

**DEVELOPMENT, PROCESSING AND CHARACTERIZATION OF ADVANCED
ALUMINA MATRIX MULTI-MATERIAL NANOCOMPOSITES REINFORCED WITH
ZIRCONIA, GRAPHENE AND CARBON NANOTUBES**

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ABSTRACT

The demand for tough materials in extreme conditions has grown due advanced technology requirements, such as high pressures ($> 90\text{GPa}$), elevated temperatures ($> 2000^\circ\text{C}$), and radiation exposure, has grown substantially. Advanced ceramics, particularly alumina (Al_2O_3), with their low weight, hardness, and chemical resistance, are promising candidates. However, their inherent brittleness (low fracture toughness) has limited their applications. To address this, researchers have incorporated sub-micron and nano-scale reinforcements like zirconia (ZrO_2), graphene (GN), and carbon nanotubes (CNTs) into alumina to create composite materials. However, challenges remain in achieving consistent mechanical properties and minimizing trade-offs between fracture toughness (K_{IC}) and strength.

This study investigates the impact of single and combined nano-scale reinforcements (ZrO_2 , GN, and CNTs) on the microstructure, mechanical properties, toughening mechanisms, tribological performance, and functional attributes of monolithic alumina. The nanocomposites were fabricated by uniformly dispersing selected optimal amounts of ZrO_2 (4wt% and 10wt%), GN (0.5wt%), and CNTs (2wt%) through a colloidal mixing process, followed by hot-press sintering. The results revealed a uniform distribution of additives within the alumina matrix, leading to significant matrix grain size reduction (up to 80%) in the Al_2O_3 -10wt% ZrO_2 -0.5wt%GN-2wt%CNTs multi-material nanocomposite compared to pure alumina.

Microhardness increased by up to 48% in the Al_2O_3 -10wt% ZrO_2 -0.5wt%GN-2wt%CNTs multi-material nanocomposites due to refined grain structures and effective load transfer capabilities. Furthermore, fracture toughness (K_{IC}) improved by up to 160%, and bending strength increased by up to 46% in Al_2O_3 -10wt% ZrO_2 -0.5wt%GN-2wt%CNTs multi-material nanocomposite, due to synergistic toughening and strengthening mechanisms involving pull-outs, crack arrest, and crack bridging by GN and CNTs. This nanocomposite also exhibited up to a 93% reduction in wear rate compared to pure alumina, attributed to wear resistance mechanisms such as micro-crack bridging and intergranular fracture restriction during sliding.

Further, the incorporation of GN and CNTs improved the electrical conductivity of monolithic alumina from 10^{-13} S/m up to 10^2 S/m (increase up to 15 orders of magnitude), with the Al_2O_3 -10wt% ZrO_2 -2wt%CNTs nanocomposite registering the highest conductivity value. This was ascribed to the intrinsic electrical properties of carbon nanostructures, percolation effect and the

refined grain structure of the nanocomposite which enhances electron mobility by forming continuous networks and pathways.

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DEDICATION

I dedicate this doctoral dissertation to the Most High King who is the source of knowledge

And

My father, Mr. Moses Hanson Duntu, my mother, Mrs. Felicia Donkor, my grandma, Mrs. Grace Tarm Sackey, my brother, Daniel Hanson Duntu, my sisters, Rose Duntu and Anthoinette Duntu

And

My beloved family

And

Lastly, I dedicate this dissertation to my beloved brother and colleague, Dr. Francis Beamish Tetteh.

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LIST OF ACRONYMS

Al₂O₃	Alumina
ZrO₂	Zirconia
npZrO₂	Zirconia Nanoparticle
SiC	Silicon Carbide
npSiC	Silicon Carbide Nanoparticle
CMCs	Ceramic Matrix Composites
CNTs	Carbon Nanotubes
HIP	Hot Isostatic Pressing
HP	Hot Pressing
FS	Flash Sintering
HFIS	High Frequency Induction Sintering
HCP	Hexagonal Closed-Pack
SPS	Spark Plasma Sintering
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscopy
HAADF	High Angle Annular Dark Field
XRD	X-ray Diffraction
α-Al₂O₃	Alpha Alumina
NaOH	Sodium Hydroxide
COF	Coefficient of Friction
K_{IC}	Fracture Toughness

σ_f	Flexural/Bending Strength
MS	Microwave Sintering

LIST OF THESIS PUBLICATIONS AND CONFERENCE PROCEEDINGS

Refereed Journal Papers:

1. **S. H. Duntu**, I. Ahmad, M. Islam, S. Boakye-Yiadom (2023), Hot-Pressed Alumina-Based Nanocomposites: A Study of Effect of Multiple Reinforcement Particles on Interfacial Behaviour, Residual Stress, Electrical and Thermal Properties (*In preparation, to be submitted: Materials Characterization*).
2. **S. H. Duntu**, J. Agyapong, I. Ahmad, M. Islam, S. Boakye-Yiadom (2022), Combined Effect of Low ZrO₂ Content and Carbon Nanostructures on Mechanical and Wear Properties of Hot-Pressed Al₂O₃/ZrO₂ Hybrid Nanocomposites, *Ceramics International*, vol 48, p. 34803-34816. (<https://doi.org/10.1016/j.ceramint.2022.08.069>).
3. **S. H. Duntu**, K. Hukpati, I. Ahmad, M. Islam, S. Boakye-Yiadom (2022), Deformation and Fracture Behaviour of Alumina-Zirconia Multi-Material Nanocomposites Reinforced with Graphene and Carbon Nanotubes, *Materials Science and Engineering A*, vol. 835, p. 142655, (<https://doi.org/10.1016/j.msea.2022.142655>).
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7. **S. H. Duntu**, I. Ahmad, M. Islam, S. Boakye-Yiadom (2023) Influence of 0.5wt%Graphene Addition on Mechanical Performance of Alumina-Graphene Nanocomposite, *Microscopy and Microanalysis*, p. 753-755, (<https://doi.org/10.1093/micmic/ozad067.372>).
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10. **S. H. Duntu**, I. Ahmad, M. Islam, S. Boakye-Yiadom (2022), Mechanical Characterization of hot-pressed alumina-zirconia hybrid nanocomposites, Canadian Society for Mechanical Engineering (CSME 2022) Edmonton, AB Canada, June 5-8, 2022.
11. **S. H. Duntu**, I. Ahmad, M. Islam, S. Boakye-Yiadom (2022), Wear and Mechanical Behavior of Hot-Pressed Alumina-based Hybrid Nanocomposites, Canadian Materials Science Conference (CMSC 2022) Toronto, ON Canada, June 22-24, 2022.
12. **S. H. Duntu**, I. Ahmad, M. Islam, S. Boakye-Yiadom (2019) Effect of Graphene and Carbon nanotubes on Wear Behaviour of Alumina-Zirconia Hybrid Nanocomposites, 31st Canadian Materials Science Canadian Conference (CMSC 2019) Vancouver, BC Canada, June 10-13, 2019.
13. **S. H. Duntu**^{*}, S. Boakye-Yiadom (2019) Effect of Zirconia and Graphene on wear properties of alumina matrix nanocomposites, 22nd International Conference on Wear of Materials, Miami, Florida, USA, April 14-18, 2019.

14. **S. H. Duntu**, M. Islam, S. Boakye-Yiadom (2018) Effect of Graphene, Carbon Nanotubes and Zirconia in Alumina Matrix Nanocomposites, Canadian Materials Science Canadian Conference (CMSC 2018).

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15. **S. H. Duntu**, S. Boakye-Yiadom (2022), Deformation and Fracture Behaviour of Alumina-Zirconia Multi-Material Nanocomposites Reinforced with Graphene and Carbon Nanotubes, *NSERC Alliance Program*.

List of Additional Publications:

16. **(In-Preparation) S. H. Duntu**, S. Boakye-Yiadom (2023), Effect of Printing Parameters on the Microstructural and Wear Properties of Lithography-based Ceramic Manufactured (LCM) Alumina and Zirconia Ceramics (*To be submitted: Journal of European Ceramics*)
17. **(In-Preparation) S. H. Duntu**, D. Mateos, S. Boakye-Yiadom (2023), Microstructural and Tensile Properties of Armox 500T Steel during Quasi-static Loading (*To be submitted: Journal of Alloys and Compounds*)
18. F. Tetteh, **S. H. Duntu**, J. Agyapong, S. Boakye-Yiadom (2023), Influence of Precipitate Distributions on Adiabatic Shear Band Formation and Flow Behavior of Heat-Treated 7050 Aluminum Alloy, *The International Journal of Advanced Manufacturing Technology*, p. 5-7, (<https://doi.org/10.1007/s00170-023-11469-z>)
19. F. Tetteh, **S. H. Duntu**, S. Boakye-Yiadom (2023), Susceptibility of Adiabatic Shear Band Formation in AZ31B Magnesium Alloy during High Strain Rate Impact, *The International Journal of Advanced Manufacturing Technology* (<https://doi.org/10.1007/s00170-023-12049-x>).
20. J. Agyapong, **S. H. Duntu**, A. Czekanski, S. Boakye-Yiadom (2022), Microstructural Evolution and Properties of Cemented Carbides Alloyed with Hexagonal Boron Nitride (h-

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22. N. Azgomi, F. Tetteh, **S. H. Duntu**, S. Boakye-Yiadom (2021), Effect of Heat Treatment on the Microstructural Evolution and Properties of 3D Printed and Conventionally Produced Medical-Grade Ti6Al4V ELI Alloy, *Metallurgical and Materials Transactions A*, vol. 52, p. 3382-3400, (<https://doi.org/10.1007/s11661-021-06310-9>).
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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The current need to make life comfortable and the desire for mankind to explore nature, advance in medicine and acquire knowledge about the universe has led to the onset of new technologies. Advanced tools and technologies are currently adopted for space explorations, deep mining, and harnessing energy from nuclear reactions. The desire to improve on these technologies and create a future with unlimited opportunities have been the main objective of industrial researchers, scientists and engineers. However, these new and advanced technologies are exposed to harsh environmental conditions such as high temperatures ($> 2000^{\circ}\text{C}$), high pressures ($> 90\text{GPa}$), harsh chemical environments and radiations [1][2]. Within these environments, the performance of the materials used in these devices and technologies is constantly challenged and eventually becomes inefficient if they are not able to tolerate such surroundings. The need to develop technologies and devices that can survive these extreme conditions has prompted scientists to design superior materials for these applications. Superior materials such as superalloys, superconductors and advanced ceramics are being developed and tested for these systems to tolerate these harsh environments [2][3]. In as much as we want these materials to withstand these conditions during in-service performance, we desire the entire system to run on the least amount of energy. Minimizing the amount of fuel consumed is a top priority because it reduces the carbon emission on the environment. Automotive and aerospace industries as well as environmental groups such as the Canadian Environmental Assessment Agency (CEAA), constantly advocate the need to reduce the overall contribution to increased carbon footprint on the environment and the effect on climate changes [4][5]. Therefore, it is essential to create a balance between the properties of these materials for the high-performance applications we seek.

One way of establishing a balance between economized fuel intake and superior performance of advanced technologies is to adapt a lightweight material. The use of lightweight materials for aerospace, automotive and other structural applications is very essential in reducing the fuel consumption of devices such as aircrafts, vehicles and spacecrafts [6][7]. In addition to cutting down energy consumption, low-density materials offer many advantages in other sectors such as

military and medicine. Present-day defense material needs suggest that a lightweight but tougher material is crucial for military personnel and defence vehicles such as armoured cars [6][8]. For military personnel to move with ease and protect against injury especially in the line of fire, a low density but high impact-resistant material which can absorb high impact loading and multiple hits is necessary. To this effect, personal armors and many protective vehicles are currently being developed with lightweight and shock-absorbing materials such as advanced alumina, silicon carbide, boron nitride, graphene, carbon nanotubes and a combination of these materials [9][10]. In addition, most human body implants require a chemical inert, high strength and low-density materials such as alumina, titanium and zirconia for effective lubrications and to prevent infections within the body [11][12].

Advanced or engineering ceramics such as alumina/aluminum oxide (Al_2O_3), silicon carbide (SiC), silicon nitride (Si_3N_4) and zirconia (ZrO_2), which have a unique combination of superior mechanical properties coupled with chemical resistance and a relatively lower density have been given a lot of attention in recent years. These materials, compared to conventional metals and polymers, offer limitless potential in equipping current technologies with reduced weight and superior mechanical properties, even in challenging environments [13][14][15][16]. Alumina as an advanced structural ceramic presents promising advantages and currently has widespread applications such as cutting tools, cylinder pistons, insulators and implants for human body due to its attractive properties such as high hardness, high temperature strength, corrosive and oxidation resistance, and low electrical and thermal conductivity. However, the inherent brittleness of monolithic alumina and most advanced ceramics largely limits their potential to be extensively adopted for further structural and high-performance applications. The brittle nature of alumina ceramic is attributed to its crystal structure (hexagonal closed-pack, HCP) and bonding nature (ionic and covalent) [17][18][19]. The need to improve the fracture toughness of alumina ceramic without compromising its lightweight property and make it most suitable for several structural applications within extreme environments such as in turbine engine parts and space materials are the main concerns of several materials researchers and engineers [13]. This has therefore presented the need to investigate ways to enhance the toughness and other mechanical properties of advanced alumina for engineering applications.

1.2 Motivation for Research

The increasing attempt to enhance the toughness and other mechanical attributes of monolithic alumina and other brittle ceramics has involved materials design and microstructural tailoring. This microstructural modification involves deliberate and effective design and tailoring of the structural ceramics by the distribution of other materials within the material to achieve maximized performance [20][21]. It is perceived that the mechanical properties of ceramics can be improved by refining the polycrystalline grain size and shape [22]. This can be achieved by embedding within the ceramic matrix phase to form a composite or a nanocomposite. By forming them into composites and nanocomposites, these materials will exhibit superior performance in harsh operating conditions whilst maintaining their lightweight attributes. Ceramic matrix composites (CMCs) are therefore monolithic ceramic matrix systems incorporated with one or more sub-micron or nano-scale reinforcement phases such as carbon nanotubes (CNTs), graphene, particulates, and second-polymers or metal phase in a ceramic matrix [20][23]. In recent years, there has been a notable focus on alumina as a ceramic matrix material due to its appealing characteristics. Alumina matrix nanocomposites can be defined as ceramic composite systems wherein an alumina matrix material is embedded with at least one reinforcement phase characterized by nanometric dimensions ($<100\text{nm}$). In addition to higher toughening attributes, alumina-based composites and nanocomposite structures also offer superior wear resistance, good strength, high-temperature stability, thermal shock resistance, electrical and other functional properties as compared to the monolithic alumina ceramic [24][25]. These remarkable physical and mechanical traits of alumina-based nanocomposites and other CMCs make them suitable for high performance applications in extreme environments including defence, aerospace, automotive, chemical and biomedical engineering industries, energy and power sectors, electronics and electricals[26]. These potential applications have therefore driven several research studies into alumina-based nanocomposites and CMCs in recent times.

Despite various research reports emphasizing the success in design and fabrication of alumina-based composites and nanocomposites with improved properties, other investigations have considerably shown that the mechanical properties of the manufactured composites are not necessarily improved by the addition of these reinforcement particles. In some cases, the additions of certain amounts of reinforcement materials and additives tend to deplete the fracture toughness and compromise the desired low-density attributes of the final composites [27]. The variation of

mechanical properties is mainly attributed to the fabrication process routes, the nature of distribution of the reinforcement particles within the ceramic matrix, amount of reinforcement phases and the final grain structure after processing [28]. Alumina-based nanocomposites are typically fabricated by dispersing and mixing reinforcement particles and alumina matrix powders followed by consolidation and high temperature sintering ($\sim 1200\text{-}1600^\circ\text{C}$) to form a dense bulk composite structure. Various processing routes and sintering techniques such as spark plasma sintering (SPS), hot pressing (HP), stir casting and hot isostatic pressing (HIP) have been adopted over the years to produce alumina matrix composites and other CMCs [23][26][29]. This fabrication approach results in refinement of the matrix grain size which can induce significant improvement on both the physical and mechanical traits of the bulk nanocomposite structure. This structure-property relationship which highlights the dependency of material properties on the grain size is known as the Hall-Petch phenomenon [20][30]. Studies on alumina-based nanocomposites reinforced with reinforcement particles such as zirconia, graphene and carbon nanotubes have shown that the superior properties of the fabricated composite also depend on the homogeneous dispersion of the reinforcement particles within the matrix phase, overall densification of composites, the retention of the structure during high temperature sintering process, the amount of the additives in the matrix phase and the interfacial bonding between additives and matrix material [28][31]. The scattered results of alumina-based composites and other CMCs despite various research highlight the need for further studies to understand the fundamentals of the structure-property relationship of ceramic composites. Studies to optimize the processing route and its effect on microstructural and mechanical properties has therefore attracted further studies into ceramic-based composites and nanocomposites.

Also, the increasing competition for sustainable designs and technologies in recent times demands the highest trait of materials with a superior combination of properties. With the use of conventional metals and alloys all but exhausted, the current approach gears towards novel hybrid and multi-material structures that can combine the attributes of these traditional materials to yield a more advanced material for high performance applications. This quest has fueled current research in the direction of hybrid and multi-material structures including multi-material ceramic composites that have the potential to exceed the performance of a single-phase composite systems [32][33]. Ceramic-based hybrid and multi-material composites are novel materials with multiple additions of second-phase particles simultaneously embedded within the monolithic matrix

structure. These multi-system composites have the tendency to offer superior properties relative to a single-phase composite due to the combination of properties from the added additives. In addition, the introduction of two or more reinforcement particles within the ceramic matrix structure can also alleviate various limitations of the single-phase composite materials and further enhance the mechanical and functional properties of for targeted applications in the aerospace, defence, automobile and biomedical field [34]. Figure 1.1 shows the interaction of multiple additions of graphene and carbon nanotubes within a matrix material. For instance, it is suggested that the processing issues such as carbon nanotube agglomeration and graphene re-stacking which lead to poor dispersion within the matrix can be minimized by simultaneous additions of both graphene (GN) and CNTs within the matrix [35][34]. It is also perceived that the multiple additions of carbon structures within the matrix can drastically improve the toughness through the synergistic contributions of the combined additives within the ceramic matrix. Hence, the incorporation of two or more additives to ceramic matrix structure has the potential to significantly enhance the overall mechanical properties of ceramic matrix composites. However, the limited availability of results in ceramic-based multi-material composite systems demands further studies and research in order to understand the microstructural evolution, toughening effect and their mechanisms, mechanisms of synergy, as well as the mechanical and tribological performance of these novel multi-material ceramic composite structures.

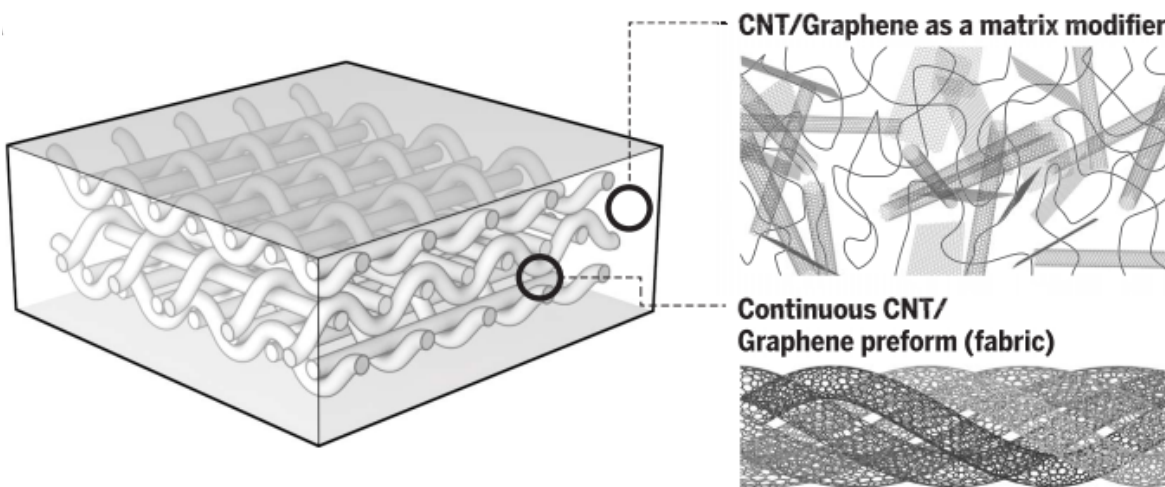


Figure 1.1: Demonstration of multiple reinforcements of graphene and carbon nanotubes in a polymer matrix [32].

1.3 Research Gaps

The deployment of alumina matrix nanocomposites and CMCs to mainstream technology and engineering application is still lacking due to processing concerns and knowledge gaps in reinforcement effects such as grain refinement and toughening mechanisms, as well as performance parameters. Despite the promising progress made with the additions of various reinforcement phases and additives to alumina matrix, there is still a need for further research in this area. A detailed literature survey shows that the combination of properties of many fabricated alumina-based nanocomposites including toughness, strength and wear attributes tend to be mutually exclusive. This is due to challenges in identifying the optimum parameters and processing conditions that will produce the superior combination of properties after sintering. This includes optimized amounts of various reinforcement particles or additives to embed within the alumina matrix structure. In effect, there is currently little consensus and consistency in the properties of processed alumina matrix composites. The trade-off in mechanical attributes such as toughness and strength properties has constantly limited the potential of alumina matrix nanocomposites to be adopted for engineering and high-performance applications such as defense, biomedical and aerospace. Figure 1.2 demonstrates the variation in bulk mechanical properties with the addition of graphene additives to the alumina matrix. The scattered results show the trade-off in properties such as flexural strength versus fracture toughness of alumina-graphene composites reinforced with a single additive. The property variation may be due to the toughening and strengthening mechanisms which may not be fully activated in the single-phase composite system as a result of the reinforcement concentrations used. This therefore suggests a need for a detailed study to identify the optimum amount of graphene nanofiller and fundamental mechanisms which can lead to simultaneous enhancement of bulk properties in graphene reinforced alumina composites.

The variation in properties is also apparent in processed alumina-carbon nanotube (CNT) composites as illustrated in Figure 1.3. Discrepancy in strength, hardness and toughness properties with different amounts of carbon nanotubes in single-phase alumina matrix composites depict that there is little consensus on the optimum amount of CNTs as an additive in alumina matrix nanocomposites. For instance, a combination of reinforcement amount and processing techniques may result in slight to no improvement in the bulk properties of the alumina-carbon nanotube

composites having higher CNT concentrations (3-5wt%), as illustrated in Figure 1.3. Therefore, a study is needed to identify the optimum reinforcement amount that will unearth the extraordinary potential of CNTs within alumina and other ceramic matrix structures for needed applications.

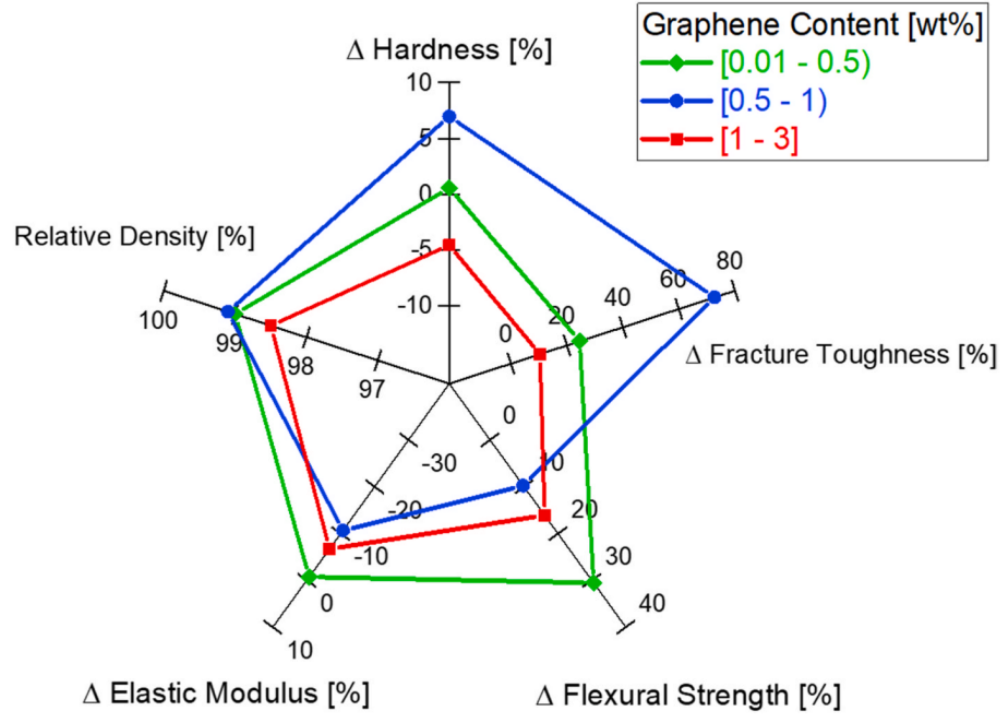


Figure 1.2: Mechanical property variations and trade-offs in processed alumina-graphene composites [36].

Also, the promising effect of incorporating two or more reinforcement materials within alumina and other ceramic matrix materials has fueled advanced research into hybrid and multi-material ceramic-based nanocomposites. However, there is still knowledge gap in the coordination and combined effects of the multiple reinforcement structures within alumina and other CMCs. This is because the fundamental understanding of the effect of single reinforcement phase within matrix is inconclusive, which has limited the mainstream adoption of these novel materials. Questions and issues with simultaneous toughening, synergy mechanisms and interfacial interactions need to be answered to illuminate strategies in tailoring multi-material nanocomposites for targeted applications. Hence further research studies will provide fundamental knowledge in toughening and synergy mechanisms of multiple additions and their effect in mechanical properties of alumina-based nanocomposite systems.

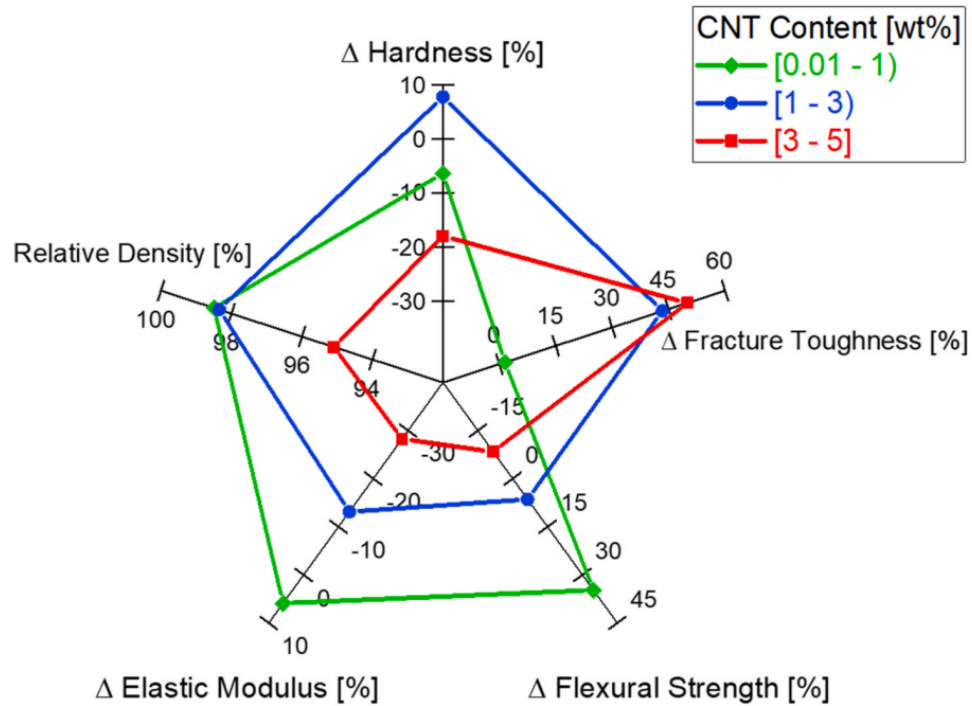


Figure 1.3: Mechanical property variations and trade-offs in processed alumina-carbon nanotube composites [36].

1.4 Research Questions and Hypothesis

The reports from literature have shown that the effect of adding a single second-phase particle to alumina matrix is all but conclusive. To achieve a more superior composite or nanocomposite material for high performance structural and functional applications that is needed, the following research questions were asked:

- What is the optimum amount of reinforcement phases such as graphene, carbon nanotubes and zirconia to give a superior property in alumina-based nanocomposites?
- What is the effect of multi-material additions on the microstructural evolution and mechanical properties of alumina-based composites?
- What is the nature of interface between the matrix and second-phase particles and how does it influence the microstructure and mechanical properties?
- Can the trade-off properties in single-phase composites be minimized with the multiple additions of nanoscale reinforcement particles within alumina matrix composites.

Response to these questions can serve as a guideline to design, develop and characterize advanced multi-material ceramic-based nanocomposites with optimized performance parameters for required applications in the aerospace, defense and biomedical industries.

The hypothesis for this study posits that the incorporation of optimal reinforcement particles into the alumina matrix can result in a synergistic enhancement of the physical, mechanical and tribological properties of structural alumina-based nanocomposites through the collaborative interaction of multiple reinforcing materials. For example, the combined effect of carbon-based structures like graphene and carbon nanotubes can significantly refine the grain structure and enhance mechanical and tribo-mechanical attributes such as hardness, wear resistance, toughness and strength by simultaneously activating toughening mechanisms and load-bearing activities within the matrix. Moreover, the electrical and thermal properties inherent in the carbon-based structures can be transferred to the alumina matrix, giving rise to a unique ceramic material suitable for multifunctional applications such as thermal management networks. By concurrently introducing and leveraging multiple reinforcement materials such as graphene, carbon nanotubes and zirconia within the matrix, the limitations associated with individual additions to ceramic nanocomposites can be mitigated. This approach enables an optimization of the trade-off between the mechanical properties (example: fracture toughness and strength) of alumina and advanced ceramic matrix nanocomposites.

1.5 Research Aims and Objectives

To answer the research questions, the following objectives have been determined for the current research as follows:

1. Develop and process advanced lightweight alumina matrix nanocomposites reinforced with zirconia, graphene and carbon nanotubes.
2. Systematically study in detail the effect of individual additions of nano-reinforcement materials on the microstructure and properties of alumina matrix.
3. Systematically study the effect of multiple additions of nano-reinforcement materials on the microstructure and properties of alumina matrix, and the mechanism of synergy effect of the multiple nano-reinforcements.

4. Investigate the interface between matrix and nano-reinforcements, and the effect of carbon nanostructures on electrical properties of alumina matrix nanocomposites.

1.6 Publication Contributions

This dissertation has been developed in a sandwich format to form a manuscript-based thesis authored by the PhD candidate (See Contributions section). I have contributed to five (5) manuscript publication as a first author in the current research during my time as a PhD candidate. These journal articles were published in highly recognized journals such as **Material Science and Engineering A**, **Ceramics International**, **Materials Characterization** and **Wear**. The following highlights my contributions as a first author to these manuscripts. For all papers, I designed and performed the experiments, from device design and implementation to data analysis. I drafted the original manuscripts and the initial responses to reviewers, and they were revised thoroughly by Prof. Solomon Boakye-Yiadom. Prof. Solomon Boakye-Yiadom was very instrumental with idea and concept development and provided constructive feedback to guide my research journey. This research has also been presented by the PhD candidate and published in international conferences including **Microscopy and Microanalysis Conference (M&M)**, **Canadian Materials Science Conference (CMSC)** and **Canadian Society of Mechanical Engineering Conference (CSME)**. A total of nine (9) conference publications and technical presentations have been achieved during my PhD program. I was financially supported by Natural Sciences and Engineering Research Council of Canada (NSERC) grants to Prof. Solomon Boakye-Yiadom for my research expenses in the entire duration of my PhD program.

1.7 Thesis Outline and Organization

This dissertation is structured into six (6) major chapters presented in a sandwich format. Chapter 1 is an introduction section of the thesis, Chapter 2 details the literature survey for the study, Chapter 3 describes the experimental procedures, materials and methodology. A summary of the published articles connected to the thesis objectives is described in Chapter 4, and Chapter 5 discusses the conclusion and future works, followed by appendices with the details of the published works and contributions. Summary of the thesis outline is described below:

- **Chapter 1: Introduction**

Chapter 1 introduces the research topic, with background of study, motivation for work, identified research gaps, research questions and hypothesis, followed by research aims and objectives and thesis outline and organization.

- **Chapter 2: Literature Review**

This chapter presents detailed literature survey of the state-of-the art of fabrication processes for ceramic matrix composites (CMCs) and alumina-based composites including various consolidation and sintering techniques. Literature studies covering the microstructural and mechanical properties of the reinforcement materials including graphene, carbon nanotubes and zirconia will also be discussed. This chapter will also provide details on reported trade-offs in mechanical properties of fabricated alumina matrix composites reinforced with graphene, carbon nanotubes and zirconia nanoparticles.

- **Chapter 3: Experimental Procedures and Methodology**

Chapter 3 introduces the experimental procedures and methods used for fabrication of the alumina matrix based multi-material nanocomposites. The fabrication procedure involves the dispersion of the nano-scale reinforcement particles including graphene, carbon nanotubes and nanoparticulate zirconia within the matrix alumina material using a colloidal mixing technique. Densification of the samples was achieved using high temperature sintering and consolidation. This chapter also details the microstructural characterization of the processed nanocomposite samples using techniques such as optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), focused ion beam (FIB) milling, transmission electron microscopy (TEM), and X-ray Diffraction (XRD). This chapter also investigates and discusses the measurements techniques used for mechanical property assessment including fracture toughness, bending strength, microhardness. Experimental details of frictional and wear properties of the fabricated nanocomposites are also captured in this chapter. More details on experimental procedures and data analysis are also discussed separately in each published paper.

- **Chapter 4: Summary of published articles**

In this chapter, a summary of the published papers resulting from this research is provided. The first paper gives a detailed study into the fabrication and dispersion process of alumina-based nanocomposites, which focuses on Objectives 1 and 2 of this research. This paper also discusses the effect of single/individual additions of graphene and zirconia on the microstructural evolution, friction and wear performance of alumina-based nanocomposites. The second paper addresses Objectives 2, which highlights the influence of single additions of reinforcement particles on mechanical properties alumina matrix, as well as toughening mechanisms by the added reinforcement phases. The third paper also demonstrates Objectives 3, which describes the simultaneous dispersion of multiple reinforcement nanoparticles such as graphene, carbon nanotube and zirconia within the alumina matrix. This article also discusses the combined effect of the multi-material additives on the matrix grain refinement, friction and wear behaviour and synergistic mechanisms by the simultaneous additions of graphene, carbon nanotubes and zirconia. The fourth paper also focuses on Objective 3, which investigates the influence of the multiple additions on mechanical properties such as fracture toughness and bending strength. Fractography studies from this paper also assessed the toughening and synergy mechanisms by the combined reinforcements particles. Fifth paper also provide comparative study of hybrid additions of zirconia and graphene, and zirconia and carbon nanotubes on alumina matrix, satisfying Objective 3 of this research. Sixth paper (manuscript in-preparation) also addresses Objectives 4, which describe the interfacial studies between multi-materials and the alumina matrix. This study also accounts the effect of carbon nanostructures on electrical conductivity of alumina-based multi-material nanocomposites.

- **Chapter 5: Summary and Conclusions**

This chapter summarizes the major findings of this research with recommendations for future work.

- **References**

All references used in this thesis are listed in this section.

- **Appendix**

The published journals used to develop this thesis into manuscript-based version is amended in the Appendix.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents a literature survey of ceramic matrix composites (CMCs), structure and properties of alumina ceramic, fabrication and sintering techniques of alumina ceramic, alumina matrix nanocomposites, properties and mechanical influence of graphene, carbon nanotube and zirconia as reinforcement phases in alumina matrix composites, toughening effects and mechanisms of reinforcements, state-of-the-art of multi-material nanocomposites and interfacial effect of matrix and reinforcements. The literature review of ceramic matrix composites is presented in Section 2.2. Section 2.3 gives a review study of the monolithic alumina matrix, its properties and applications. The literature studies and overview of alumina-based composites reinforced with graphene, carbon nanotubes and zirconia reinforcements are also detailed in Sections 2.4-2.7. Section 2.8 details state of the art of multiple and hybrid additions of nano-reinforcements on alumina matrix.

2.2 Overview of Ceramic Matrix Composites (CMCs) and their Applications

Ceramic Matrix Composites (CMCs) are composite materials that have ceramic matrix with embedded reinforcements which can be a fiber, whiskers or particulates [23][37][38][39]. The ceramic matrix material serves as the binding agent, ensuring the cohesion of all components, while the reinforcement particles impart their distinctive properties to the matrix. Although advanced monolithic ceramics exhibit appealing properties such as high melting point, hardness, stiffness, corrosion resistance, thermal and electrical insulation, and low density, their application in high-performance scenarios is often constrained due to their inherent low fracture toughness under loading conditions [37][40]. CMCs were consequently developed to address the inherent brittleness of monolithic ceramics and enhance their effectiveness in demanding loading and environmental conditions. Over the years, the design and development of CMCs with reinforcement particles has led to the significant improvement in monolithic ceramics including toughness, shock resistance, wear resistance and reliability [37][38][39][41]. CMCs, therefore, hold immense potential for application in areas that demand exceptional mechanical and thermal performance, including space structures, aircraft turbines, land transportation systems, chemical

plants, and nuclear facilities [42]. CMCs employ diverse matrices integrated with a range of reinforcements to optimize their properties for targeted applications. Most common ceramic matrices used include oxide-based CMCs and non-oxide-based CMCs such as silicon-carbide based CMCs, Carbon-based CMCs and Boride-based CMCs. Major reinforcement materials mostly used also include graphene, carbon nanotubes (CNTs), silicon carbide (SiC) and zirconia [43]. Figure 4 illustrates the commonly used matrix material for CMCs and examples of reinforcement particles used for oxide CMCs. Figure 5 also provides an overview of the primary categories of CMCs based on their matrix materials, accompanied by illustrative examples of industrial applications.

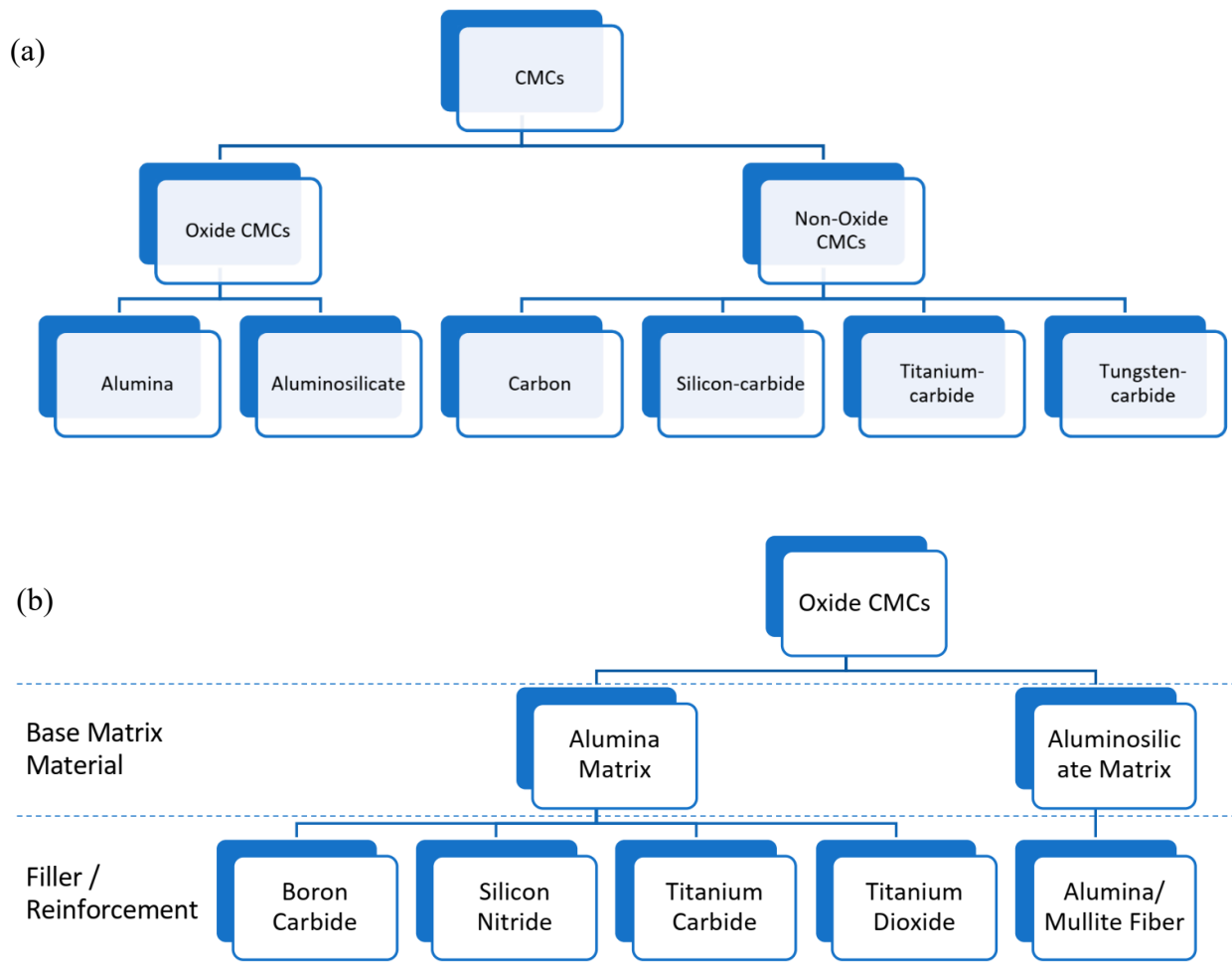


Figure 2.1: (a) Examples of oxide and non-oxide CMCs (b) Commonly used oxide CMCs and their reinforcements [43].

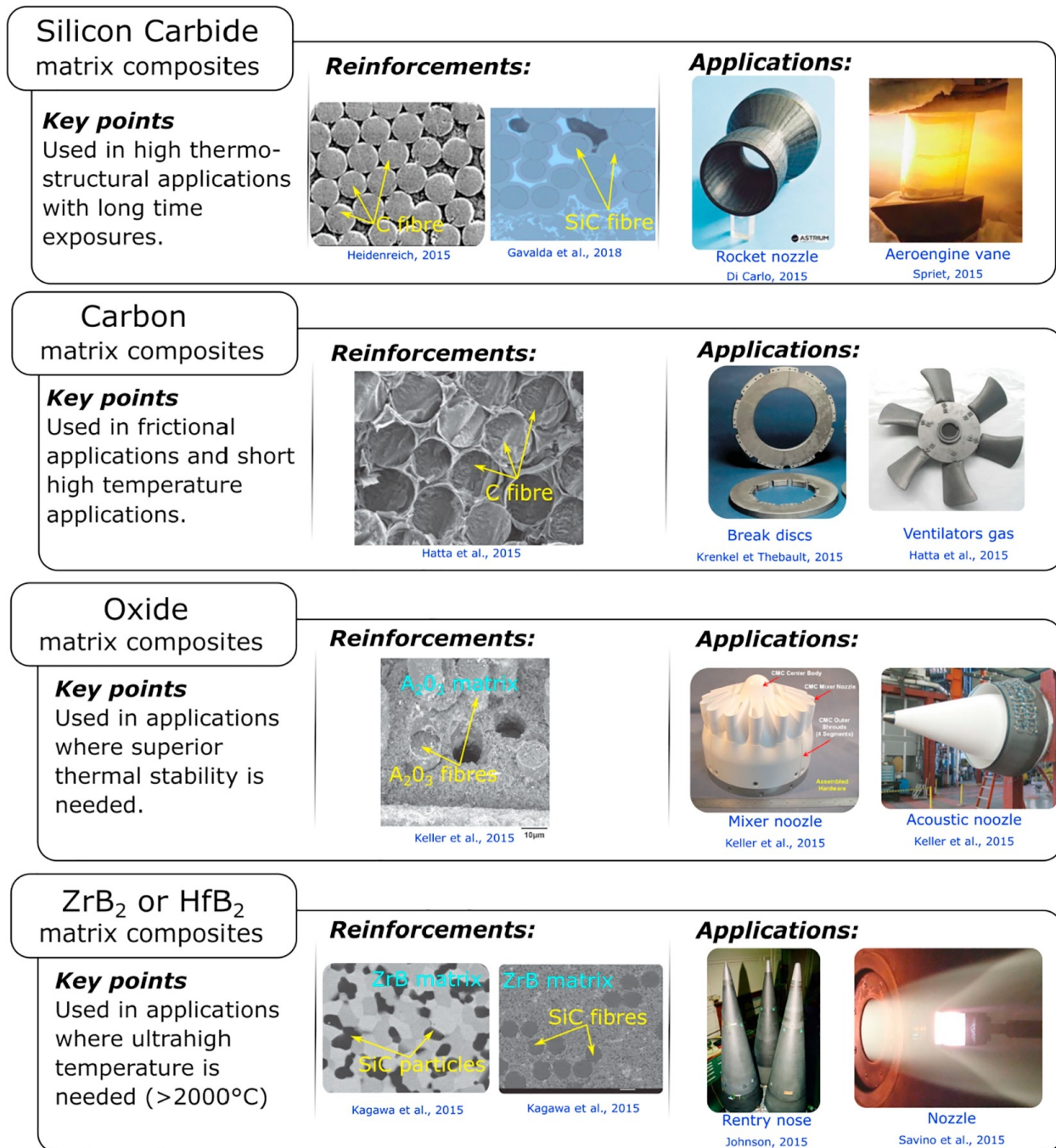


Figure 2.2: An overview of key Ceramic Matrix Composites (CMCs) matrices, common reinforcements, and prominent industrial applications [29][37][38][39].

2.3 Alumina as an Oxide Ceramic

Alumina also referred to as aluminum oxide (Al_2O_3) is a natural occurring ceramic oxide which is formed by the metal aluminum [44]. Alumina as a multifunctional advanced ceramic has many metastable polymorphs occurring at low temperature (up to 500°C) and high temperature ($\geq 800^\circ\text{C}$). The low temperature polymorphs include χ - Al_2O_3 , γ - Al_2O_3 and η - Al_2O_3 , whilst κ - Al_2O_3 , δ - Al_2O_3 , θ - Al_2O_3 and α - Al_2O_3 form the high temperature Al_2O_3 polymorphs. However, α - Al_2O_3 (also known as corundum or sapphire) is the only thermodynamically stable Al_2O_3 phase which has wide range of commercial and industrial applications including coating, optical, and electrical insulation. Upon thermal treatment, all metastable polymorphs of Al_2O_3 undergo irreversible transformation into α - Al_2O_3 [45][46]. The crystal structure of α - Al_2O_3 consists of a hexagonal closed-packed (HCP) array of oxygen anions (O^{2-}) and aluminum cations (Al^{3+}) with a rhombohedral or trigonal unit cell ($a=3.56 \text{ \AA}$ and $\alpha=55.333^\circ$) (Figure 2.3). The O atoms have 4 Al neighbours, whilst each Al atom is coordinated by 6 O atoms. Hence, the O^{2-} in the HCP system fills $2/3$ of the octahedral interstices. The reported lattice parameters are given as $a=b=4.760 \text{ \AA}$ and $c=12.989 \text{ \AA}$ [47][48][49]. The predominant bond in α - Al_2O_3 is ionic for two-thirds of the lattice structure and covalent for the remaining third. The presence of strong ionic bonding in structural ceramics, including α - Al_2O_3 , results in their hardness and brittleness, along with high melting points and elastic moduli. Furthermore, these ceramics exhibit limited plastic deformation, even at elevated temperatures [50].

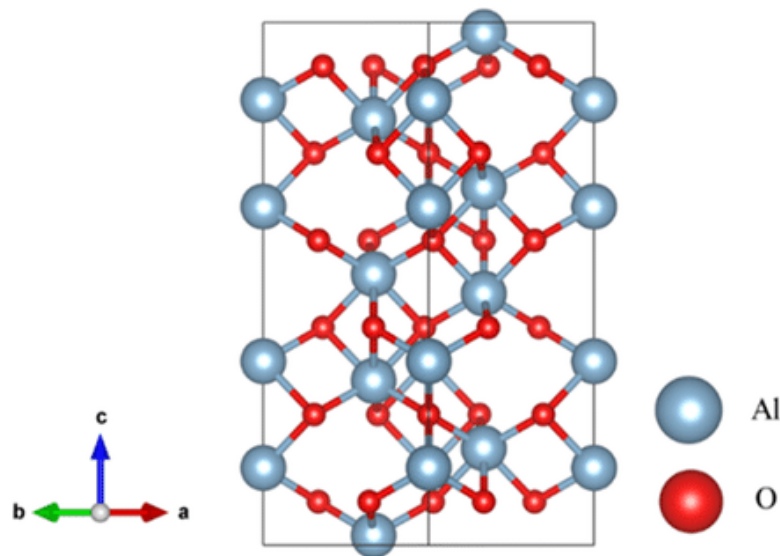


Figure 2.3: The crystal lattice of α - Al_2O_3 [49]

2.3.1 Fabrication Process of Alumina Ceramic

As an advanced structural material, the final performance of alumina and other technical ceramics are dictated by the processing-structure-property relationship. Hence, the processing techniques/routes of advanced ceramics influence their properties and structural attributes. Due to their low ductility, poor resistance to thermal shock and high melting temperatures, bulk engineering ceramics including (α - Al_2O_3) are mainly produced using powder metallurgy technique [51][52]. Figure 2.4 details the powder processing route for forming advanced ceramics. Ceramic powder processing involves the dispersion and formation of ceramic powders into slurries, which are dried and shaped into final dense structures using high temperature sintering techniques. The ceramic slurries are formed by the dispersion and distribution of the powders within a liquid medium to create a colloidal ceramic slurry consisting of ceramic particles suspended in a solvent. This slurry can be utilized for various manufacturing processes such as tape casting and slip casting, which involve wet forming techniques. Alternatively, a plastic forming method can be used where the powder is mixed with wax to enable injection molding [52][53]. The formed part at this stage is referred to as the “green body”. Following the formation/shaping process, a controlled heating rate is employed to execute a de-binding step, which aims to eliminate the organic binders during dispersion. This results in the formation of a “brown body”. Subsequently, the brown body undergoes sintering, a crucial stage where it is subjected to elevated temperatures in a furnace. Typically, the sintering temperature ranges between 50%-90% of the ceramic melting temperature. This controlled heat treatment induces a physicochemical transformation, leading to the development of the component's desired material properties and microstructure [54].

2.3.2 Powder Synthesis of Alumina (α - Al_2O_3)

Polycrystalline monolithic alumina ceramics are fabricated using this powder process route. The starting raw material which is alumina powder is commercially produced from bauxite ore via a conventional method known as the Bayer process. The Bayer process, developed by the Austrian chemist Carl Josef Bayer in 1887 during his time in Saint Petersburg, Russia, was a significant invention aimed at providing the textile industry with a reliable supply of alumina. The flowchart for this process is illustrated in Figure 2.5. Common bauxite ores (precursors) used normally exist in the form of boehmite (γ - $\text{AlO}(\text{OH})$), gibbsite ($\text{Al}(\text{OH})_3$ or $\text{AlO}(\text{OH}) \cdot \text{H}_2\text{O}$) and diaspor (α -

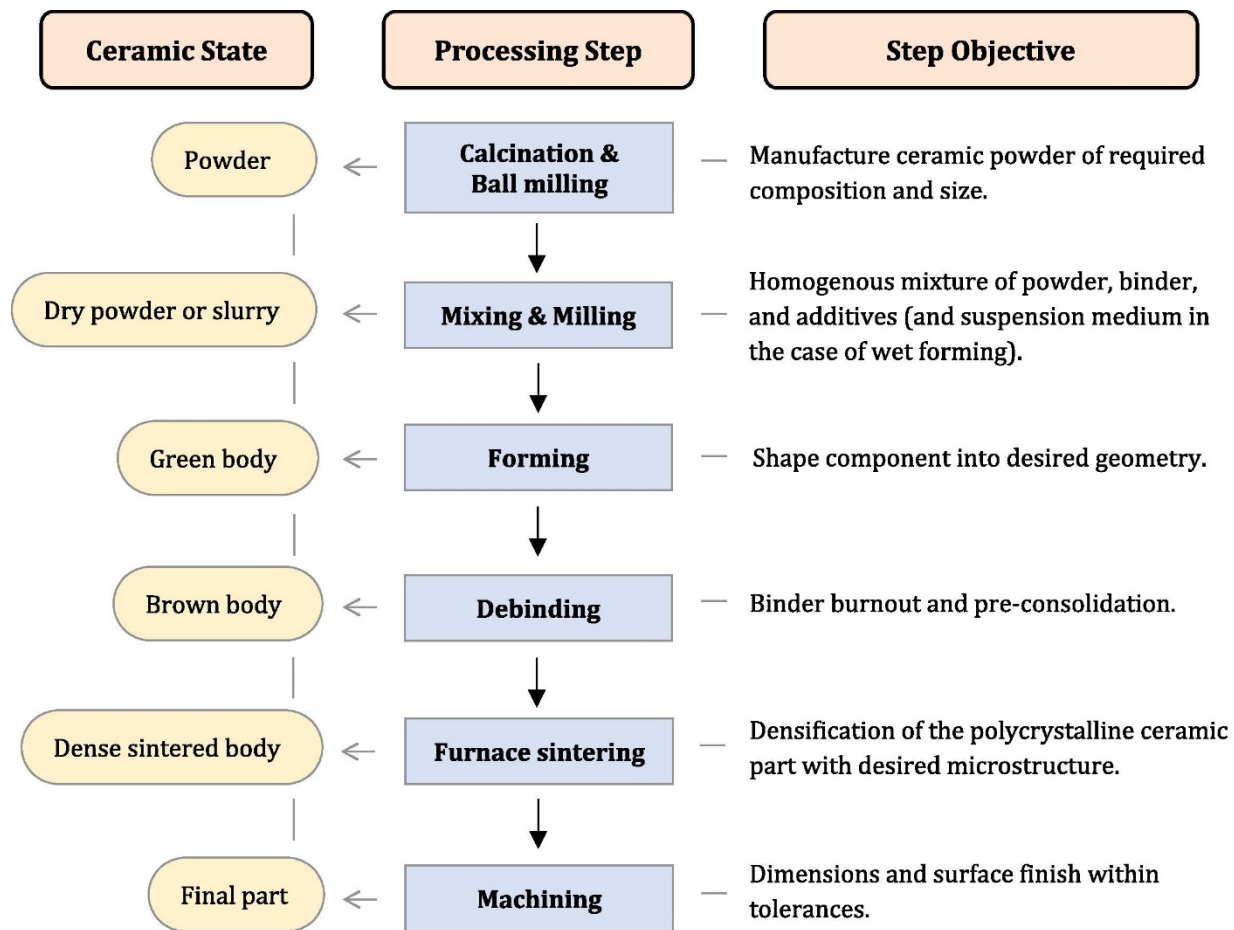
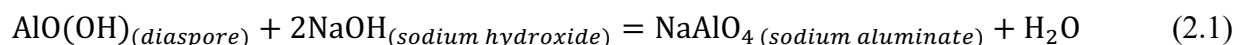
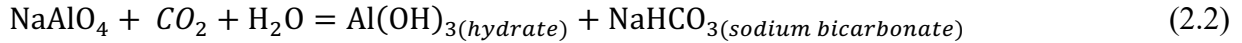


Figure 2.4: Flowchart of ceramic processing route for alumina and advanced ceramics [54].

AlO(OH)) [55]. The Bayer powder synthesis method begins by dissolving or digesting crushed/milled bauxite ore in sodium hydroxide (NaOH), at elevated temperatures (150-200°C) and pressures. This step facilitates the separation of alumina (Al₂O₃) from the bauxite ores by effectively washing out the waste components such as red muds or sands. Finally, the hydrated alumina is subjected to crystallization and subsequently dried in a furnace through a process known as calcination. The calcination (at high temperatures: 1000-1260°C) step leads to the formation of solid alumina [56][57]. This powder synthesis technique can produce high quality alumina powders (purity of 99.6 - 99.9%), having particle sizes of >50nm [58]. Summary of the chemical reactions during the synthesis with the Bayer process using diaspore ore (α -AlO(OH)) is presented by equations (2.1)-(2.3) below [55]:

Diaspore digestion stage:



Precipitation stage:**Calcination stage:**

Processing and synthesis of nano-sized $\alpha\text{-Al}_2\text{O}_3$ powder processing requires high temperatures for phase transition of to $\alpha\text{-Al}_2\text{O}_3$. To initiate phase transformation, temperatures exceeding 1200°C are necessary to surpass the activation energy barrier. However, it is important to note that such elevated temperatures can also lead to swift grain growth or the aggregation of alumina particles, thereby hindering the formation of nanoparticles using these techniques. This has therefore motivated several researchers and powder manufacturing industries to develop methods to synthesize $\alpha\text{-Al}_2\text{O}_3$ at low temperatures [59]. Different precursors (including natural occurring ores) coupled with relatively lower temperatures ($\leq 1200^\circ\text{C}$) have been used to synthesize micro and nano-sized $\alpha\text{-Al}_2\text{O}_3$ powders with high purity ($>99\%$). Most common $\alpha\text{-Al}_2\text{O}_3$ powder synthesis techniques include sol-gel, vapor deposition, hydrothermal, combustion methods, precipitation, microemulsions, spray pyrolysis, solvothermal and mechanical milling [60][61][62][63]. Table 2.1 shows examples of low temperature powder synthesis techniques used for processing $\alpha\text{-Al}_2\text{O}_3$ powders and the range of powder/particle sizes yielded.

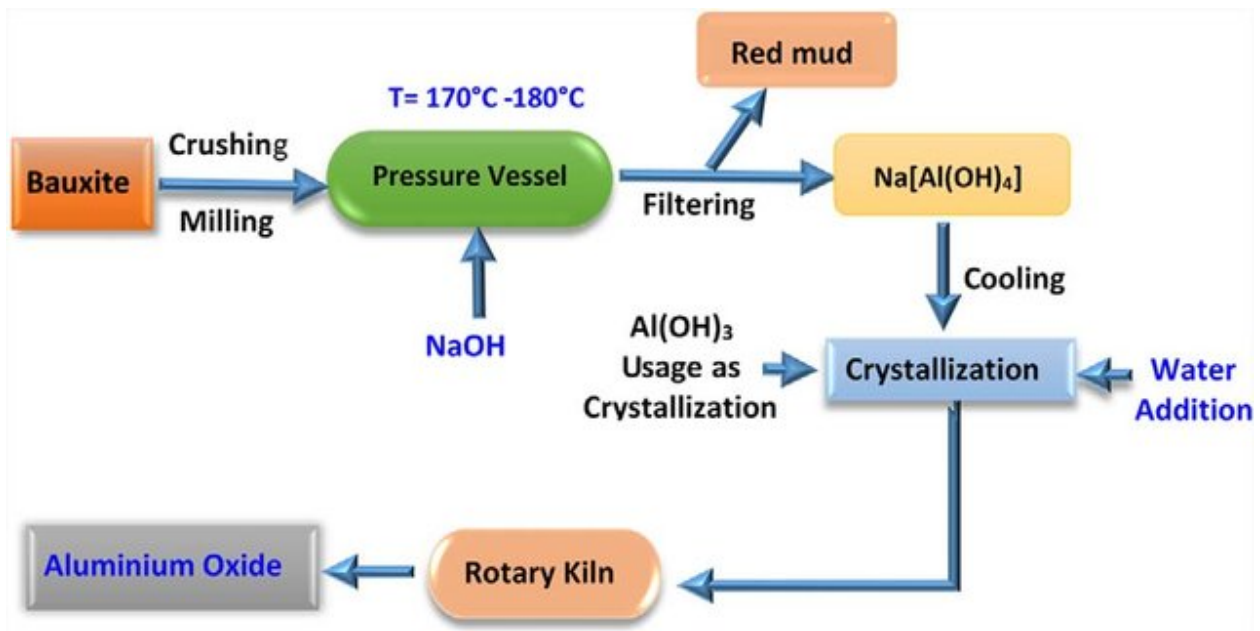


Figure 2.5: Commercial processing route of alumina powder using the Bayer process [64].

Table 2.1: Various powder sizes from derived synthesis of α -Al₂O₃

Purity of α -Al ₂ O ₃ (%)	Precursor	Powder Synthesis Technique	Calcination Temperature (°C)	Powder Sizes (nm)	Refs.
>99.99	Aluminum alkoxide (Aluminum isopropoxide) Al (OC ₃ H ₇) ₃	Hydrolysis	1200	100-700	[58]
	Aluminum isopropoxide Al (OC ₃ H ₇) ₃ + aluminum nitrate nonahydrate	Sol-gel	100-1200	20-30	[65]
up to 99.98	Gibbsite (γ -Al(OH) ₃) Boehmite (γ -AlO(OH))	Hydrothermal	380-435	100-40000	[60]
—	Aluminum isopropoxide Al (OC ₃ H ₇) ₃ + absolute ethanol and nitric acid	Sol-gel	400-1000	36-50	[59]
—	Aluminum nitrate nona- hydrate (98%), aluminum chloride hexahydrate (99%) and ammonium acetate (99.99%)	Precipitation	700-1100	80-300	[66]
high purity	Aluminum formate (Al(O ₂ CH) ₃)	Thermal decomposition	1100	20-800	[67]
high purity	Cyclohexane	Microemulsion	900-1150	30-100	[68]
high purity	Aluminum chloride (AlCl ₃) powder (99.6%)	Spray pyrolysis	1100	80-100	[69]

2.3.3 Consolidation and Forming/Shaping of Alumina Ceramic

Consolidation and forming/shaping stages are essential part of the fabrication process of alumina and advanced ceramics. These two stages dictate the final geometry and structure of the ceramic part. Consolidation refers to the process of transforming alumina (α -Al₂O₃) and advanced ceramic powders (polycrystalline and nanocrystalline powders) into uniform and dense structures [70]. Consolidation is done to ensure homogeneous packing of the powder particles in the green state. The consolidation process which is accompanied by mechanical compaction (pressure pressing) of dry or semi-dry powders in a die is mostly used to commercially process advanced ceramics. The distribution of pressure/stress and friction of powder particles in the die during consolidation determines the density variation and packing uniformity of the alumina (α -Al₂O₃) and ceramic powders [52]. Other consolidation and shaping/forming techniques used for advanced ceramics include tape casting, slip casting, extrusion, freeze casting, injection molding, cold isostatic pressing and uniaxial die pressing [18][71].

2.3.4 Sintering of Alumina Ceramic

The sintering process, which follows the forming/shaping and consolidation stages determines the final densification and microstructure of the bulk ceramic. Sintering refers to the thermal process that facilitates the cohesive bonding of ceramic powder particles, resulting in the formation of a solid structure through atomic-scale mass transport phenomena. This bonding mechanism reduces the overall energy of the system and enhances the mechanical and physical properties [72]. The sintering process of advanced ceramics including alumina, typically occurs below their melting temperatures, and encompasses multiple stages, as illustrated in Figure 2.6. These stages are controlled by mechanisms and driving forces, as well as the influence of key processing variables such as particle/powder size, temperature and applied pressure, all of which are crucial in the densification of the final sintered part [52][72]. The first stage is characterized by the interaction of the loose ceramic powder particles randomly distributed. This is followed by the initial stage which depicts a more pronounced contact between powder particles, accompanied by formation and growth of particle bonds known as sinter bonds. The interactions of the randomly distributed powder particles result in high volume of pores, which are reduced drastically at the intermediate stage during densification. The presence of pores is also due to the burning of the remnant binders during the temperature sintering. During the final stage, a dense structure is achieved by complete

closure and migration of the pores by the application of temperature and pressure [73][74]. Typically, as the sintering process progresses at the microstructural level, the growth of necks at particle interactions becomes apparent, indicating the formation of the sinter bonds. These bonds are established through atomic-level interactions, where the particles work to minimize the surface energy of the interacting particles. Therefore, predominant driving force during the powder particle interactions depends on the curvature of the particles coupled with the applied pressure. The kinetics of matter transport during sintering is governed by the diffusion of the atoms, ions and other charged species of the ceramic structure [52][75]. The sintering conditions such as temperature, time and pressure influence the rate of diffusion and thus control the grain growth during sintering. For alumina (α -Al₂O₃), the diffusion of aluminum and oxygen atoms across the grain boundary during sintering leads to growth of the Al₂O₃-Al₂O₃ particle bonding, which inspires grain coarsening [76][77][78].

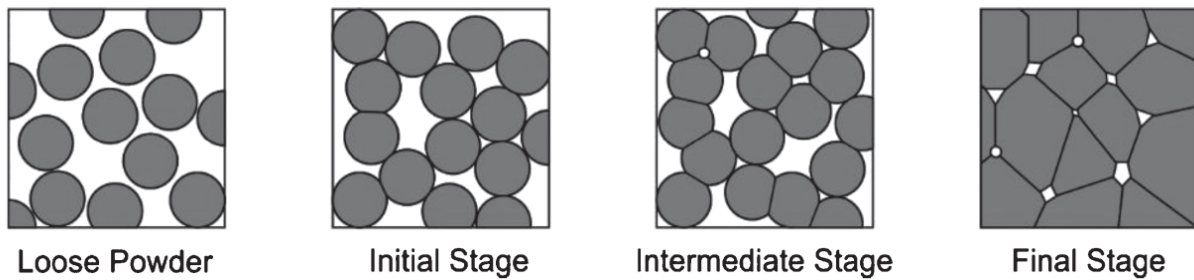


Figure 2.6: Stages of the sintering process of alumina and advanced ceramics [73].

Sintering processes can be categorized into two types: solid state sintering and liquid phase sintering. These sintering types are widely used for processing advanced ceramics including alumina(α -Al₂O₃) for high-performance engineering applications. During the process of liquid phase sintering, it is observed that at the sintering temperature, at least one phase experiences melting. This melting leads to the wetting of the remaining powder particles with the liquid phase, which facilitates particle bonding [73]. The solid-state sintering process entails compacting a green body into a solid object of high density at temperatures ranging from 1500-1800°C, without reaching the melting point (2050°C) [79]. Several sintering techniques have also been developed to fabricate bulk ceramic materials for structural and multifunctional applications. Traditional sintering methods including hot pressing (HP), hot isostatic pressing (HIP) and gas-pressure sintering (GPS) typically involve extended time durations due to the utilization of relatively low

heating and cooling rates (usually <50 °C/min). Other non-conventional/fast sintering techniques that require relatively lower energy and less time have been adopted in recent times. Spark plasma sintering (SPS), flash sintering (FS), induction sintering (HFIS), microwave sintering (FS) are examples of these advanced sintering. These techniques are however cost-intensive as compared to the conventional sintering technique [80][81].

2.3.5 Properties of Alumina Ceramic

Polycrystalline and nanocrystalline α -Al₂O₃ as a structural ceramic have many attractive properties that make it appealing for high-performance applications. The combination of its physical, chemical, and mechanical properties, along with its ready availability, provides Al₂O₃ ceramic with a competitive advantage over other structural ceramics. The remarkable hardness of α -Al₂O₃ (≥ 18 GPa) is ascribed to the strong ionic bonding between aluminum and oxygen atoms in its hexagonal crystal structure (HCP). As a result, α -Al₂O₃ is recognized as one of the hardest known materials in existence. Also, due to its high melting point and exceptional thermal stability, α -Al₂O₃ maintains its mechanical and structural integrity even when exposed to extreme temperatures. This property enables it to withstand and perform reliably in high-temperature environments [82][83]. α -Al₂O₃ also exhibits excellent chemical inertness and resistance to acids and alkalis, making it an ideal material for use in corrosive environments. Its ability to withstand chemical attack, coupled with high hardness make it a suitable candidate as a biomaterial. In addition, the electrical insulating properties, transparency to infra-red radiation and high dielectric strength of α -Al₂O₃ offer distinct advantages in electrical, optical and other functional applications [84][85]. These unique combinations of properties therefore enhance the broad use of α -Al₂O₃ in a wide range of technological applications, including electronics, optics, high-temperature and chemical environments. Tables 2-4 details the reported mechanical, wear/tribomechanical, thermal and electrical attributes of commercially produced α -Al₂O₃ for structural and multifunctional applications.

2.3.5.1 Mechanical Properties

The mechanical properties of bulk sintered α -Al₂O₃ such as density, hardness, bending and tensile strength, and elastic modulus determine their performance in structural and engineering

applications. The lightweight and mechanical characteristics of α -Al₂O₃ has merited several applications in recent technologies. For instance, high compressive strength at elevated temperatures confers the ability to withstand appreciable load without deformation or failure in harsh conditions. Nevertheless, the inclusion of pores in the structure of ceramics leads to a notable reduction in their mechanical properties including fracture toughness and strength. Employing nanosized powders (particle sizes <100nm) to fabricate alumina ceramic tend to enhance the strength of advanced ceramic materials such as alumina by forming fine-grained structures [86]. Examples of mechanical properties of fabricated α -Al₂O₃ is summarized in Table 2.2 below:

Table 2.2: Reported mechanical properties of alumina (α -Al₂O₃)

Sintering Technique	Grain Size (μm)	Density (g/cm^3)	Hardness (GPa)	Bending Strength (MPa)	Fracture Toughness (K_{IC}) ($\text{MPa}\cdot\text{m}^{1/2}$)	Elastic Modulus (GPa)	Refs.
Hot Pressing (HP) @ 1500°C	5	3.834	15	300	2.5	338	[87]
Spark Plasma Sintering (SPS) @ 1250°C	1.40	-	19.20	-	4.37	430-550	[88]
-	-	-	18-20	-	2-40	300-400	[89]
Hot Pressing (HP) @ 1650°C	-	-	15	250	3	-	[89]
SPS @ 1450 °C	-	3.90	9.21	-	3.88	-	[90]
Hot Isostatic Pressing (HIP) @ 1300 °C	1.23	-	21.3	-	3.5	382	[91]
Hot Pressing (HP)	10	3.70	13.73	290	4.3	380	[92]
Hot Isostatic Pressing (HIP)	0.44	3.98	21.26	-	3.7	436	[93]

2.3.5.2 Wear and Tribomechanical Properties

The wear and tribomechanical characteristics of alumina (Al_2O_3) makes it an exceptional candidate for various structural and tribological components. This is because alumina ceramic demonstrates good resistance to wear, making it well-suited for applications involving components that experience high levels of friction and wear including bearings, cutting tools, grinding disks, biomedical components, valves and nozzles [94][95]. Wear is a phenomenon characterized by the gradual erosion of material from the surfaces of a body as a result of their relative motion and contact. This process involves a combination of mechanical, chemical, and thermal processes and mechanisms, leading to both brittle fracture and plastic deformation of the solid surfaces involved. Furthermore, alumina and other advanced ceramics exhibit various wear modes, including adhesive wear, fatigue wear, flow wear, mild wear, and severe wear. [96][97]. The wear resistance properties of alumina ceramic can be attributed to its microstructure, such as the grain size, as well as its physical and mechanical properties hardness. Research has indicated that sintered monolithic alumina with a finer grain structure tends to exhibit superior tribological properties, emphasizing the importance of microstructure in determining wear resistance [94][96]. Meng et al. conducted studies that clearly showed a significant difference in wear performance between coarser and finer-grained alumina ceramic samples prepared via spark plasma sintering (SPS). Specifically, the coarser-grained alumina exhibited a 50% higher volume loss and low wear resistance compared to the finer-grained counterpart [98]. The low friction coefficient of alumina ceramics, which is accompanied with minimal frictional forces is an essential trait in applications where reducing friction and minimizing energy losses such as in sliding bearings or grinding tools [97]. The wear response of alumina ceramic is dependent on various contact conditions. These conditions include the contact pressure and load, the nature of the contacting surface (including its texture, roughness, topography), the material of the counter-body, the sliding velocity, the shape of the contact, the stiffness of the suspension, the presence of lubricant, and the environmental factors such as temperature and humidity [96][97][98]. Various wear test configurations including reciprocating sliding wear, rotary wear test, block-on-ring, pin-on-disk, ring-on-disk, plane bearing and crossed cylinders are utilized to characterize the access tribological properties of alumina and other advanced ceramics (Figure 2.7) for specific applications such as biomedical and automotive [99]. Table 2.3 summarizes reported wear and tribological properties of monolithic alumina ceramic.

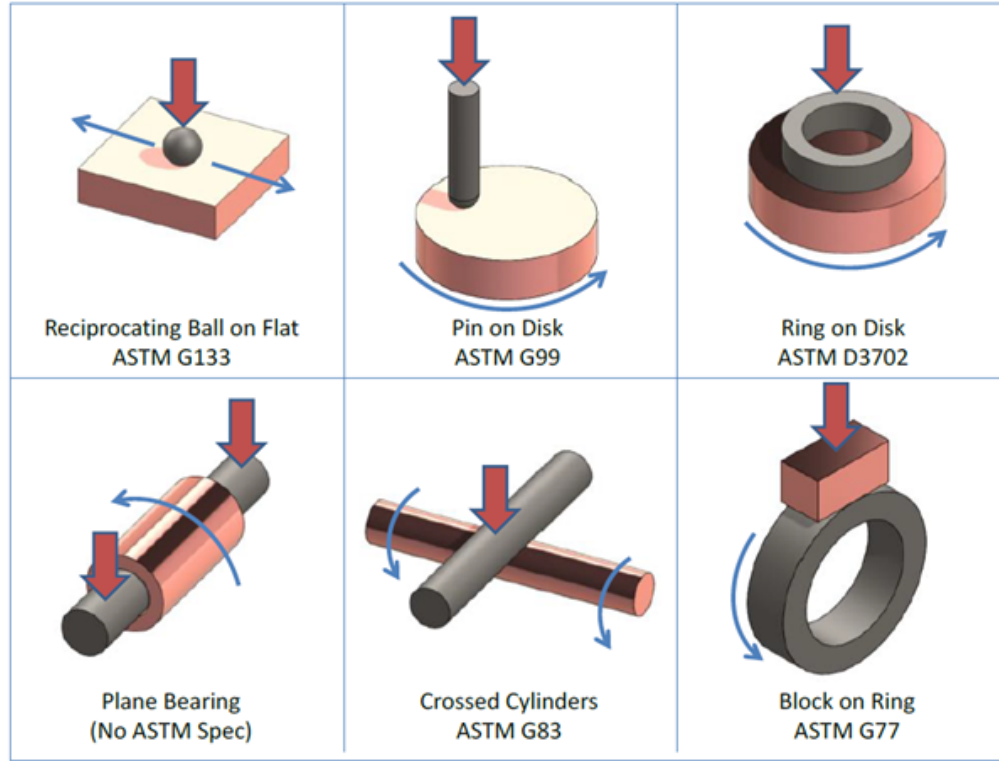


Figure 2.7: Friction and wear test configurations used for alumina (Al_2O_3) ceramics [99].

Table 2.3: Literature survey on wear and tribological properties of monolithic alumina Al_2O_3

Sintering Technique	Grain size (μm)	Friction coefficient (COF)	Wear rate ($\text{mm}^3/\text{N.m}$)	Wear testing configuration	Normal load (N)	Counter-body and environment	Ref.
HP @ 1300 °C	0.7, 5 and 25	0.2-0.65	10^{-13} - 10^{-10}	Reciprocating (Ball-on-flat)	8-40	Diamond Dry sliding	[100]
HP @ 1550 °C	13.0	0.44-0.77	10^{-6}	Block-on-ring	4.9, 14.7, 24.5	Tool steel Dry and water	[101]
HIP @ 1450 °C	0.16	0.19-0.55	10^{-3}	Ball-on-disk	2, 8, 16	Alumina ball Fluid	[102]
HP @ 1275 °C	4, 0.45 and 0.95	~0.155	10^{-7}	Pin-on-disk	10 and 50	Bovine serum fluid	[103]
-	0.098	0.24	10^{-6}	Reciprocating (Ball-on-flat)	9.81	Tungsten carbide ball	[104]

2.3.5.3 Thermal and Electrical Properties

Thermal and electrical properties are useful physical properties of alumina (Al_2O_3) ceramic that merits several multi-functional applications. These functional attributes, coupled with attractive mechanical characteristics make advanced alumina ceramic ideal for a wide range of applications including electronics, power generation, aerospace, automotive, and high-temperature processing components. Specific thermal properties such as high melting temperature ($\sim 2050^\circ\text{C}$), good thermal conductivity, thermal diffusivity, low thermal coefficient of friction, thermal shock resistance and stability, good specific heat capacity are favorable in many applications [105][106]. For example, the combination of low coefficient of thermal expansion, thermal shock resistance and stability attributes are essential in limiting thermal stress, cracking and deformation during high-temperature environments [107]. Further, alumina ceramic has appealing electrical properties including high electrical resistivity ($10^{14} \Omega \cdot \text{cm}$), good dielectric strength, low electrical conductivity and low dielectric loss. Excellent insulating material for use in electrical and electronic applications due to high resistivity to electric current flow. Alumina ceramics can tolerate high voltages without damaging as a result of their high dielectric strength. Low dielectric loss property enables minimum dissipation of energy in the presence of electric field [105][107]. Combination of these functional properties makes them ideal candidates in many industries where thermal and electrical performances are needed. Summary of thermal and electrical properties of monolithic alumina is presented in Table 2.4:

Table 2.4: Thermal and electrical properties of alumina (Al_2O_3)

Coefficient of thermal expansion ($10^{-6} / \text{K}$)	Thermal conductivity (W/m.K) at 20°C	Specific heat capacity (J/kg.K)	Thermal shock resistance (K)	Electrical resistivity at 20°C $\Omega \cdot \text{cm}$	Dielectric constant	Dielectric strength (kV/mm)	Ref.
8.5	30	900	190	$10^4 - 10^{14}$	-	>25	[92]
8.3	29	900	180	10^{14}	-	19	[108]
-	33	800	-	$>10^{14}$	-	>30	[92]
5.8	41.9	753	-	$>10^{16}$	7.5-10.5	17	[109]
8.0	28-35	-	-	$>10^{14}$	9-10	10-35	[109]
8.0	34	780	-	$>10^{14}$	9.9	15	[92]

2.4 Alumina Matrix Nanocomposites

Alumina matrix nanocomposite is a type of oxide-based CMCs that combines a monolithic alumina (Al_2O_3) ceramic matrix with at least one nano-scale reinforcement phase ($<100\text{nm}$) or additives with nanometric dimensions. Through microstructural tailoring and design, the inclusion of nanometric reinforcement materials to the alumina ceramic matrix confers superior physical (thermal and electrical), mechanical and biomedical properties and functionalities relative to the pure or monolithic alumina structure [20][25]. The concept of ceramic structural design to form nanocomposite systems was introduced in 1991 by K. Niihara [110]. Figure 2.8 shows the distribution of various nano-phase reinforcement with different geometries in a typical ceramic matrix ranging from nano-fillers (nanospheres and nanoparticles), fibers and particulate powders [20]. The nanometric reinforcement phases commonly used for alumina matrix include carbon-based nanostructures (carbon nanotube, graphene, nanofibers), zirconia nanoparticles (npZrO_2) and silicon carbide nanoparticles (npSiC) [20][25]. These low-density reinforcement particles enhance the fracture toughness and other mechanical and physical properties of alumina-based nanocomposites whilst maintaining their desirable lightweight attributes. The enhanced properties of the nanocomposites are dependent on several factors such as initial powder/particle size, particle distribution within the matrix, amount of the reinforcement phases (wt%, vol%), final grain structure, interfacial interactions between matrix and the reinforcement particles and active toughening mechanisms [111]. The dispersion of reinforcement particles within the alumina ceramic matrix is accomplished through the utilization of nanocomposite fabrication and sintering techniques, which closely resemble the processing method employed for monolithic ceramics.

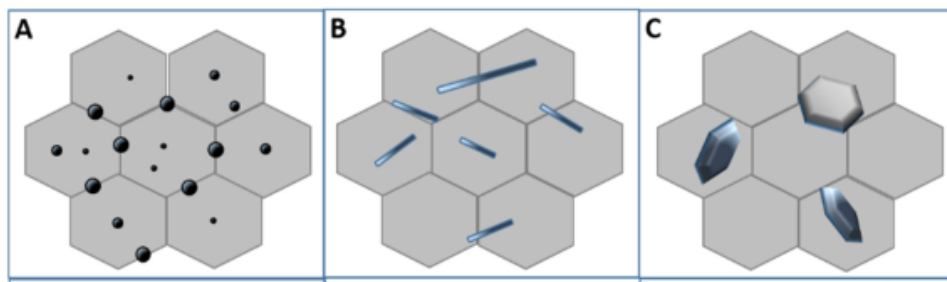


Figure 2.8: Distribution of different reinforcement morphologies illustrating the dispersion of (a) particulates (b) elongated/fiber and (c) platelet-like nano-reinforcement particles within ceramic matrix grains and on grain boundaries [20].

2.4.1 Properties of Alumina Matrix Nanocomposites

The addition of different nano-reinforcement materials with specific physical and mechanical properties to alumina matrix confers exceptional properties to the nanocomposites for wide range of applications including cutting tools, wear-resistant coatings, biomedical, defense and aerospace components. The improved mechanical strength, hardness, fracture toughness, wear resistance, chemical stability, high-temperature resistance, thermal and electrical properties compared to pure monolithic alumina is credited to the inherent nature of inclusions, matrix microstructure and mechanisms introduced by the nano-reinforcement structures. The effect on the nano-reinforcement particles on the properties of alumina matrix nanocomposites is dependent mainly on the distribution and optimum amount of the reinforcement within the alumina matrix.

The final grain structure with the inclusion of nano-reinforcement phases is essential for the bulk property enhancement of processed alumina matrix nanocomposite. According to the Hall-Petch phenomenon, the mechanical attributes such as strength and microhardness have inverse relationship with the grain size of the structural material, as presented in equation (2.4) below [112]:

$$\sigma_s = \sigma_o + \frac{k}{\sqrt{d}} \quad (2.4)$$

where σ_s represents strength, σ_o is the yield stress, k is a constant and d represents the grain size of the polycrystalline or nanocrystalline material. The anticipated increased strength in alumina and ceramic nanocomposite structures can be attributed to the load-transfer and load-bearing capabilities of nanostructures including carbon nanotubes, graphene and nanofibers. The dissemination of applied load and stress to the surrounding matrix structure leads to increased strength properties in alumina-based nanocomposites [20][113]. Other micro-strengthening mechanisms such as dislocation motion inhibition and obstruction by reinforcement particles at convenient sites within the matrix grains, as well as the grain boundaries, enhance the flexural and bending strength properties of the nanocomposites. These strengthening mechanisms is also associated with intergranular (along grain boundary) and transgranular (within grains) fracture modes which is predominant in alumina and ceramic nanocomposite systems [113]. The presence of a robust interface facilitates efficient load transfer between the reinforcement and the matrix, thereby reducing the occurrence of interfacial debonding or failure. This, in turn, enhances the overall strength of the ceramic nanocomposite structure [41].

However, the fracture toughness property of ceramic nanocomposites is not always dependent on grain size and grain structure of the matrix but rather on the toughening mechanisms and interfacial response in the presence of applied load. Fracture toughness can be defined as the capacity of a material or nanocomposite system to absorb energy in the presence of a flaw or crack without experiencing failure. Brittle ceramics such as monolithic alumina experiences little or no plastic deformation and exhibit catastrophic failure in the presence of propagating crack due to low resistance to crack propagation. The critical crack which results in failure of brittle ceramics such as alumina is characterized by the stress intensity factor expressed by Griffith's relation in equation 2.5 below [114]:

$$K_{IC} = \sigma_f \times Y \times \sqrt{\pi \cdot a} \quad (2.5)$$

where K_{IC} is the fracture toughness, σ_f represents the critical stress, Y denotes the calibration factor which is dependent on configuration of the crack and loading geometry, and a is the crack size/length. The dispersion of nano-reinforcement materials such as zirconia, graphene and carbon nanotubes produce better resistance and impedance to crack initiation, growth and propagation within the alumina matrix material, and consequently result in higher fracture toughness properties as compared to the monolithic matrix. Predominant toughening mechanisms including crack deflection, crack bridging, micro-cracking, crack branching and phase transformation toughening are achieved by the inclusion of optimum amount of the nano-reinforcement phases in the nanocomposite system [40][41][113].

Alumina matrix nanocomposite structures also exhibit improved thermal and electrical properties with the addition of carbon-based nanostructures such as graphene, carbon nanotubes and carbon fibers. The addition of thermally and electrically conductive nano-reinforcements forms heat transfer and electrical pathways within alumina ceramic matrix for efficient transport of thermal (heat transfer and dissipation) and electrical charges. The enhanced thermal and electrical conductivity makes these nanocomposites suitable for applications in the thermal and electronic industries [115][116].

The lubricating properties coupled with excellent mechanical attributes of nano-reinforcements such as graphene, carbon nanotubes and zirconia can also result in good tribo-mechanical performance of alumina-based nanocomposites. The dispersion of the nano-reinforcement

particles act as barriers to minimize friction, surface deformations and abrasions by effectively transporting and distributing load or wear-induced stresses during localized sliding, which enhances the overall wear resistance of the nanocomposite system and improves their tribological performances [36][117].

Summary of mechanical, tribo-mechanical, thermal and electrical properties of fabricated alumina matrix nanocomposites is illustrated in Table 2.5.

Table 2.5: Summary of reported properties of fabricated alumina (Al_2O_3) matrix nanocomposites

Mechanical Properties						
Processing conditions	Alumina matrix Nanocomposite	Grain size (μm)	Hardness (GPa)	Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	Flexural strength (MPa)	Refs.
Hot pressing	Monolithic Al_2O_3	0.99	~19.8	~4.5	~470	
(HP)	$\text{Al}_2\text{O}_3 + \text{GN}(1\text{wt}\%)$	0.55(44%↓)	21.3(7.6%↑)	7.4(65%↑)	764(55%↑)	[118]
@ 1550°C	$\text{Al}_2\text{O}_3 + \text{GN}(3\text{wt}\%)$	0.86(13%↓)	~16(19%↓)	~4.8(7%↑)	~560(19%↑)	
Pressureless	Monolithic Al_2O_3	1.4	14.3	4.2	425	
sintering	$\text{Al}_2\text{O}_3 + \text{CNT}(0.1\text{wt}\%)$	1.1(21%↓)	15.2(6.3%↑)	4.3(2.3%↑)	439(3.3%↑)	[120]
@ 1600°C	$\text{Al}_2\text{O}_3 + \text{CNT}(0.5\text{wt}\%)$	0.98(30%↓)	15.7(9.7%↑)	4.8(4.7%↑)	443(4.2%↑)	
Pressureless	Monolithic Al_2O_3	1.4	14.3	4.2	425	[120]
@ 1600°C	$\text{Al}_2\text{O}_3 + \text{ZrO}_2(20\text{wt}\%)$	1.2(14%↓)	12.4(13%↓)	4.6(9.5%↑)	403(5.1%↓)	
Hot pressing	Monolithic Al_2O_3	28	14.8	2.8	220	[121]
@ 1550°C	$\text{Al}_2\text{O}_3 + \text{SiC}(5\text{wt}\%)$	~8(71%↓)	20.8(41%↑)	5.9(111%↑)	230(4.5%↑)	
Thermal and Electrical Properties						
Processing conditions	Alumina matrix Nanocomposite	Grain size (μm)	Electrical conductivity (S/m)	Thermal conductivity (W/m.K)	Thermal diffusivity (cm^2/s)	Refs.
Hot pressing	Monolithic Al_2O_3	1.4	10^{-6}	28	0.093	
@ 1350°C	$\text{Al}_2\text{O}_3 + \text{SiC}(10\text{vol}\%)$	2.2 (57%↑)	10^{-3} ($10^{50}\%$ ↑)	~32 (14%↑)	0.11(18%↑)	[122]
	$\text{Al}_2\text{O}_3 + \text{SiC}(20\text{vol}\%)$	1.5 (7%↑)	10^{-2} ($10^{60}\%$ ↑)	~40 (42%↑)	0.14(51%↑)	

Spark plasma sintering	Monolithic Al ₂ O ₃	3	-	~21	0.54	
1500°C	Al ₂ O ₃ +GN(0.5wt%)	~1 (67%↓)	-	~30 (43%↑)	~0.78(44%↑)	[123]
	Al ₂ O ₃ +GN(2wt%)	~1(67%↓)	-	~27 (29%↑)	~0.72(8%↑)	
Spark plasma sintering	Monolithic Al ₂ O ₃	0.89	-	-	-	
@ 1375°C	Al ₂ O ₃ +GN(0.58wt%)	0.47(47%↓)	0.85×10 ²	-	-	[124]
	Al ₂ O ₃ +GN(0.77wt%)	0.46(48%↓)	1.84×10 ²	-	-	
Hot pressing	Monolithic Al ₂ O ₃	2.15	10 ⁻¹³	32.7	-	
@ 1550°C	Al ₂ O ₃ +CNT(0.5wt%)	0.4(81%↓)	10 ^{1.5} (10 ¹⁶⁰ %↑)	25.5(22%↓)	-	[125]
	Al ₂ O ₃ +CNT(1.5wt%)	0.26(88%↓)	10 ² (10 ¹⁷⁰ %↑)	22.5(31%↓)	-	
Sintering	Monolithic Al ₂ O ₃	-	-	24	0.0108	[126]
@ 1350°C	Al ₂ O ₃ +ZrO ₂ (20wt%)	-	-	15(38%↓)	0.014(30%↑)	

Tribo-mechanical properties

Processing conditions	Alumina matrix Nanocomposite	Grain size (μm)	Coefficient of friction (COF)	Wear mass loss (μg)	Wear volume loss (mm ³)	Refs.
Hot pressing	Monolithic Al ₂ O ₃	1.3	0.5	~32.5	-	
@ 1600°C	Al ₂ O ₃ +CNT(2wt%)	0.45(65%↓)	0.47(6%↓)	~17(47%↓)	-	[127]
	Al ₂ O ₃ +CNT(5wt%)	0.37(72%↓)	0.43(14%↓)	~11(66%↓)	-	
Sintering	Monolithic Al ₂ O ₃	1.8	0.68	-	~0.95	[128]
@1300°C	Al ₂ O ₃ +ZrO ₂ (15wt%)	0.8(72%↓)	0.67(14%↓)	-	~0.1(89%↓)	
Spark plasma sintering	Monolithic Al ₂ O ₃	0.96	0.45	-	~0.17	
@ 1400°C	Al ₂ O ₃ +GN(0.5vol%)	0.80(17%↓)	0.35(22%↓)	-	0.06(53%↓)	[129]
	Al ₂ O ₃ +GN(5vol%)	0.77(20%↓)	0.5(11%↑)	-	~0.3(76%↑)	

NB: %↑ denotes percentage increase, %↓ denotes percentage decrease, Al₂O₃ denotes alumina, GN denotes graphene, CNT denotes carbon nanotubes, ZrO₂ denotes Zirconia, SiC denotes silicon carbide.

2.4.2 Potential Applications of Alumina Matrix Composites and Nanocomposites

Alumina matrix nanocomposite as an advanced material merits wide range of applications in current and future applications. These applications include but not limited to cutting tools,

aerospace, automotive, ballistic and defense, electronics, chemical, biomedical, energy and power generation and environmental. Through the deliberate design and customization of the microstructure of the monolithic alumina matrix, incorporating nano-reinforcement structures, a diverse range of physical, mechanical, and tribological properties can be achieved. These enhanced properties make these nanocomposite systems well-suited for structural and multifunctional applications. Therefore, the specific application of nanocomposites relies on the selection of the appropriate nano-reinforcement material. Figure 2.9 presents a depiction of different nano-reinforcements employed in alumina matrix nanocomposites along with their potential applications.

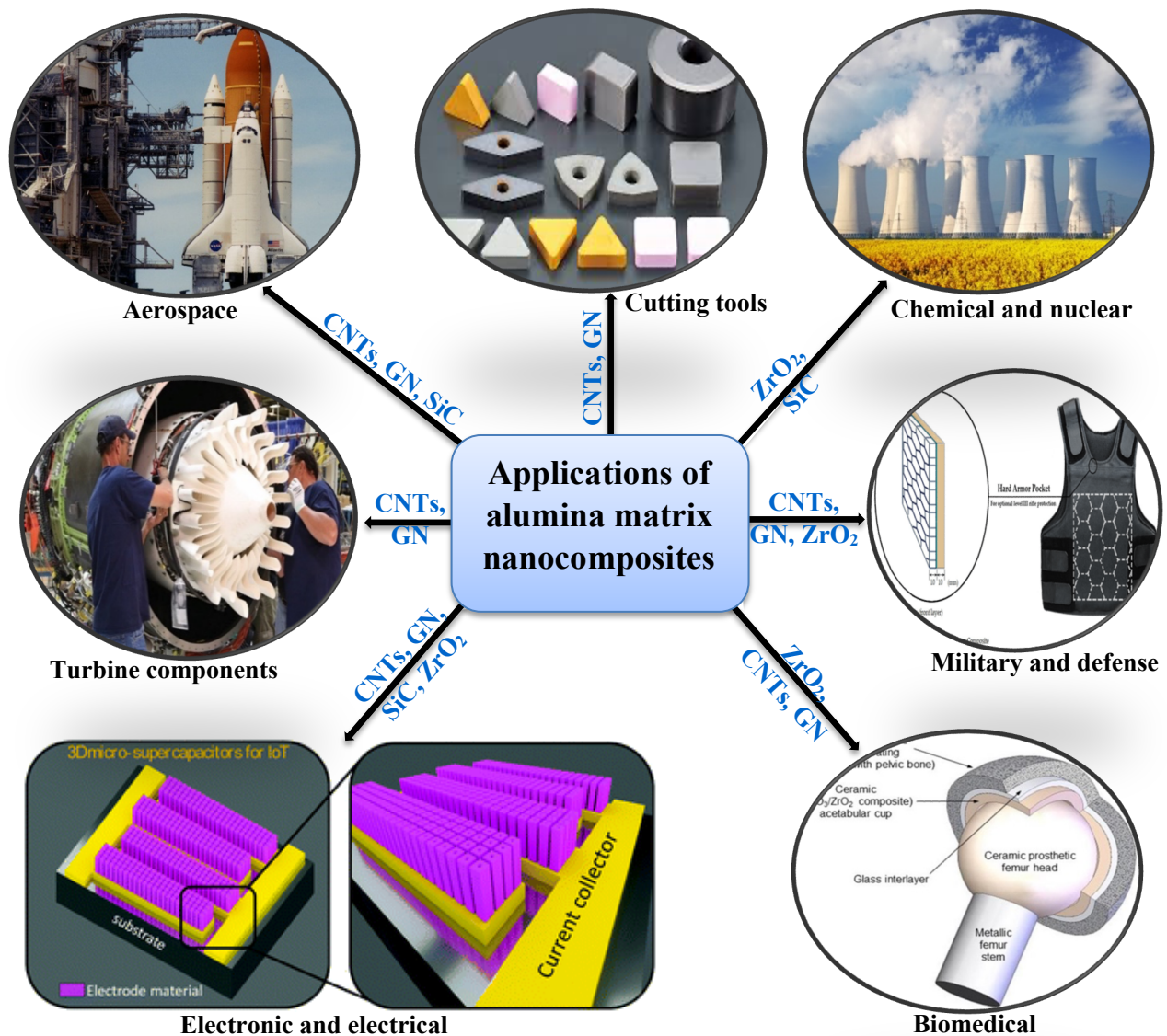


Figure 2.9: Potential applications of alumina matrix nanocomposites [130][131][132][133]

2.5 Fabrication Approach of Alumina Matrix Nanocomposites

Manufacturing of alumina (Al_2O_3) matrix nanocomposites which involves the dispersion of nano-reinforcement materials within the alumina matrix follows similar powder route as monolithic alumina fabrication. The quality of the final nanocomposite structure depends on the concentration of the nano-reinforcements and their dispersion approach, the consolidation and final sintering technique. Effective dispersion of nano-reinforcements in alumina and other ceramic matrices lead to high density structures with improved mechanical properties. Over the years, dispersion issues including agglomeration have been identified with nanometric additives such as graphene and carbon nanotubes [134][111]. High agglomeration due to van der Waals forces within these carbon-based nanostructures results in inhomogeneous dispersions leading to porosities and defects after sintering. In addition, the high surface area and aspect ratio of carbon nanotubes and graphene, although advantageous in certain aspects, pose a significant challenge in terms of achieving proper dispersion. This limitation has prompted the exploration of various techniques aimed at enhancing the dispersion of graphene, ultimately facilitating effective load transfer from the ceramic matrix to the graphene nanofillers [134][135][136]. Hence, mixing and consolidation methods are essential in dictating the final structural integrity and properties of alumina-based nanocomposites. Figure 2.10 summarizes fabrication approach for alumina and ceramic-based nanocomposites.

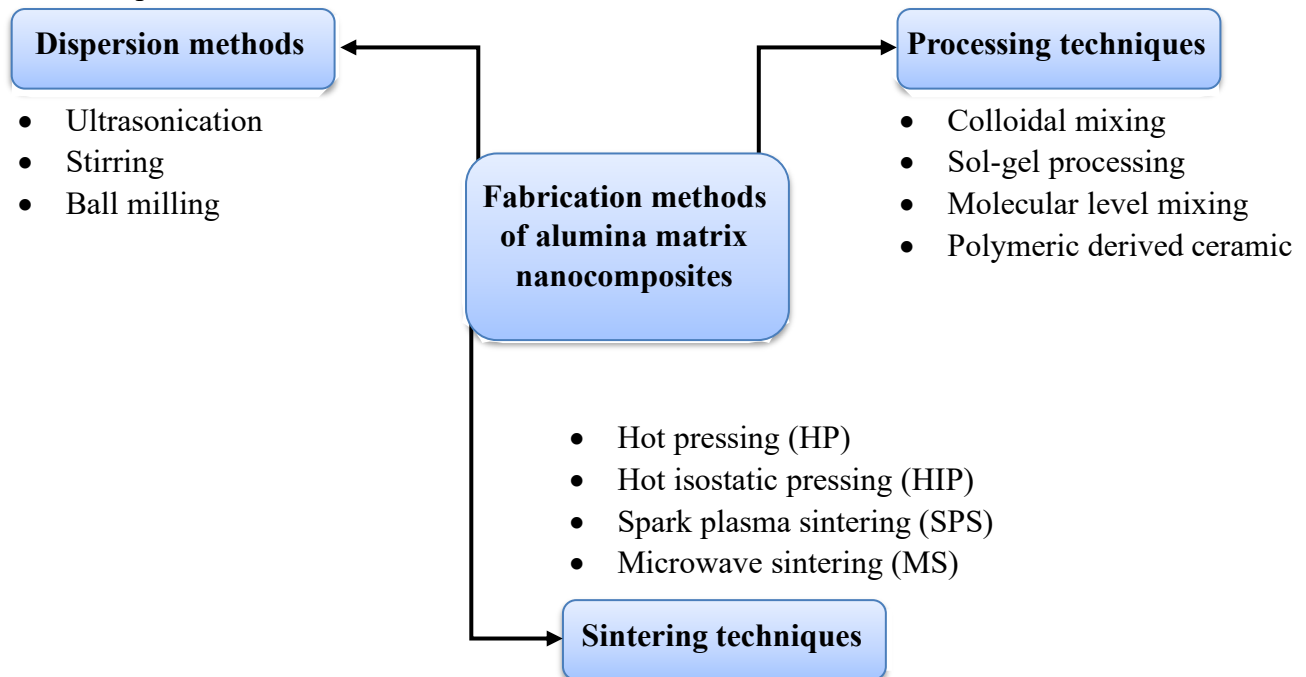


Figure 2.10: Fabrication methods for alumina-based nanocomposites

2.5.1 Colloidal Processing Method

Colloidal processing is a wet method employed to consolidate particles with a high density and achieve a homogeneous microstructure. This is accomplished by controlling the interparticle interaction within a suspension. Colloidal processing has been used in recent years to fabricate alumina and ceramic-based nanocomposites to produce high performance nanocomposite structures with high degree of microstructural homogeneity and minimum defects from the mixing to the green compact stage [137]. A multiphase system is formed by dispersing one or more phases (normally in powder form) in liquids for either direct consolidation of the suspensions or as an intermediate step for subsequent processing operations. The size of the dispersed phase typically falls within the nanometer (10^{-9} m) to micrometer (10^{-6} m) range, making colloidal dispersions predominantly composed of large molecules and/or small particles. The interface between the dispersed phase and the dispersing medium plays a critical role in determining surface properties, such as adsorption, surface charge, and electrical double layer. In colloidal suspensions, particles are dispersed within a surrounding medium, and the overall interaction involves particle-particle interactions, as well as interactions between the medium and particles or between different components of the medium [138][139]. Typically, a colloidal process for alumina and ceramic-based nanocomposites involves five stages: (i) powder synthesis (ii) preparation of suspension (iii) consolidation into desired shape and geometry (iv) solvent phase removal and (v) densification process to produce final microstructure [140][141]. Figure 2.11 illustrates colloidal processing of ceramic matrix nanocomposites.

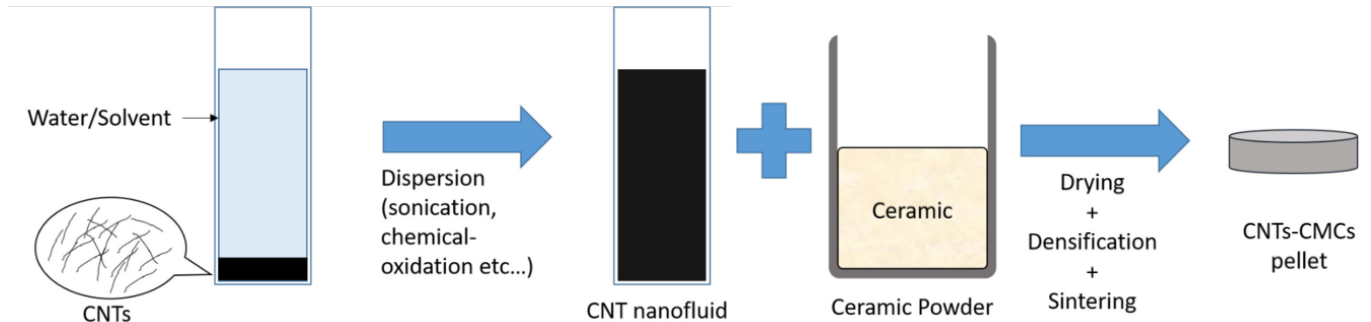


Figure 2.11: Schematic diagram of colloidal processing illustrating the dispersion of CNTs into CNT suspension and ceramic powder mixed for densification and sintering into CNTs-CMCs pellets [142].

2.5.2 Sintering Techniques for Alumina Matrix Nanocomposites

Final bulk alumina matrix nanocomposite structure with high density is achieved using high temperature sintering techniques. Achieving full or nearly full density during the sintering of nanocomposite powders without significant grain growth remains a considerable practical challenge. In alumina and other ceramic-based nanocomposites, conventional sintering techniques that require high temperatures ($\sim 1300^{\circ}\text{C}$ - 1600°C) for complete densification often led to the formation of large grain sizes. Sintering parameters such as applied pressure, temperature, powder size and time have been optimized via several sintering techniques to overcome this densification challenge during sintering of ceramic nanocomposites [111][143]. Hot pressing (HP), hot isostatic pressing (HIP), spark plasma sintering (SPS) and microwave sintering have been adapted in recent years to achieve high densification and limited grain growth in alumina and oxide ceramic nanocomposites. The identified sintering parameters can be applied simultaneously to achieve a fully dense nanocomposite structure for high performance applications. The mechanisms during sintering such as driving force and mass diffusion is similar to that of the monolithic ceramic previously discussed in section 2.3.4. However, the rate of these mechanisms including diffusion rate are influenced by the addition of the nano-reinforcement dispersed within the matrix material. The choice of the sintering method is dependent on cost, nanocomposite material, conditions of sintering and availability of sintering equipment.

2.5.2.1 Hot Pressing (HP)

Hot pressing is widely employed as the primary technique for manufacturing dense, non-oxide monolithic ceramics and their composites. Hot-pressing techniques typically require demanding processing conditions, which involve high temperatures (around 1600°C), high pressure, and extended holding times ranging from minutes to hours. These conditions are necessary to achieve effective densification of the nanocomposite material [88]. During hot pressing, both temperature and pressure are applied simultaneously to the powder compact within a die. Induction coils and a graphite die are commonly used for heating, while hydraulic systems are often employed for applying pressure. The application of pressure leads to the development of high stress at the contact points between particles, which in turn increases local diffusion rates. Various factors including particle size, temperature, pressure, heating rate, and holding time influence the density and microstructure of the hot-pressed compacts. It is important to note that a controlled atmosphere is

typically necessary for hot pressing non-oxide materials to limit contamination and reaction in the chamber [111][144][145]. Figure 2.12 presents a schematic representation of hot-pressing.

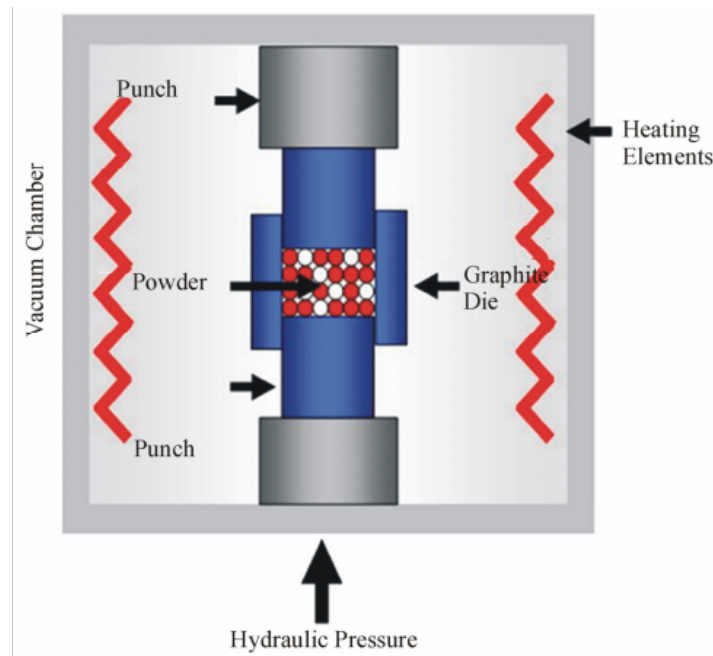


Figure 2.12: Schematic illustration of hot-pressing sintering technique used for alumina matrix nanocomposites [146].

2.5.2.2 Spark Plasma Sintering

Spark Plasma Sintering (SPS) has gained significant attention in the past two decades due to its exceptional effectiveness in achieving rapid sintering and densification. It has proven particularly advantageous for materials that are challenging to sinter, including highly refractory materials, metastable phases, and nanomaterials. SPS technique involves the simultaneous application of uniaxial pressure and high-intensity, low-voltage, pulsed current. It can be viewed as a modification of hot pressing, where the traditional furnace is replaced by a mold that contains the sample [147]. The mold and the sample are directly heated by the current passing through them during the SPS process. The design of the direct current heating in SPS enables higher ramp rates and shorter holding times, which are crucial for preserving the fine microstructure of the starting powder in the final sintered nanocomposite [148]. The SPS technique can be applied to both conducting and non-conducting composites to achieve a poreless state under optimal sintering conditions. In the case of a high-resistance powder, a significant portion of the current passes

through the conductive die, resulting in minimal direct current Joule heating of the sample itself. Figure 2.13 illustrates the spark plasma sintering (SPS) technique.

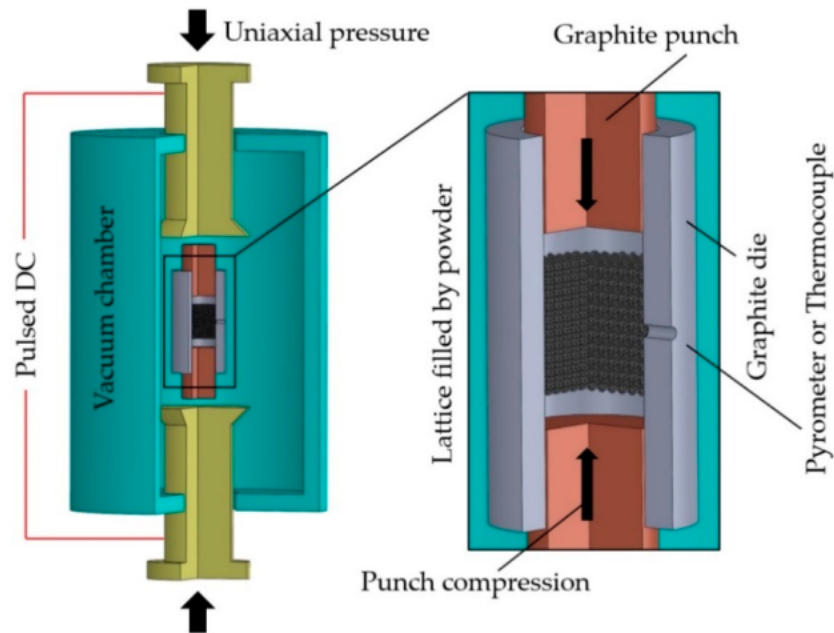


Figure 2.13: Schematic illustration of spark plasma sintering technique used for alumina matrix nanocomposites [149].

2.6 Properties of Zirconia (ZrO_2) Reinforcements

Zirconia (ZrO_2) is a highly desirable structural ceramic that is frequently employed to enhance the fracture toughness of structural alumina. The superior fracture toughness, low thermal and ionic conductivity, as well as its biocompatibility, make zirconia ceramic an appealing choice for a wide range of applications. These properties also make it an attractive reinforcement phase when combined with alumina [150]. In addition to restraining the abnormal grain growth of alumina during sintering, the inclusion of the zirconia particles also provides the improved strength and toughness of alumina (K_{IC} from $3\text{--}8\text{MPa}\cdot\text{m}^{1/2}$) in the form of phase transformation [151][152]. The metastable tetragonal to monoclinic phase transformation ($t\text{-ZrO}_2$ to $m\text{-ZrO}_2$) of the added zirconia reinforcements is accompanied with substantial volume expansion (about 3-5%) which causes constraint of the matrix grains and provide toughening effect to the composites [153][154]. The level of increase in the fracture toughness property of alumina/zirconia composites is however dependent on the distribution of the zirconia particles, grain size of the particulate zirconia phase and the concentration of the zirconia added [150][155]. Figure 2.14 shows the distribution of ZrO_2

reinforcement materials within alumina (Al_2O_3) matrix. Homogeneous dispersion of an optimum amount ($>8\text{vol}\%$) of zirconia phases within alumina have been reported by several studies to yield significant increase in the fracture toughness and other mechanical properties of the fabricated composites [156][157]. A sufficient amount of zirconia incorporated within the alumina provide substantial inhibition of the matrix grain movements during sintering and decrease the grain size, as reported by several works [156]. Rao et al used co-precipitation route to prepare $\text{ZrO}_2\text{-Al}_2\text{O}_3$ composites and estimated the fracture toughness (K_{IC}) value using the Vickers micro-indentation method, and recorded an increase from $4.45\text{MPa}\cdot\text{m}^{1/2}$ to about $7.6\text{MPa}\cdot\text{m}^{1/2}$ when $10\text{wt}\%\text{ZrO}_2$ was added to the alumina matrix. The 71% improvement in the toughness was attributed to the fine distribution of the ZrO_2 phase and smaller grain size of the matrix [157]. Ganesh et al also reported an approximate increase in fracture toughness up to $7.38\text{MPa}\cdot\text{m}^{1/2}$ in zirconia toughened alumina (ZTA) composites prepared by gel casting method with different zirconia compositions ($30\text{wt}\%$ and $60\text{wt}\%\text{ZrO}_2$) [158]. Naglieri et al also studied the mechanical properties of alumina-zirconia composites (with ZrO_2 amounts varying from $5\text{-}20\text{vol}\%$), which were prepared using a combination of wet chemical method and pressureless sintering at 1500°C for 60 minutes. The composite with $10\text{vol}\%\text{ZrO}_2$ had the highest fracture toughness value with finer grains as compared to the $5\text{vol}\%\text{ZrO}_2$ which recorded the lowest toughness due to the coarsened microstructure [159].

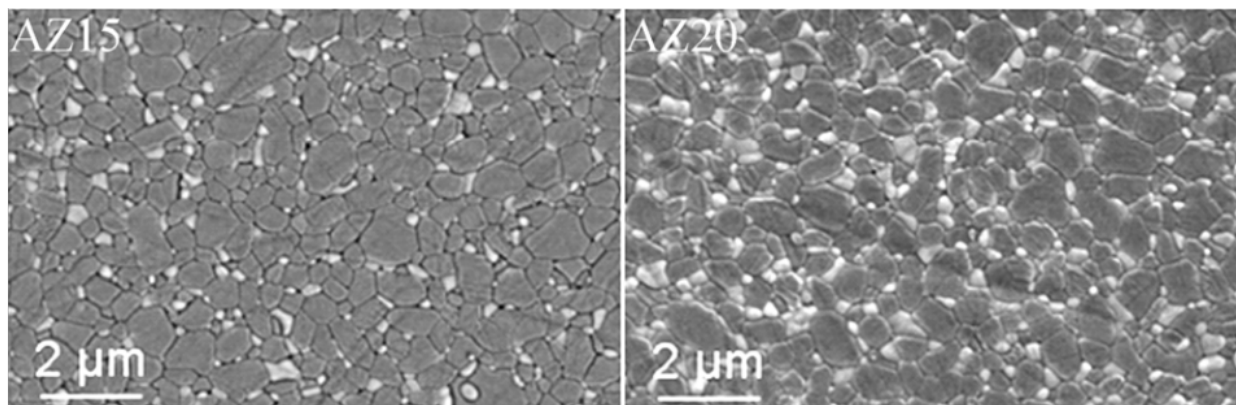


Figure 2.14: Microstructure of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ nanocomposite system showing distribution of ZrO_2 particles within the matrix [159].

2.6.1 Toughening Effect of Zirconia (ZrO_2) in Alumina-Zirconia Nanocomposites

The toughening influence in zirconia (ZrO_2) ceramic make it an essential reinforcement material for alumina matrix nanocomposites. The relatively high toughness exhibited by ZrO_2 can be attributed to its inherent toughening mechanisms, which are closely associated with its metastable phase. As a polymorphic ceramic material, monolithic ZrO_2 can exist in 3 crystalline phases namely: monoclinic, tetragonal and cubic (Figure 2.15) [153]. Phase transformations occur in the presence of temperature or applied stress. In its unmodified state, ZrO_2 undergoes crystallization in a specific sequence during cooling from high temperature. Initially, it crystallizes in the cubic phase (c- ZrO_2) at temperatures below $2,680^\circ\text{C}$. As the temperature decreases further, it undergoes a transformation to the tetragonal phase (t- ZrO_2) at $2,370^\circ\text{C}$. Lastly, at temperatures below $1,770^\circ\text{C}$, it transitions to the monoclinic phase (m- ZrO_2) [153][154]. However, in the presence of crack or applied stress, the localized transformation results in toughening. This is known as stress-induced transformation toughening. The phase transformation from the metastable t- ZrO_2 to the

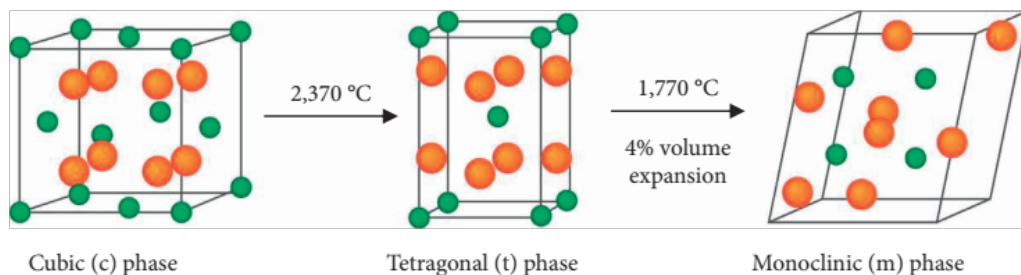


Figure 2.15: Temperature dependent polymorphic phases in ZrO_2 [153].

stable monoclinic structure (m- ZrO_2) under the influence of mechanical stress/propagating crack front is accompanied by volume expansion ($\sim 4\%$) and a shear strain. This process can induce a net compressive force in the surrounding zone of the propagating crack tip (Figure 2.16). This mechanism hinders the propagation of cracks and enhances the overall toughness of the Al_2O_3 - ZrO_2 nanocomposite systems [160].

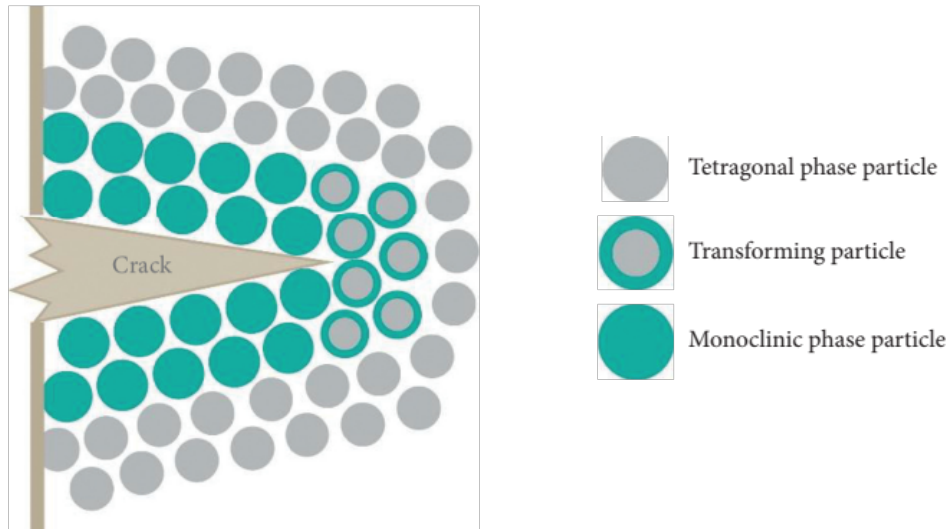


Figure 2.16: Transformation toughening of ZrO_2 in the presence of crack [153].

2.6.2 Deteriorating Effect of ZrO_2 Addition to Alumina Matrix Nanocomposites

Even though the ideal composition of added ZrO_2 (8vol% and above) within the monolithic Al_2O_3 matrix yields improved toughness and strength, other mechanical properties accompanied such as hardness, strength and wear resistant properties are not necessarily improved relative to that of the monolithic Al_2O_3 [159][161][162]. In the work of Naglieri et al, it was shown that the Vickers hardness decreased gradually with the addition of ZrO_2 with compositions from 10-20vol% despite the significant improvement in matrix grain refinement and fracture toughness. The addition of 5vol% ZrO_2 rather had the highest hardness value regardless of the larger Al_2O_3 grain size recorded [159]. Also, Ifthikar et al recently prepared Al_2O_3 - ZrO_2 nanocomposites and reported a fairly small decrease in the hardness of Al_2O_3 -8vol% ZrO_2 even though the fracture toughness was largely enhanced. He suggested that microstructural defects and the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfacial micro-cracking might be the possible cause of the decline in the hardness property [163]. Clearly, the effect of these nano-phase particles on the microstructure and its direct influence on the mechanical properties are still not very well understood, even though extensive studies have been carried out on Al_2O_3 - ZrO_2 matrix composites.

2.7 Properties of Graphene and Carbon Nanotube Reinforcements

The addition of carbon-based materials such as graphene and carbon nanotubes have been used recently to reinforce alumina matrix. Exceptional properties of two-dimensional (2D) graphene including high stiffness ($\sim 1\text{TPa}$) and strength (up to 130GPa), good flexibility, low density, higher electrical and thermal conductivity and higher surface area ($\sim 2600\text{ m}^2/\text{g}$) makes it a potential nanofiller for producing tough, wear resistant and electrically conductive alumina composites for industrial applications [123][124][111]. Carbon nanotubes which are one-dimensional (1-D) rolled graphene sheets also exhibit combined physical and mechanical properties such as high aspect ratio (length/diameter aspect ratios of about 1250–3750 is typical for MWCNTs), tensile strength ($20\text{--}100\text{GPa}$), high thermal ($>3000\text{W/mK}$) and electrical ($>10^5\text{ S/m}$) conductivity, high Young's modulus (up to 1000GPa) which presents significant toughening in ceramic structures [32][90][115]. In the last decades, the addition of these nano-scale reinforcements in alumina-based composites have become an interesting field due to their effect on the matrix grain structure and the enhanced mechanical properties generated. For example, reports have shown that the addition of low content of carbon nanotubes ($<2\text{wt}\%$) results in fine-grained structure with improved mechanical properties. It is also perceived that the addition of certain amounts of graphene (less than $1.0\text{wt}\%$) refines the matrix grain structure and improves the wear resistance and mechanical properties [164][165][166].

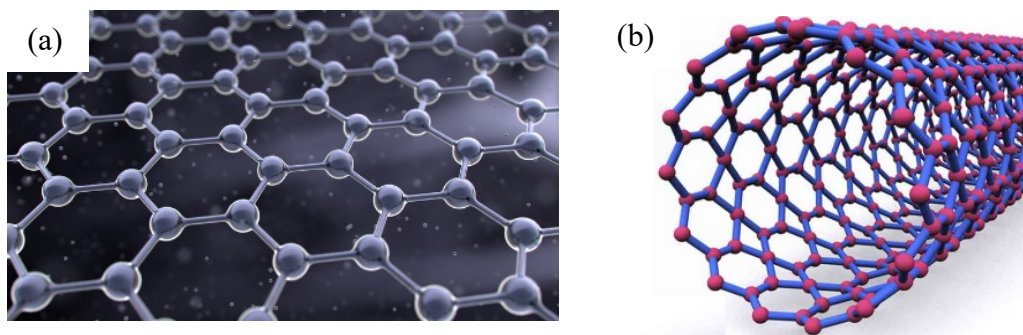


Figure 2.17: Structure of (a) graphene and (b) carbon nanotube [9]

2.7.1 Toughening Effect of Graphene and Carbon Nanotubes in Alumina Nanocomposites

Carbon-based nano-reinforcements such as graphene and carbon nanotubes have been widely used to reinforce alumina ceramic due to their toughening and strengthening capabilities. The addition of these nano-scale structures can activate these mechanisms and improve the interfacial bonding with the matrix if an optimal amount ($\text{wt}\%$ and $\text{vol}\%$) are used. The potential of these carbon-

based additives to impart toughness, strength and improve electrical and thermal conductivity increases the structural and multifunctional applications of ceramic matrix composites [167][168]. In recent years, the use of single addition of either graphene or CNTs within alumina matrix has shown interesting results. More specifically, the enhancement in fracture toughness and bend strength by these additives has piqued attention [20][169][170]. In addition, literature has reported on various toughening mechanisms displayed by these individual carbon-based additives within the ceramic matrix including crack bridging, graphene/CNTs pull-out, and crack deflection [20][111]. For instance, Centeno et al demonstrated about 50% increase in fracture toughness of alumina composite reinforced with 0.22wt% graphene. Crack bridging action by the graphene was identified as the main phenomena for inducing toughening in the composite [171]. Further, the pull-out and crack bridging mechanisms illustrated by CNTs (0–3vol%) in the alumina matrix yielded improved fracture toughness (K_{IC}) value up to 40% (from 3.32–4.68MPa^{1/2}), as demonstrated in the work by Kim et al [172]. In a more recent study by Guo et al, both the fracture toughness and bending strength of CNTs/alumina having different CNTs amounts (0-2wt%) were evaluated using 3-point bending and Single Edge Notched Beam (SENB) tests. They reported about 182% and 55% increment in the toughness and strength of the composite with 0.5wt% CNTs concentration, as compared to the monolithic alumina. High load-bearing capacity, as well as CNT pull-outs, and bridging of cracks within grains were outlined as the main toughening and strengthening mechanisms in the fabricated CNTs/alumina composites [173]. Other literature studies have however concluded a decline or comparable bulk fracture toughness values after dispersing either graphene or carbon nanotubes within the Al₂O₃ matrix [174][175]. In Aguilar's report, after 0.05-0.1wt% of CNTs were added to pure alumina matrix to form alumina/CNTs composites via pressureless sintering, both the hardness and toughness lowered, with the K_{IC} values declining up to about 41% [175]. A similar trend was also identified in alumina-GNPs system incorporated with 1.33vol%GNPs by Liu et al, who realized no significant increment in the hardness and K_{IC} values [176]. In both reports, poor dispersion, agglomeration of GNPs and CNT bundles, and pore formation restricted the toughening efficiency of the composites and its constituents, which degraded the mechanical properties. Hence, it is obvious that the single addition of either CNTs or GN to ceramic matrix have not yielded conclusive result. Figure 2.18 illustrates the toughening mechanisms of graphene and carbon nanotubes in alumina matrix.

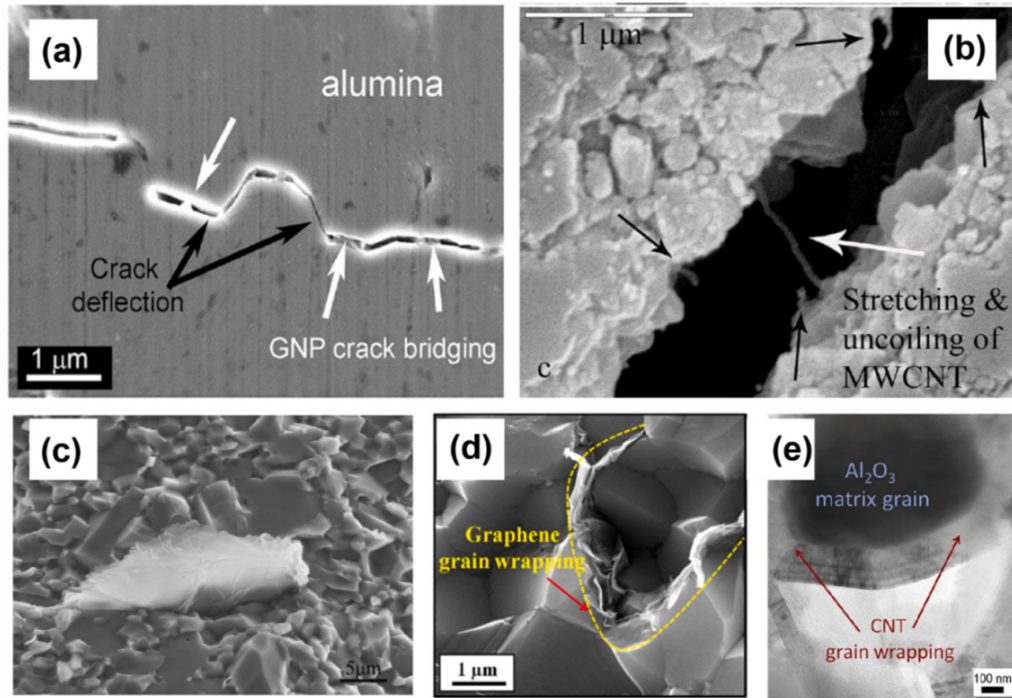


Figure 2.18: Demonstration of toughening effect of graphene and carbon nanotubes in alumina and ceramic matrix nanocomposites [36].

2.7.2 Tribo-mechanical Effect of Graphene and Carbon Nanotubes in Alumina Nanocomposites

The effect of graphene and carbon nanotubes on the wear and tribological properties of alumina nanocomposite systems has also received enormous attention in recent years. In both carbon-based systems, a carbon-rich tribofilm formed from the wear-induced action increases the wear response of alumina and other ceramic-based nanocomposite structures by acting as a lubricant to protect the contacting surfaces. This is also accustomed to the exceptional lubricating properties of graphite which merits these carbon-based composites with high wear resistance [177]. Yazdani et al added 0.5wt% of graphene to alumina matrix and achieved about 75% increase in the wear rate with a 23% decrease in the friction coefficient. This was due to the formation of a smooth tribofilm on the worn surface which decreased the friction between contact bodies when the low content graphene was added [34]. Winarto et al also used a cold spray process on Al-Si surface to fabricate alumina-CNT nanocomposites and recorded an improvement in both hardness and wear properties with the addition of 2wt% CNT. A uniform distribution of the CNT particles with increased load-bearing capacity contributed to the enhanced mechanical properties [178]. Gutierrez-Gonzalez et

al. also reported about half the wear rate and ~10% decline in the coefficient of friction of alumina-graphene composite, as compared to the parent alumina under similar reciprocating wear testing conditions when 0.22wt% added to the matrix. This was ascribed to the presence of a self-lubricating layer of the embedded graphene platelets that provided sufficient lubrication in the alumina-graphene composite [179].

2.7.3 Deteriorating Effect of Graphene and Carbon Nanotube Addition to Alumina Matrix Nanocomposites

Contrary to the improvements in mechanical and wear properties by the additions of these nanofillers to a ceramic matrix, other studies have also shown that the individual additions result in the depletion of the properties. The decline in both the physical and mechanical properties are mainly due to the problems with homogeneous dispersion of the individual nano-scale additives and their interfacial bonding with the matrix [180][181]. For instance, the Van der Waals forces and large specific surface area of graphene nanoplatelets (GNPs) lead to inhomogeneity in the dispersion by promoting agglomeration and limiting matrix-graphene interface bonding. Agglomeration of carbon nanotubes and graphene in the reinforced nanostructures also limits their effect on matrix grain refinement, weakens bond formation and hampers sintering activities to produce denser structured composites [117][111]. In addition, graphene re-stacking which is caused by the strong sheet-to-sheet Van Der Waals interactions tend to limit the inter-sheet contact area and results in small gaps between sheets. This phenomenon reduces the active surface properties of graphene and consequently leads to pore formation in the composite [182]. Bernal et al reported about 8-40% decrease in the fracture toughness of Al_2O_3 -CNT composite with 0.1 wt% synthesized via spark plasma sintering (SPS). Agglomeration of the CNT, increased grain size and weak interfacial bonding accounted for the decline in the fracture toughness [27]. Wang et al also claimed a comparable fracture toughness value of alumina/CNT composite with the brittle monolithic alumina, when reinforced with 10vol% CNT [183]. In the work of Ruthowski et al, adding graphene content of more than 2wt% increases the material wear rates, which can be a result of the graphene removal process and filling of voids by the wearing off of fine silicon nitride particles on the track after the friction test [184]. Therefore, it is clear that the addition of single-phase carbon-based nano-reinforcements (having various amounts) to the alumina matrix still presents challenges that need further studies.

2.8 State of the Art of Multiple and Hybrid Reinforcements used in Alumina

Matrix Nanocomposites

There is a growing interest in the utilization of hybrid and multiple reinforcements in alumina and ceramic-based nanocomposites. In the case of alumina-based multi-material nanocomposites, at least two nano-reinforcement phases can be incorporated simultaneously within the alumina matrix. This approach leads to the development of improved physical and mechanical properties compared to monolithic alumina and single-reinforced alumina-based nanocomposites. Consequently, several research efforts have been made to concurrently reinforce these advanced ceramic materials with carbon-based structures such as graphene and carbon nanotubes, aiming to enhance their toughness. This concept is based on the belief that by combining the exceptional properties of both graphene and carbon nanotubes, these ceramic structures can benefit from a synergistic effect, resulting in superior performance for high-demand structural applications [185]. Other studies also suggest that the limitations of reinforcing a matrix with either GN or CNTs only, such as agglomeration and graphene re-stacking can be minimized when both carbon-based structures are combined in the matrix [33][186][182]. Figure 2.19 depicts the simultaneous dispersion of graphene (GN) and carbon nanotubes (CNTs) within an alumina matrix. Up till now, there have been few reports on the toughening effects of these multiple reinforcement phases within the ceramic matrix. In the studies of Rahman et al, about 250% increase in fracture toughness was achieved in consolidated alumina/1wt%GNPs/0.5wt%CNTs nanocomposites, which were prepared via spray drying followed by spark plasma sintering (SPS). The abrupt toughness enhancement was associated with known toughening mechanisms such as CNT pull-out, crack-bridging and deflection, CNT embedded graphene and CNT yarning [186]. In another similar work, Yazdani et al utilized ultrasonication and hot-pressing to reinforce alumina-based nanocomposites with both 0.5wt%GNPs and 1wt%CNTs, and reported about 63% and 18% increase in the fracture toughness and flexural strength respectively, relative to the parent alumina. Though there was no significant reduction in the grain size, the improved mechanical properties were accustomed to the unique structural morphologies of the combined carbon-based materials, and toughening effects including GNP pull-out, CNT pinning and pull-out, and CNT crack bridging [187]. The concept of reinforcing ceramic matrices with multiple additives can, therefore, offer drastic improvement to the mechanical properties. However, more studies are needed to further understand the microstructural and mechanical performance of these novel ceramic-based

multi-material nanocomposites. Research work focusing on the effect of selected optimal amount of each nano-reinforcement to disperse within an alumina-based multi-material system is essential to understand the synergistic effect of these nano-inclusions within the ceramic.

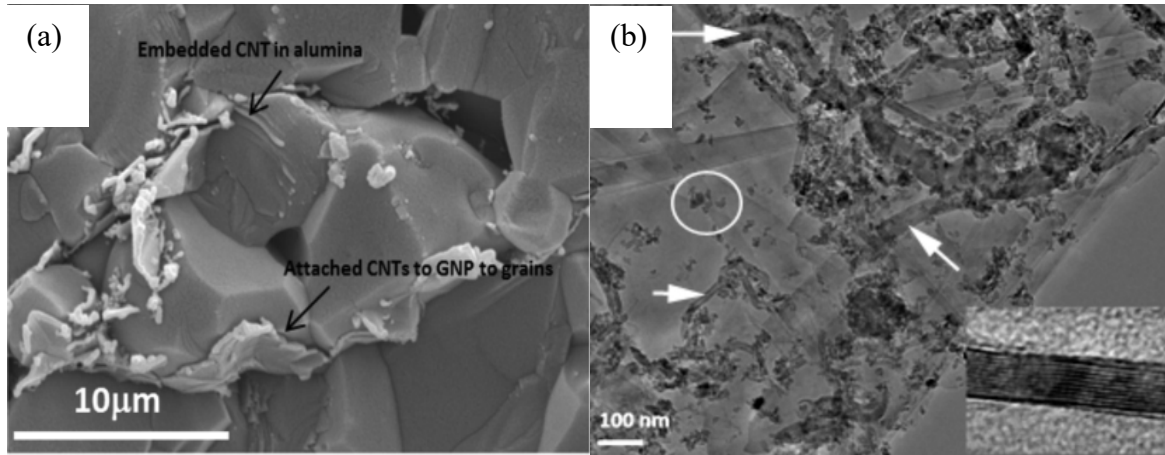


Figure 2.19: (a) Scanning electron microscopy (SEM) micrograph of hybrid additions of graphene (GN) and carbon nanotubes (CNTs) (b) Transmission electron microscopy (TEM) showing the distribution of both GN and CNTs within Al_2O_3 matrix [35].

CHAPTER 3

EXPERIMENTAL PROCEDURES AND METHODOLOGY

3.1 Introduction

This chapter details the materials, experimental procedures and methods used in this research. The fabrication procedure used for the alumina (Al_2O_3) matrix multi-material nanocomposites with the identified optimum nano-reinforcement concentrations and sintering parameters are presented in section 3.2. Colloidal mixing followed by hot-pressing sintering at high temperature (1600°C) were used to consolidate and achieved near-dense bulk structural nanocomposites. The objective of this research is to study the effect of these selected optimal nano-reinforcement amounts on the microstructural evolution, mechanical, tribological, thermal and electrical properties of alumina matrix. Hence, the systematic characterization of the microstructural, mechanical, tribological and physical and functional properties of the alumina matrix nanocomposites is also detailed in sections 3.3-3.5. Detailed experimental set-ups are also presented in this chapter.

3.2 Fabrication of Alumina Matrix Nanocomposites

Figure 3.1 below illustrates the flow process of the fabrication of the alumina (Al_2O_3) matrix multi-material nanocomposites. The fabrication route adopted in this research is the colloidal mixing route followed by hot-pressing sintering procedure. Selected amounts of zirconia (4wt% and 10wt% ZrO_2), graphene (0.5wt%GN) and carbon nanotubes (2wt%CNTs) were selected as the nano-reinforcement phases for the alumina matrix after thorough literature studies. The as-received α -alumina powder (commercially procured from Sigma Aldrich), having an average particle size of $<50\text{nm}$ and purity of 99.96% was uniformly dispersed in distilled water to form an alumina suspension. The graphene was prepared from graphite oxide(GO), which was obtained from fine graphite flakes using the Hummer's method discussed elsewhere [55]. The as-received surface enhanced graphite flakes (Grade-3775, Asbury Graphite Mills Inc., NJ, USA) were first chemically modified to graphite oxide (GO) followed by thermal exfoliation upon heating to 1600°C at $1000^\circ\text{C}/\text{min}$ and 4.5×10^2 Torr pressure in an induction-heat furnace. Carbon nanotubes (Multi-walled) with length $15\mu\text{m}$ and diameter about 50nm were also obtained from MK Imprex, Canada. To enhance interfacial bonding and remove impurities, the CNTs were functionalized by

treating in acidic solution. The carbon nanotubes (CNTs) were subsequently suspended in distilled water and subjected to continuous sonication to ensure their continuous dispersion.

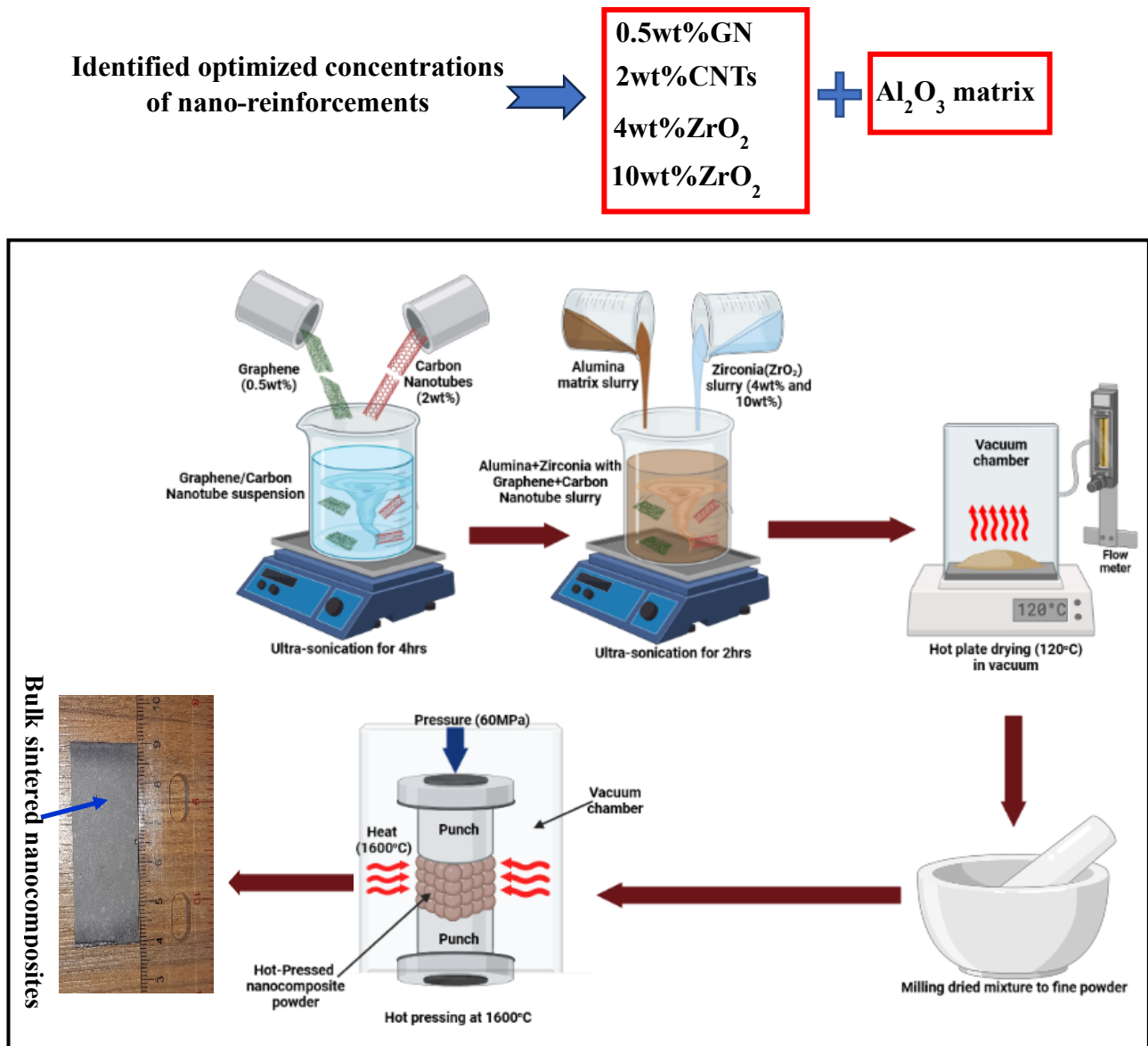


Figure 3.1: Flow diagram of hot-pressing technique used to fabricate alumina (Al₂O₃) matrix nanocomposites with identified optimum nano-reinforcement materials

Concentrations of 4wt% and 10wt% of zirconia (<80 nm in diameter, Sigma Aldrich, UK), 0.5wt%graphene and 2wt%CNTs were separately dispersed in distilled water. A surfactant was used together with ultrasonic vibrations to enhance uniform dispersion of both graphene and CNTs by decreasing the Van der Waal's attractive forces. The alumina slurry was added to both zirconia and the carbon nanofiller suspensions whilst continuously stirred using ultra-sonication to obtain

a homogeneous mixture. The slurry formed were then dried on a hot plate at temperatures between 120-150°C under sonication to obtain the powder mixture. Dried powder mixture was constantly milled in a mortar to obtain very fine and uniform nanocomposite powders. Consolidation was then carried out by hot-pressing in a graphite die at 1600°C at a constant 60 MPa pressures for 1 hour holding time. The final processed alumina-based nanocomposites which are rectangular shaped with approximate dimensions of about 50mm×40mm×2mm were then subjected to mechanical and microstructural characterization.

Table 3.1: Summary of prepared Alumina (Al_2O_3) matrix multi-material nanocomposites

Fabricated Hot-Pressed Alumina (Al_2O_3) Matrix Nanocomposite Samples	Alumina (Al_2O_3) Matrix (wt%)	Zirconia (ZrO_2) (wt%)	Graphene (GN) (wt%)	Carbon Nanotubes (CNTs) (wt%)
1. Monolithic/Pure Al_2O_3 (Aa)	0	0	0	0
2. Aa+4wt%ZrO_2	96	4	0	0
3. Aa+10wt%ZrO_2	90	10	0	0
4. Aa+0.5wt%GN	99.5	0	0.5	0
5. Aa+4wt%ZrO_2+0.5wt%GN	95.5	4	0.5	0
6. Aa+4wt%ZrO_2+2wt%CNTs	94	4	0	2
7. Aa+10wt%ZrO_2+0.5wt%GN	89.5	10	0.5	0
8. Aa+10wt%ZrO_2+2wt%CNTs	88	10	0	2
9. Aa+10wt%ZrO_2+0.5wt%GN+2wt%CNTs	87.5	10	0.5	2

3.3 Structural and Microstructural Characterization of Fabricated Alumina Matrix Multi-Material Nanocomposites

The bulk as-sintered alumina (Al_2O_3) matrix multi-material nanocomposites were also subjected to various characterization techniques to assess the effect of single, hybrid and multiple additions of nano-reinforcement materials including graphene (GN), carbon nanotubes (CNTs) and zirconia on the density, defects (porosity) and microstructural evolution of the alumina matrix. Various characterization techniques via the scanning electron microscope (SEM), energy dispersive

spectroscopy (EDS) and X-ray diffraction (XRD) have been used to determine the evolved crystallite phases, structural morphology, topography, grain sizes and their distributions after the high temperature sintering procedure.

3.3.1 Density and Relative Density Measurements

Bulk densities of the as-sintered nanocomposites were determined using the Archimedes method, with distilled water as the medium of immersion. Relative density values were then estimated by dividing the measured density by the theoretical density. Rule of mixture was used to calculate the theoretical densities using literature density values of 3.97gcm^{-3} , 5.87gcm^{-3} , 2.21gcm^{-3} and 1.85gcm^{-3} for monolithic alumina (Al_2O_3), zirconia (ZrO_2), Graphene(GN) and Carbon Nanotubes (CNTs) respectively [35][189]. Figure 3.2 shows the experimental set-up for the density and relative density estimation using the Archimedes principle.

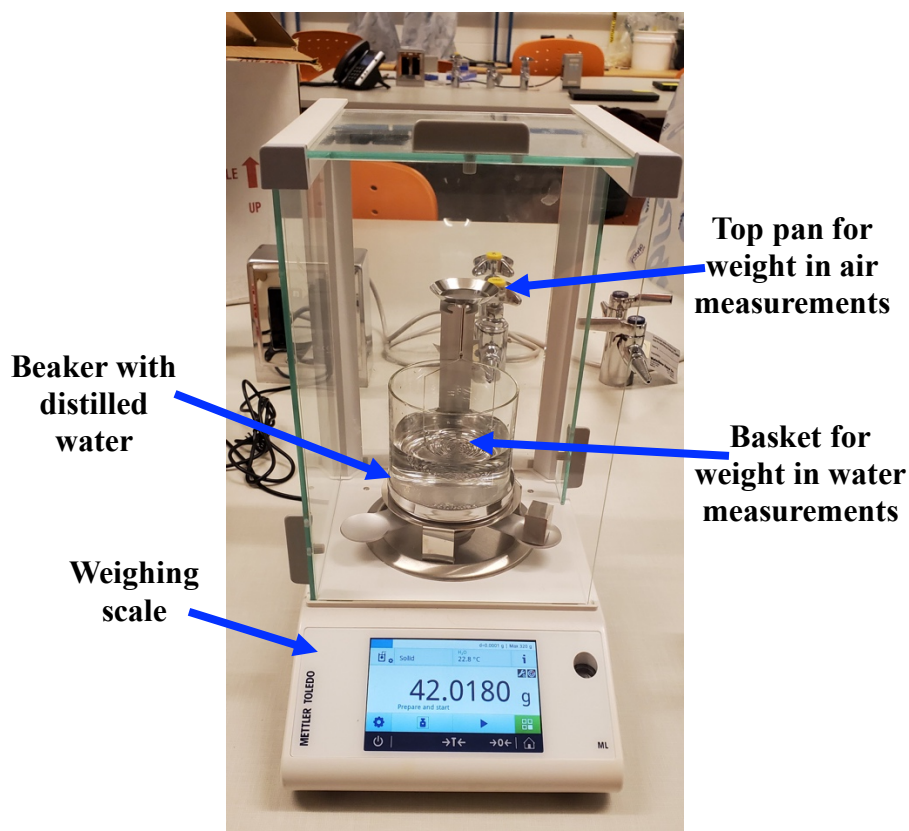


Figure 3.2: Experimental set-up for density and relative density measurements of fabricated nanocomposites using Archimedes principle.

3.3.2 X-Ray Diffraction (XRD) Analysis and Crystallite Phases

The different phase compositions of the sintered monolithic alumina and alumina-based multi-material nanocomposites were detected using X-ray diffraction (XRD) (Rigaku Miniflex 600), as shown in Figure 3.3. The XRD system was equipped with Cu-K α radiation of $\lambda = 1.54056 \text{ \AA}$. XRD patterns were collected in a 2θ range from $5-110^\circ$, at a $1.4^\circ/\text{min}$ scanning rate. Post-processing of the XRD patterns was also done using MDI JADE 6.0 to identify the crystallite phases and their corresponding planes.

The content of the monoclinic ($m\text{-ZrO}_2$) and tetragonal ($t\text{-ZrO}_2$) were also determined and compared to analyse the possible effect of GN and CNTs additions on the phase transformations of the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ nanocomposites reinforced with ZrO_2 amounts (4wt% and 10wt%). The XRD intensities were used to quantitatively estimate the $m\text{-ZrO}_2$ and $t\text{-ZrO}_2$ amounts in the alumina-zirconia multi-material nanocomposites. The respective volume fractions were approximately calculated using reflections of the various patterns coupled with equations proposed by Toraya and Garvie below [190]:

$$X_m = \frac{[I_m(\bar{1}11) + I_m(111)]}{[I_m(\bar{1}11) + I_m(111) + I_t(111)]} \quad 3.1$$

$$V_{m\text{-ZrO}_2} = \frac{1.311X_m}{1 + 0.311X_m} \quad 3.2$$

where X_m is the integrated intensity ratio of the $t\text{-}m$ ZrO_2 phases, V_m is the monoclinic ZrO_2 phase volume fraction, $I_m(\bar{1}11)$ and $I_m(111)$ are the intensities of the monoclinic phase at planes $(\bar{1}11)$ and (111) respectively, and $I_t(111)$ denotes the tetragonal (111) reflection. The tetragonal volume fraction (V_t) was approximately estimated from the relation:

$$V_{t\text{-ZrO}_2} = 1 - V_{m\text{-ZrO}_2} \quad 3.3$$

3.3.2.1 Crystallite Size Estimation from XRD Spectrum

The crystallite sizes of the fabricated monolithic Al_2O_3 and nanocomposite samples were estimated from the XRD patterns by measuring the full width at half-maximum (FWHM) of the various diffraction peaks within each sample. The measured FWHM values were coupled with Scherrer equation below to calculate the crystallite sizes [191],

$$D = \frac{K\lambda}{B \cos \theta} \quad 3.4$$

where D is the crystallite size in nm, K is the crystallite shape factor, with a known value of ~ 0.9 , λ represents the wavelength of the incident X-rays given as 0.154056nm , B is the FWHM value of a specific diffraction peak in radians, and θ is the peak position (Bragg angle) in radians.

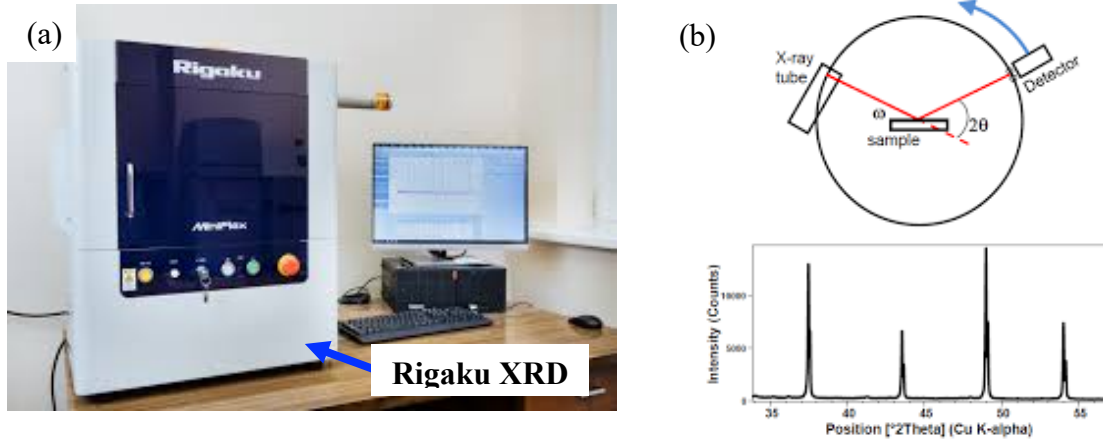


Figure 3.3: Illustration of X-ray diffraction (XRD) working principle [192]

3.3.3 Metallographic and Microstructural Analysis

The sintered multi-material nanocomposites were subjected to routine metallographic procedures involving grinding using silicon carbide (SiC) pads (from 400grits up to 1200 grits) and polishing down to $0.5\mu\text{m}$ with a diamond suspension and polishing cloths. The polished sections of the fabricated samples were also observed using a Field Emission Scanning Electron Microscope (FE-SEM, Quanta 3D, Thermofisher) operating at an accelerating voltage of 10kV to reveal the morphology of the grain and structural features of the prepared nanocomposites. Attached to the SEM is an EDS detector which was used to analyse the chemical and elemental composition of the multi-material nanocomposites. The distribution of the nano-reinforcements such as ZrO_2 particles were also analysed in detail using a backscattered electron (BSE) imaging mode to give contrast and topographical information.

3.3.4 Grain Size Estimation and Distributions

The Al_2O_3 matrix grain size and distributions within the sintered nanocomposites were also estimated from the captured SEM micrographs via the linear intercept method, in conjunction with image J software, according to the ASTM E112-13. At least 10 different micrographs were used

for each nanocomposite sample and the mean grain size value recorded. The ZrO_2 grains were also measured for each $\text{Al}_2\text{O}_3\text{-ZrO}_2$ nanocomposites using similar technique described above.

3.4 Mechanical Property Characterization

3.4.1 Micro-Hardness Property

Vickers micro-hardness of the polished rectangular samples were also measured by means of a diamond indenter installed on a Vickers microhardness tester (METLAB, Canada) (Figure 3.4). The diamond indenter was used to apply a load of 9.807N (1 kg) on the flat sample surface at a dwell time of 15s, in accordance with the ASTM C1327-15. The diagonal lengths of the diamond-shaped indent made on the sample surface after removal of the indenter was measured by means of an optical microscope attached to the microhardness equipment. The Vickers hardness (H_v) was estimated according to equation:

$$H_v = 0.0018544 \times \left(\frac{P}{d^2} \right) \quad 3.5$$

where P is the applied load in N and d is the average diagonal length in mm . Ten separate indentations were made using similar load and dwell time, at appreciable distance apart on the sample surface to avoid cracks connecting and ensuring accuracy. Also, the indents were carefully made at fresh regions without visible pores or cracks to prevent poor indent formation.

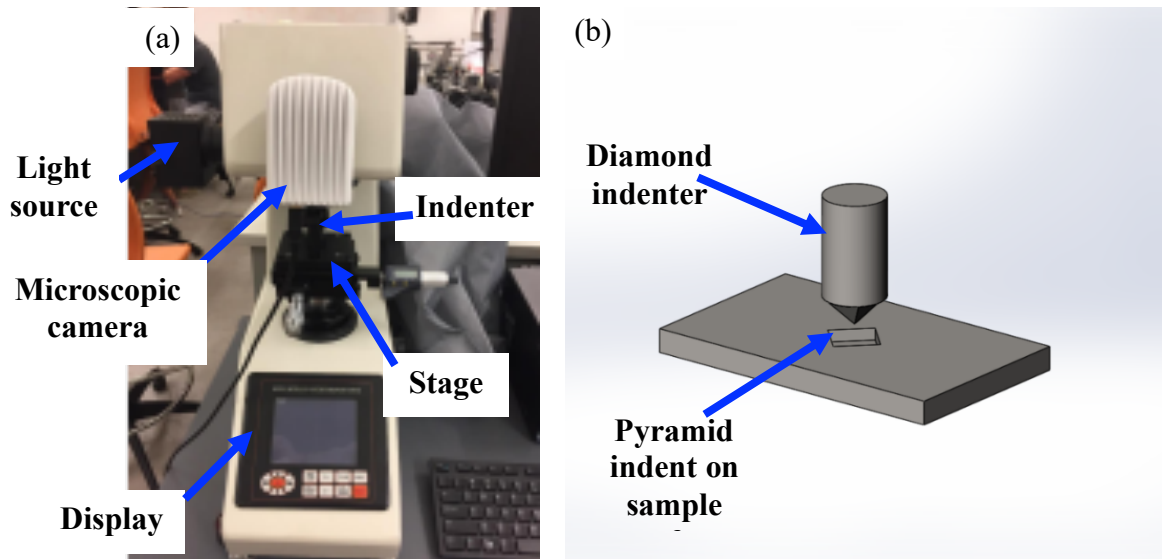


Figure 3.4: (a)Vickers micro-hardness tester (b)Schematic illustration of Vickers Hardness Testing

3.4.2 Fracture Toughness Measurements

3.4.2.1 Fracture toughness (K_{IC}): Single Edge Notched Beam (SENB) Test

Single edge notched beam (SENB) test (Figure 1(a)) was used to evaluate the fracture toughness (K_{IC}) values of the nanocomposites under ambient conditions using the Hybrid Rheometer (Discovery 3, Canada) (Figure 3.5). A 30mm (length) $\times$ 2mm (width) $\times$ 2mm (thickness) was used as the test sample, which was sectioned from the bulk fabricated nanocomposite. A notch was created in the centre part of the test specimen with the aid of a diamond saw, having a typical notch-depth ratio (a/W) of ~ 0.45 – 0.55 [187]. Three samples with similar geometry were tested for each nanocomposite. A span length of 25mm and crosshead speed of 0.05mm/min were applied to each test specimen during the test. The fracture toughness (K_{IC}) was subsequently calculated using the following equations [193][194]:

$$K_{IC} = \left(\frac{3 \times L_{max} \times S}{2 \times B \times W^{3/2}} \right) \times \alpha^{1/2} \times Y \quad 3.6$$

where L_{max} is the maximum applied load during fracture, S is the span length, B and W are the width and thickness (height) of the test specimen respectively, a is the notch depth, α is the notch ratio (a/W) and Y is a coefficient (calibration factor) estimated from the equation [193][194]:

$$Y = \frac{1.99 - \alpha(1 - \alpha)((2.15 - 3.93\alpha + 2.7\alpha^2))}{(1 + 2\alpha)(1 - \alpha)^{3/2}} \quad 3.7$$

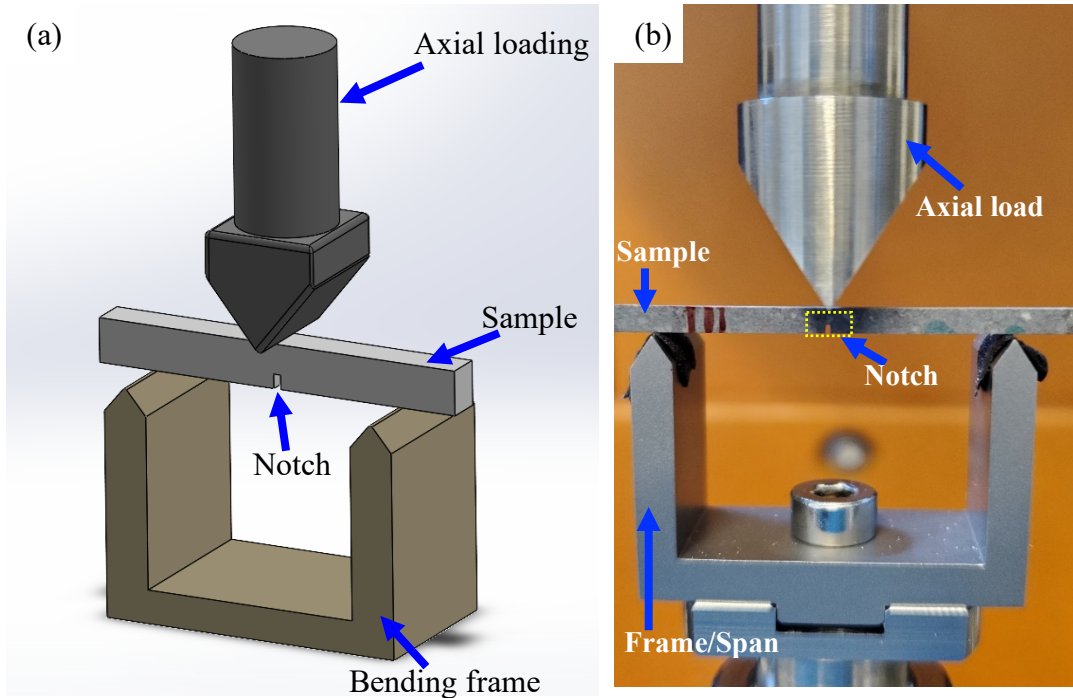


Figure 3.5: (a) Schematic illustration and (b) experimental set-up for single edge notch beam (SENB) test

3.4.2.2 Fracture Toughness (K_{IC}): Direct Crack Measurement (DCM) Technique

Another method used to estimate the fracture toughness (K_{IC}) is the direct crack measurement (DCM) using various theoretical equations. The K_{IC} values were calculated by measuring crack extensions from the indents made on samples' surface during the Vickers hardness measurements. With the aid of an attached optical microscope and Image J software, the lengths of the emerging cracks were determined for the indents made. The measured crack lengths were combined with known theoretical equations to estimate the K_{IC} values as follows:

$$\text{Niihara equation [195]:} \quad K_{IC} = 0.203 \left(\frac{c}{a} \right)^{-1.5} \cdot H \cdot a^{0.5} \quad 3.8$$

$$\text{Lawn equation [196]:} \quad K_{IC} = 0.028 (H \cdot a^{0.5}) \left(\frac{E}{H} \right)^{0.5} \cdot \left(\frac{c}{a} \right)^{-1.5} \quad 3.9$$

where a is half of the length of Vickers indent diagonal (mm), H is the Vickers microhardness (GPa), c is the length of the measured crack (mm) from the crack tip to the center of the diamond-shaped indent and E is the Young's modulus estimated from literature values of Al_2O_3 , ZrO_2 , CNTs and GN. The results of the estimated K_{IC} values from the SENB test and theoretical equation (DCM) were also compared and discussed in this study.

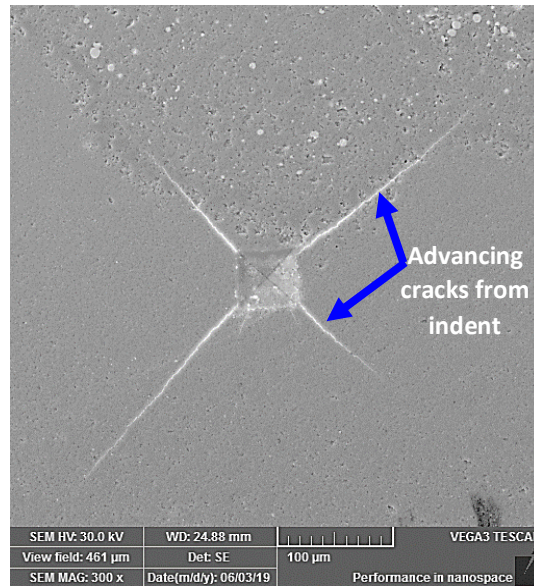


Figure 3.6: Sample with emanating radial cracks from indent after micro-hardness test.

3.4.3 Flexural/Bending Strength

The bending strength (α_f) of the nanocomposites was determined using the 3-point bending configuration on the Hybrid rheometer (Discovery 3, Canada), as shown in Figure 1 (b). The dimension of the test samples was 50mm (length) $\times$ 2mm (width) $\times$ 2mm (thickness). A bending span of 40mm was used, with an axial loading speed of 0.5mm/min. Crack initiation and subsequent fracture occurred at regions closer to the applied axial load during the bending. Three different test samples were used for each fabricated nanocomposite and the bending strength evaluated from the equation below [197]:

$$\alpha_f = \frac{3 \times P_{max} \times L}{2 \times b \times h^2} \quad 3.10$$

where P_{max} is the fracture load, L is the bending span, b and h denote the sample width and thickness, respectively.

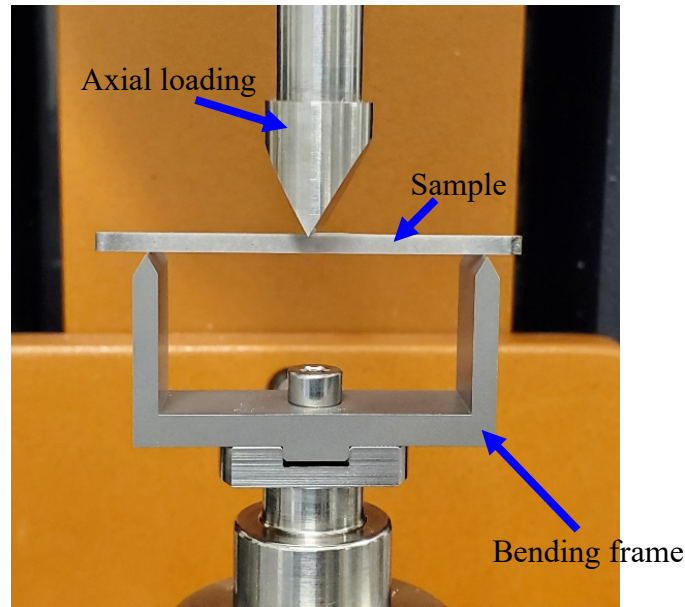


Figure 3.7: Experimental set-up for the 3-point bending test.

3.4.4 Analysis of Fractured Surfaces (Fractography)

To critically analyse the toughening mechanisms of the nano-reinforcements and the nature of fracture of the Al_2O_3 nanocomposites, the fractured surfaces were studied under a high-resolution field-emission scanning electron microscope (FE-SEM, Quanta-3D). The fractured surfaces of the nanocomposites were mounted on an SEM angular mounts to expose the cross-section of the

fractured surfaces within the SEM. These surfaces were also coated with the thin layer of platinum to enhance conductivity and prevent charging in the SEM chamber. Detailed fractography of these surfaces was conducted using both lower and higher resolutions (50x-100kx) in the FE-SEM to elucidate and document the influence of the nano-reinforcements during bending and subsequent fracture of the nanocomposites.

3.5 Tribological Property Characterization

3.5.1 Surfaces Roughness Measurements Prior to Wear Test

Prior to wear test, surface roughness of the polished composites was measured by a Non-contact White Light Interferometry using a Bruker Contour GT Optical profilometer system. The surface roughness of each specimen was investigated using the ISO 25178, which utilizes a high pass and low pass filter to reveal the asperities of the polished composite surface. Ten separate measurements were made on each sample surface over an area of $961 \times 721 \text{ um}^2$ and the average 3D surface roughness value (S_a) was calculated.

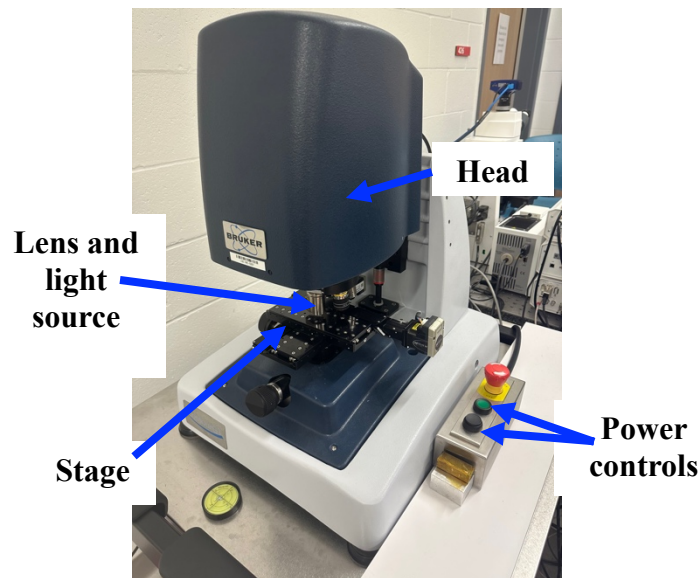


Figure 3.8: Bruker contour GT optical profilometer used for surface property measurements.

3.5.2 Ball on-Flat Reciprocating Wear Test

A ball-on-flat configuration (Figure 3.9) was used to conduct a dry sliding wear test on a flat polished specimen using the UMT tribolab (Bruker Tribometer, Canada). The specimens were

prepared for the test in accordance with the conditions described in ASTM G133-10. A 9.525mm diameter spherical silicon nitride (Si_3N_4) ball with purity of 99.9% and surface roughness (S_a) of 5.11 ± 0.25 nm was used as the counter body during the experiment. Si_3N_4 against Al_2O_3 is one of the ceramic-on-ceramic material combinations proposed for artificial joint or joint replacement. The counter ball was cleaned in an ethanol ultrasonic bath for about 5minutes prior to the wear test as prescribed by the standard. The ball was then secured in an appropriate customized holder which was suspended normally to the specimen stage. The tip of the ball was closely examined to prevent ball movements in the holder during the test. The finely polished alumina specimens with dimensions (15mm $\times$ 10mm $\times$ 2mm) was also cleaned ultrasonically and secured on the reciprocating stage using a pair of rectangular holders to limit vibrations. A preload of 5N was applied to the Si_3N_4 ball at the initiation of each test for 5s, to ensure smooth engagement of the contact surfaces before the sliding and to ensure safe condition of the sensitive loading force sensor. A constant normal load of 25N was applied to the stationary ball immediately after the pre-load sequence for 1000s, using a to and fro sliding velocity of 100mm/s of the sample stage, which represents the testing frequency of 0.5Hz according to the ASTM standard [198]. The stroke length used was 10mm which gave a total sliding distance of 100m equivalent to 5000cycles which was calculated according to equations 3.11 and 3.12 below:

$$\text{Total sliding distance(m)} = 0.002 \times t \times f \times L \quad 3.11$$

$$\text{Total number of cycles} = t \times f \quad 3.12$$

where t is test time, f is oscillating frequency and L is stroke length. The experiment was repeated three times on each sample surface by changing the position of the counterball and moving to an unworn area on the sample surface. The test was conducted in a dry sliding condition at room temperature of 22 ± 3 °C and relative humidity of 40-60%. The coefficient of friction (COF) and frictional forces were determined from the tribometer at every 0.01s during the test operations. Three separate tests were done for each sample and on unworn regions of the polished surface. The mean coefficient of friction (COF) was estimated for all the 3 tests.

Post-wear testing analysis of each sample having wear tracks were carried out to determine the volume loss and consequent wear rate of each sample. The optical profilometer was utilized to generate the 2D and 3D wear track profiles in order to measure their wear width and depth. Prior

to these measurements, the tracks covered with debris were thoroughly cleaned and dusted using air pressure to reveal the true depth and width for accurate measurements. The wear rate (W_R) was calculated using the relation in equation (9) [198].

$$W_R = \frac{V}{F \times L} \quad 3.13$$

with V as the volume loss (mm^3), F represents the applied load (N) and L is the total sliding distance (m). The worn surfaces and wear debris of each nanocomposite were also studied after the wear test using the FE-SEM, to determine various wear mechanisms during the dry sliding tests.

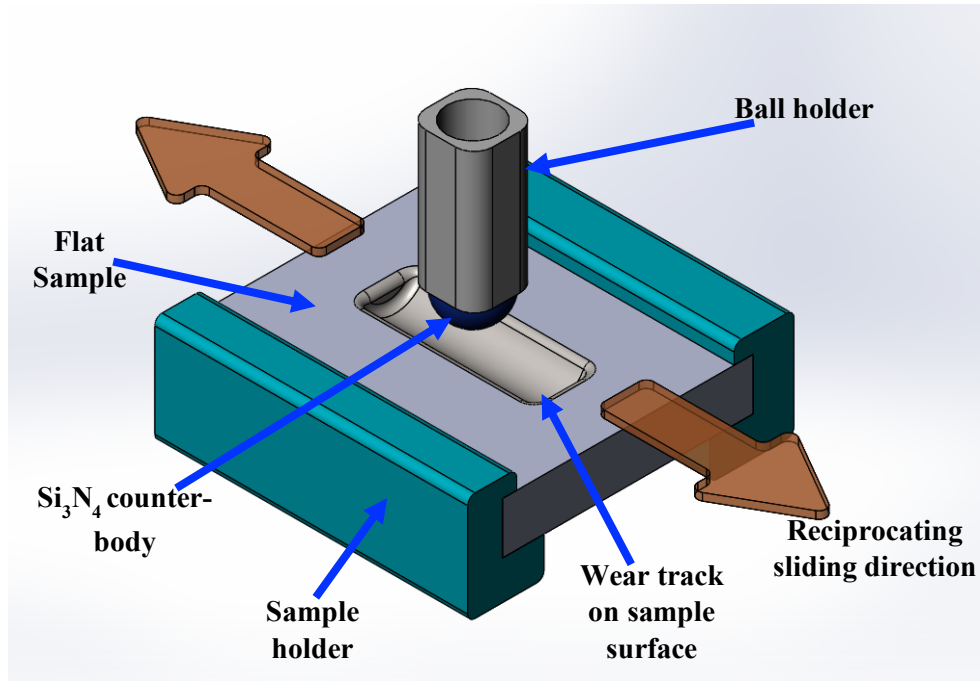


Figure 3.9: Illustration of ball-on-flat sliding wear test configuration according to ASTM G 133.

3.6 Functional Property Characterization

The functional properties of the fabricated alumina matrix multi-material nanocomposites were also estimated to assess their electrical conductivities. This is essential to maximize the full potential of carbon nano-reinforcements via the simultaneous dispersions of CNTs and GN within the bulk alumina matrix. The prospect of achieving a stiffer, stronger and more electrically conductive bulk Al_2O_3 matrix structure by incorporating the exceptional properties of CNTs and

GN can generate even wider spectrum of applications for demanding but extreme environmental conditions.

3.6.1 Electrical Resistivity and Conductivity using Four-Point Probe

The electrical properties of the Al_2O_3 based multi-material nanocomposites were estimated by measuring the electrical resistivity and conductivity. The electrical resistivity was measured using the Four-Point Probe method. The experimental set-up for the four-point measurement is illustrated in Figure 3.10. The four-point probe system (Lucas/Signatone Model SP4 4-Point Probe Head, S-32 Test Stand) used for the experiment consists of four collinear probes made of tungsten carbide (WC), with 1.016mm (0.040 inch) tip spacing and 0.254mm (0.010inch) tip radius. The probes are mounted into the probe head and made to gently contact the sample surface. The electrical resistivity is determined by passing direct electric current (I_{DC}) through the outer probes and measuring the corresponding voltage (V_{DC}) across the two inner probes.

Prior to the measurements, all samples were ground and polished to minimize undulated surfaces and ensure good contact of probe tips with sample surface. The tips of the four probes were lowered gently to contact the surface of the polished Al_2O_3 nanocomposite samples. A current measurement of 5mA was applied to the two outer probes by a precision DC current source (KEITHLY 2231A-30-3 Triple Channel DC Power Supply), as illustrated in Figure 3.10. The applied current was increased from 5mA to 35mA in a range of 5mA for each measurement. Care was taken to ensure a constant contact force applied between the probe pins and the sample surface for every measurement. Every sample was measured 10 times and the corresponding DC voltage was recorded by a multi-voltmeter (KEITHLY 2110 5 1/2 Digit Multimeter). Each of the ten measurements is derived from three separate measurements, which were automatically executed with a change in polarity between each single measurement. This procedure ensures that the polarity or electrical charging does not influence the measured voltages. The average value of the measured voltages was employed to calculate the bulk resistivity and conductivity of the nanocomposites. This calculation was performed in accordance with Ohm's law and Smits' relation [199], which incorporates a correction factor in equation 3.14 and 3.15 below:

$$\rho = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \cdot t \cdot k = 4.532 \cdot \frac{V}{I} \cdot t \cdot k \quad 3.14$$

$$\sigma = \frac{1}{\rho} \quad 3.15$$

Where ρ is the bulk resistivity ($\Omega\cdot\text{cm}$), σ is the electrical conductivity (S/m), V denotes the voltage measured between the two inner probes (v), I is the magnitude of the source current applied (A), t represents the thickness of the sample (cm) and k denotes the correction factor, which is based on the ratio of sample thickness (t) to probe spacing (d).

During the measurements, there were instances where the detectable voltage exceeded the measurable range of the device due to high resistivity of the ceramic nanocomposites devoid of carbon nano-structure additions, namely: Al_2O_3 matrix, Al_2O_3 -4wt% ZrO_2 and Al_2O_3 -10wt% ZrO_2 nanocomposites. An overflow reading was therefore detected. If so, the resistivity of these nanocomposites was assumed to be $10^{13} \Omega\cdot\text{cm}$ according to literature [92][108]. This value represents the limit of the measurement device and can be regarded as an approximation.

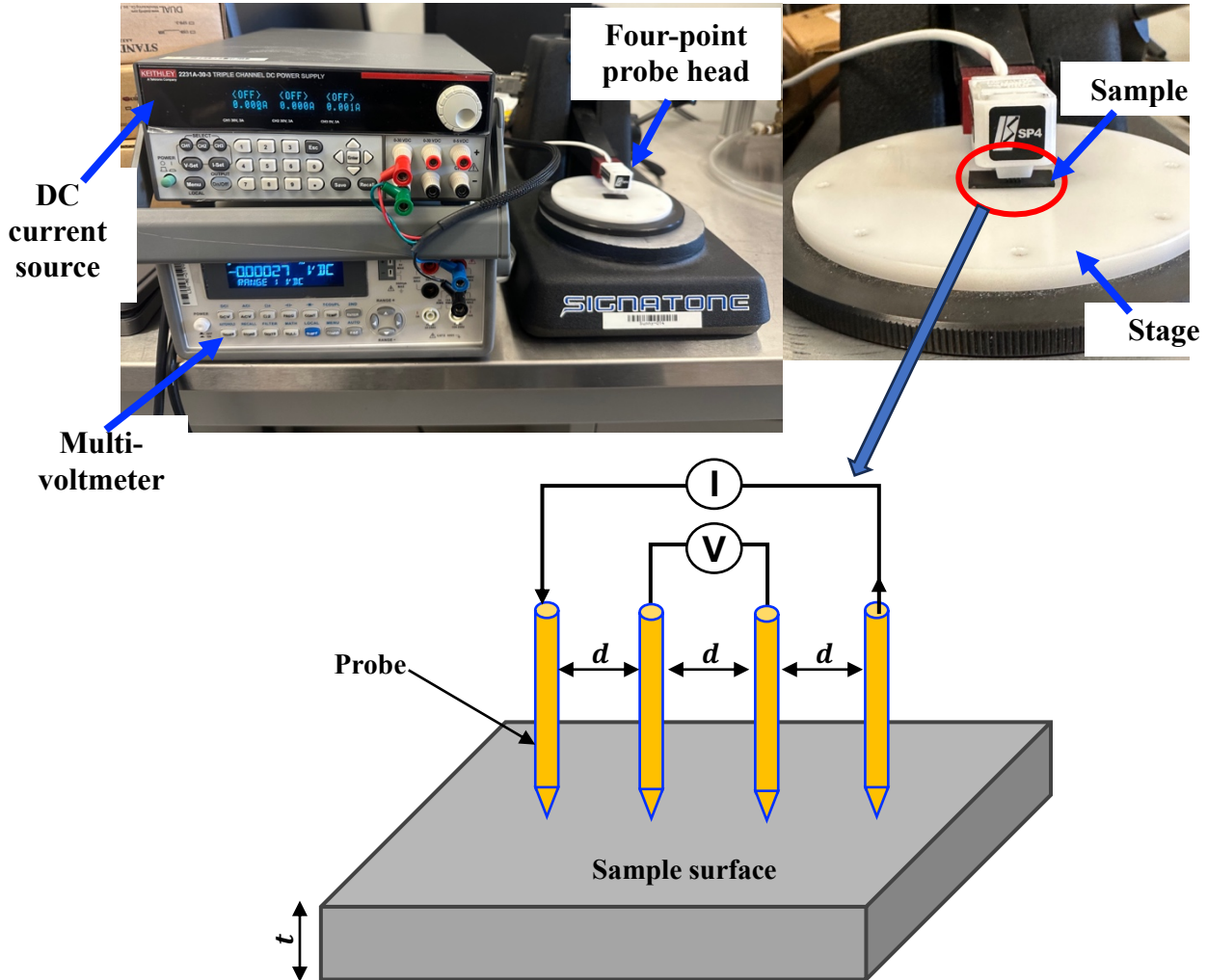


Figure 3.10: Experimental set-up and schematic illustration for electrical conductivity measurement using the Four-Point Probe.

3.7 Interfacial Characterization using Transmission Electron Microscopy (TEM)

3.7.1 Preparation of Electron Transparent Lamella for TEM Analysis using Focused Ion Beam (FIB) Milling

Details of the nature of the ceramic Al_2O_3 matrix and the nano-reinforcements' interface at the nano-scale are essential to assess the interfacial characteristics of fabricated nanocomposites. To this effect, thin transparent lamellae were prepared for analysis on the transmission electron microscope. The thin lamella was prepared using advanced focused ion beam (FIB) milling technique. The focused ion beam (FIB) milling process is a highly precise and maskless nano-fabrication technique utilized for creating 3D nano-structures, commonly referred to as lamella, with a thickness of less than 200nm. This unique method involves gradually removing material from a bulk sample through the application of a focused beam of ions (gallium ions) and sculpting into a thin lamella for TEM characterization [200]. This method was adopted due to the difficulty and limitation with conventional thin lamella preparation technique such as double-jet polishing and ion milling, which can also cause distortion and damage to thin specimen [200]. The FIB technique gives the flexibility to fabricate site-specific thin lamellae for TEM analysis without inducing stresses, cracking and permanent damage to FIB specimen. For this study, the Helios 5 UC DualBeam FIB milling system (ThermoFisher Scientific, McMaster University, Canada) was used to create the transparent lamella from the bulk Al_2O_3 -10wt% ZrO_2 -0.5wt%GN-2wt% CNTs sample. The Helios FIB-SEM uses high-resolution imaging and high material contrast to produce fast and precise high-quality milling and deposition of complex structures with dimensions less than 10nm. A site-specific step by step milling, lift-out and thinning during the FIB process is illustrated in Figure 3.11.

The ceramic Al_2O_3 nanocomposite sample surface was initially gold (Au) sputtered (up to 15nm) to make surface and region of interest conductive for imaging in the FIB-SEM system by dissipating charges. Pt layer was deposited on the surface of interest with carbon nano-structure distributions within the Al_2O_3 matrix using the gas injection system (GIS). The purpose of these platinum stripes is to act as protective barriers for the sensitive regions of the sample during further processing or imaging. By strategically placing the platinum stripes, potential damage or unwanted interactions with the specimen's surface can be limited, allowing for more precise and controlled manipulation in the FIB system. Following the Pt stripe, an amorphous thin carbon electron

deposition with 15 kV and 13 nA was done. The carbon layer was deposited to protect the surface from the ion beam before the thick W deposition, as the 15 nm of Au was not enough to protect

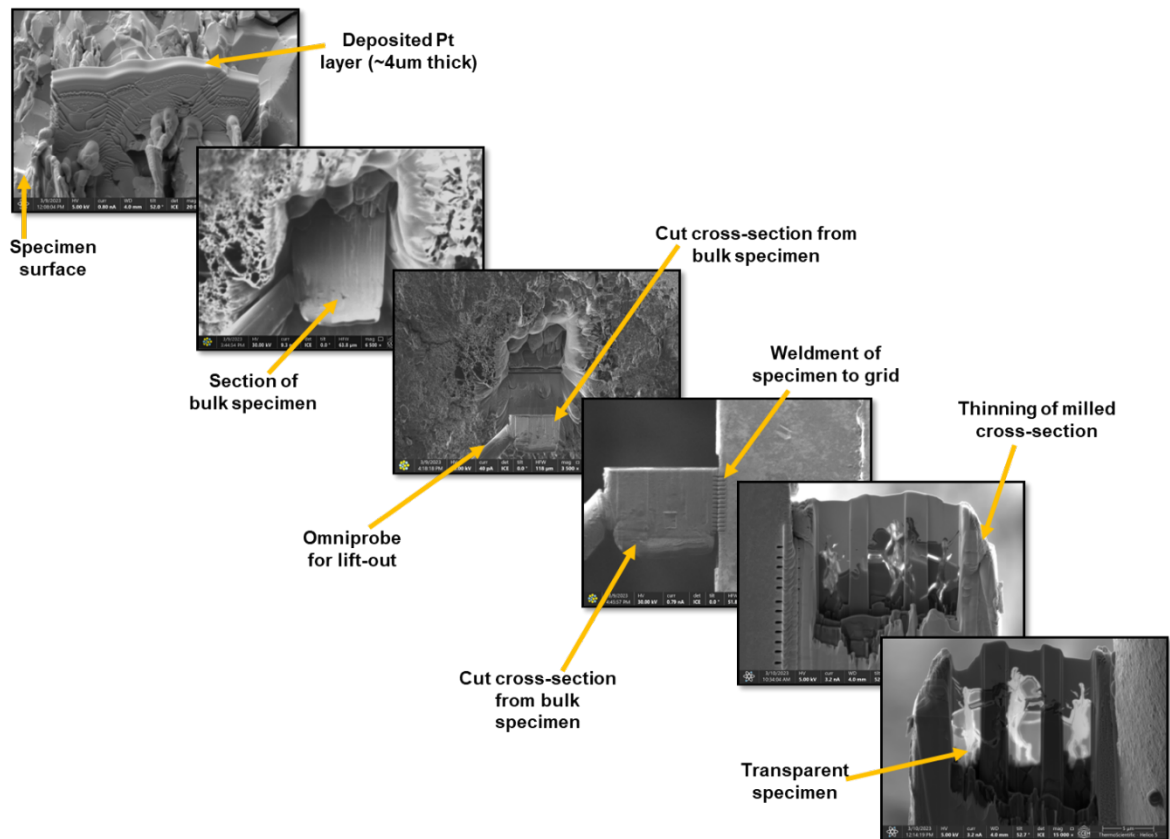
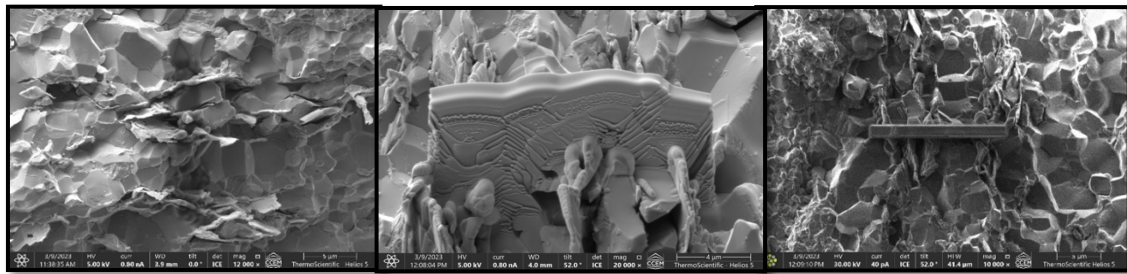


Figure 3.11: Step-by-step lift-out process during focused ion beam (FIB) milling of ceramic lamella.

the surface against the ion beam. As soon as the sample is loaded, a region of interest is located, then locally a pad of amorphous carbon is deposited with the electron beam at a stage tilt of 0° . This electron deposition happened at 15 kV first to allow any pores to get filled with carbon then

an energy of 5 kV was used for the rest of the coating. Then a thick W pad is deposited with the ion beam at a stage tilt of 52° (30 kV, 0.43nA). The thickness of the carbon layer is around 200 nm. It is noteworthy that the thickness of W was 5-6 μm (thicker than needed for most TEM sample preparations but it was necessary for the ceramic sample to planarize the surface).

A high current Ga beam was used to trench around the region of interest (30kV, 65 nA) to form a thick membrane of the sample at a stage tilt of 52°. Then the beam current was decreased to 9.3nA to get closer to the region of interest and continue trenching. Sample is then carefully lifted out with a micromanipulator (microprobe) at a stage tilt of 0° and attached to a Cu grid, as demonstrated in Fig 3.11. Sample is then thinned out with at a stage tilt of 52.7° from both sides using a 30kV Ga beam with different beam currents. The thinner the sample gets, the lower the beam current used. After thinning and reaching a thickness of 700 nm, some holes are filled with W with the electron beam, 13 nA and 5 kV as thinning continued. TEM sample preparation was concluded with a final cleaning step by exposing each side of the TEM lamella to a 2 kV and 0.19 nA Ga FIB beam for a few minutes per side. Redeposition of material is associated with FIB milling and TEM sample prep. which can't be fully avoided. The purpose of the last cleaning step is to clean the sample from both sides removing the damaged/amorphized layer due to the thinning with the high energy Ga beam (30 kV) and to remove any redeposited material. Three separate electron-transparent TEM windows were ion-milled in the FIB by thinning three sides of the membrane.

3.7.2 Structural and Interfacial Characterization using Transmission Electron Microscopy (TEM)

High resolution transmission electron microscopy (HRTEM) analysis carried out on the FIB lamella (thin electron transparent sample, thickness < 200nm) using the Talos HRTEM (Canada) operating at an accelerating voltage of 300kV. Different imaging modes of the TEM including high resolution transmission electron microscopy (HRTEM), high-angle annular dark field (HAADF), selected area electron diffraction (SAED), were used to observe and study the details of the interface between Al_2O_3 matrix and multi-material reinforcements including zirconia (ZrO_2), graphene (GN) and carbon nanotubes (CNTs). Further analyses were done using the TEM micrographs and the Gatan's Digital Micrograph software.

CHAPTER 4

SUMMARY OF PUBLISHED JOURNAL PAPERS PRESENTED IN FULL IN APPENDICES

4.1 Introduction

In this chapter, the summary of the published papers and prepared manuscripts related to this research are presented. The purpose of this chapter is to provide a concise overview of the main findings from each paper and how they contribute to the overall research objectives. These published articles are presented in full detail in the Appendix section of this thesis for a comprehensive understanding of my findings. By summarizing and relating these papers to the research gaps and objectives outlined in Chapter 1, I aim to demonstrate the coherence and significance of our research. This chapter serves as a critical link between our research work and the broader context of the academic and scientific community. Below are the list of published papers targeting the set objectives in this research:

- I. **S. H. Duntu**, I. Ahmad, M. Islam, S. Boakye-Yiadom (2019) Effect of Graphene and Zirconia on Microstructure and Tribological Behaviour of Alumina Matrix Nanocomposites, *Wear*, 438-439, (<https://doi.org/10.1016/j.wear.2019.203067>).
- II. **S. H. Duntu**, F. Tetteh, I. Ahmad, M. Islam, S. Boakye-Yiadom (2020) Characterization of the Structure and Properties of Processed Alumina-Graphene and Alumina-Zirconia Composites, *Ceramic International*, p. 135577, (<https://doi.org/10.1016/j.ceramint.2020.08.142>).
- III. **S. H. Duntu**, A. Eliasu, I. Ahmad, M. Islam, S. Boakye-Yiadom (2021), Synergistic effect of Graphene and Carbon Nanotubes on Wear Behavior of Alumina-Zirconia nanocomposites, *Materials Characterization*, vol. 175, p. 111056. (<https://doi.org/10.1016/j.matchar.2021.111056>).

- IV. **S. H. Duntu**, K. Hukpati, I. Ahmad, M. Islam, S. Boakye-Yiadom (2022), Deformation and Fracture Behaviour of Alumina-Zirconia Multi-Material Nanocomposites Reinforced with Graphene and Carbon Nanotubes, *Materials Science and Engineering A*, vol. 835, p. 142655, (<https://doi.org/10.1016/j.msea.2022.142655>).
- V. **S. H. Duntu**, J. Agyapong, I. Ahmad, M. Islam, S. Boakye-Yiadom (2022), Combined Effect of Low ZrO₂ Content and Carbon Nanostructures on Mechanical and Wear Properties of Hot-Pressed Al₂O₃/ZrO₂ Hybrid Nanocomposites, *Ceramics International*, vol. 48, p. 34803-34816, (<https://doi.org/10.1016/j.ceramint.2022.08.069>).
- VI. **S. H. Duntu**, I. Ahmad, M. Islam, S. Boakye-Yiadom (2023), Hot-Pressed Alumina-Based Nanocomposites: A Study of Effect of Multiple Reinforcement Particles on Interfacial Behaviour, Residual Stress, Electrical and Thermal Properties (*To be submitted: Materials Characterization*).

The focus of this research is to develop, design and fabricate advanced ceramic alumina (Al₂O₃)-based multi-material nanocomposites by dispersing nano-reinforcement phases such as zirconia (ZrO₂), graphene (GN) and carbon nanotubes (CNTs). To understand the effect of these multiple nano-phase additives to the ceramic Al₂O₃, it was crucial to identify the concentration of these nano-reinforcements with the potential to yield a high-performance structure with superior mechanical properties and multi-functionalities. To bridge the identified gaps in Chapter 1 and provide concise response to the research objectives, systematic studies were carried from design, processing, microstructural, mechanical and functional characterization before and after subjecting the processed nanocomposite structures to various experimental conditions. **Objective 1** was achieved by fabricating the alumina (Al₂O₃)-based multi-material nanocomposites using colloidal mixing of the dispersing nano-phases coupled with identified optimum sintering conditions (through literature studies) to yield a near-dense advanced ceramic nanocomposite structure.

In **Paper I**, we studied the effect of single additions of nano-reinforcement particles on the microstructure and tribological properties of the Al₂O₃ matrix, which focuses on **Objective 2** of

this research. The alumina-based nanocomposites were fabricated by homogeneously dispersing zirconia (4wt% and 10wt%) and graphene (0.5wt%) using colloidal mixing. The next step involved hot-pressing the mixture at 1600°C for 1 hour. To understand the microstructure of the processed nanocomposites, we extensively observed it under high-resolution electron microscopes (FESEM). Additionally, we investigated the effects of zirconia (ZrO_2) and graphene (GN) on the mechanical and tribological properties of the nanocomposites. The microstructural analysis revealed that the addition of 0.5wt%GN and 10wt% ZrO_2 led to extensive grain-refinement in the parent alumina matrix. However, the introduction of 4wt% ZrO_2 resulted in a coarse-grain microstructure due to insufficient inhibition of alumina grain growth during the sintering process.

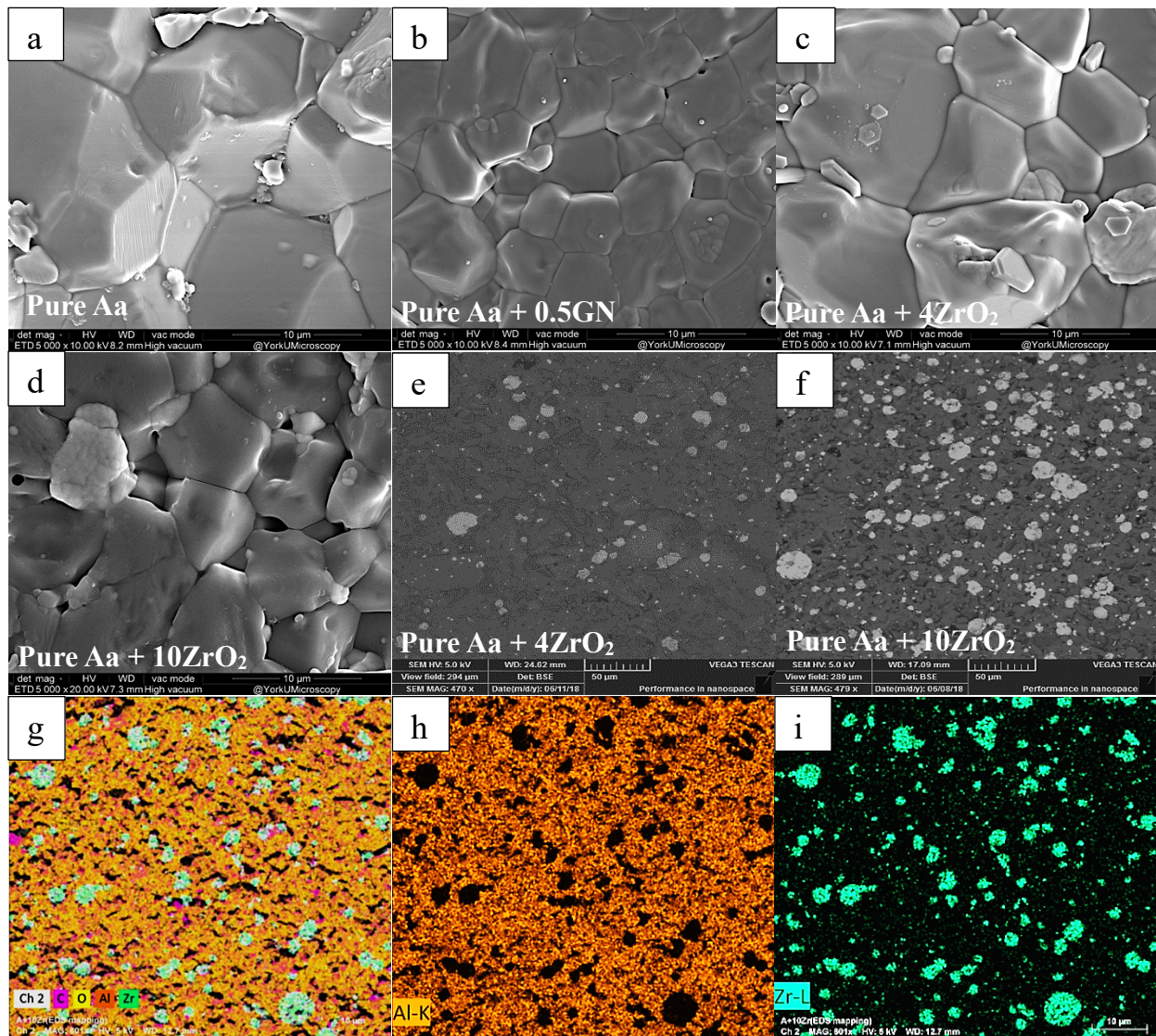


Figure 4.1: SEM micrographs of as-sintered (hot-pressed) samples under the same magnifications illustrating Al_2O_3 matrix refinement with the addition of reinforcement materials (a) Pure Al_2O_3 with relatively coarse microstructure (b) Al_2O_3 with 0.5wt% graphene addition showing grain-refinement of Al_2O_3 matrix (c) Al_2O_3 with 4wt% ZrO_2 with relatively coarse-grain structure (d) Al_2O_3 with 10wt% ZrO_2 showing a refined Al_2O_3 matrix. (e)-(f) Backscattered Electron SEM micrographs showing ZrO_2 phase distribution within Al_2O_3 matrix (e) Al_2O_3 with 4wt% ZrO_2 (f) Al_2O_3 with 10wt% ZrO_2 showing a relatively refined alumina matrix. (g)-(i) EDS mapping of elements in Al_2O_3 - ZrO_2 samples (g) overall mapped data (h) EDS mapping of element Al (i) EDS mapping showing Zr elements and ZrO_2 distribution within the Al_2O_3 matrix.

For the tribological properties, we conducted wear tests using a UMT Tribolab equipment with a constant normal load of 25N and a sliding velocity of 100mm/s for 1000 seconds, following the ASTM G133-05 standard. Interestingly, we observed a steep increase in the coefficient of friction for the addition of 4wt% zirconia, while a significant decrease was observed for the addition of 10wt% ZrO_2 . Consequently, the incorporation of 10wt% ZrO_2 led to an impressive ~98% reduction in the wear rate, attributed to its refined microstructure and effective load-bearing properties due to the uniformly dispersed ZrO_2 precipitates. On the other hand, the addition of 0.5wt% graphene resulted in a fine-grained microstructure and a consequent lower wear rate of approximately ~90.5%. However, we noted a relative increase in the coefficient of friction with graphene addition, suggesting a direct relationship between the microstructure and wear behavior rather than the coefficient of friction itself.

In conclusion, our study demonstrated the significance of carefully controlling the nanocomposite microstructure by incorporating optimal amounts of zirconia (ZrO_2) and graphene (GN). These findings shed light on the connection between microstructure and wear behavior, providing valuable insights for the development of advanced alumina (Al_2O_3) matrix nanocomposites with tailored mechanical and tribological properties.

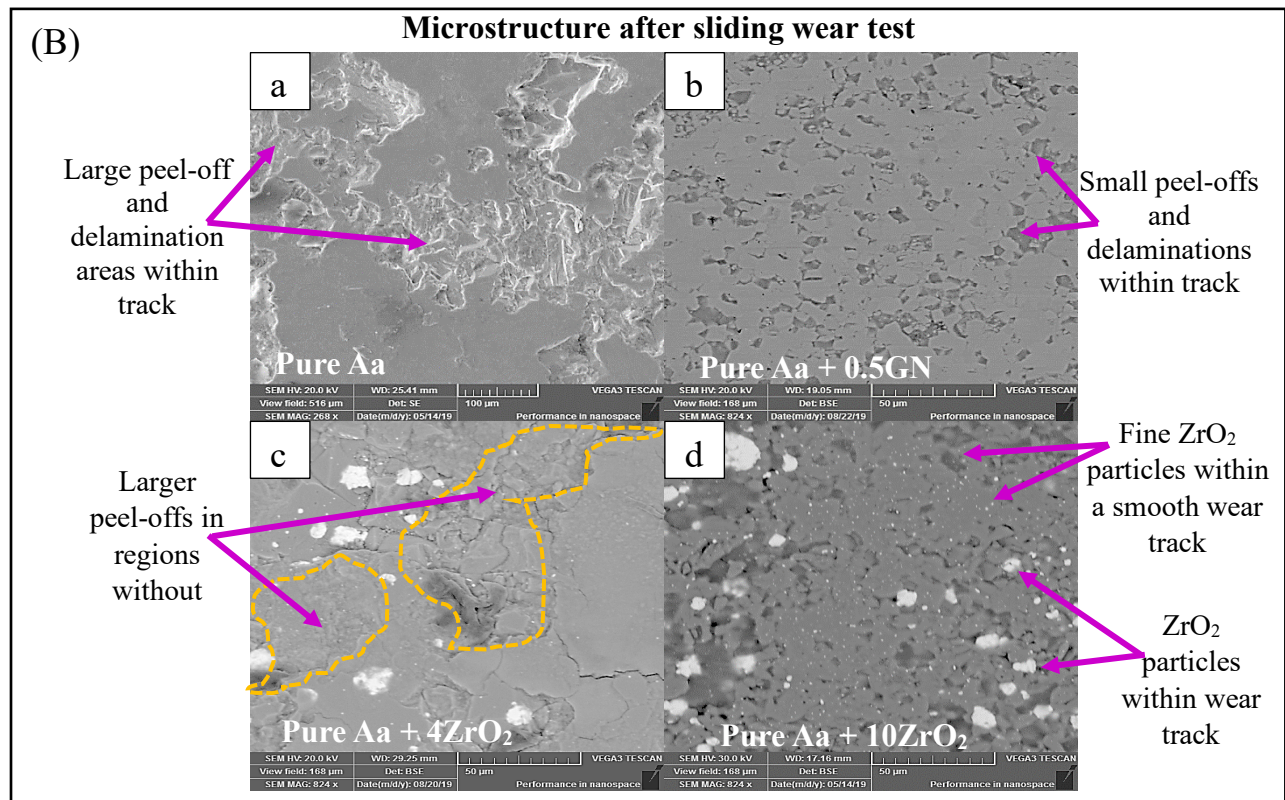
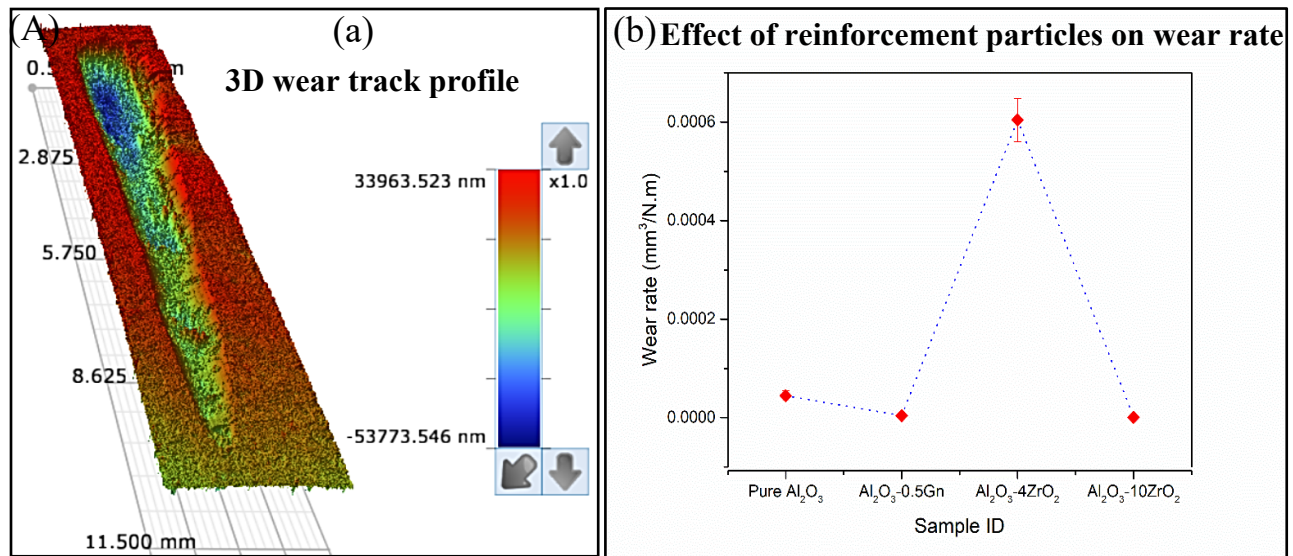


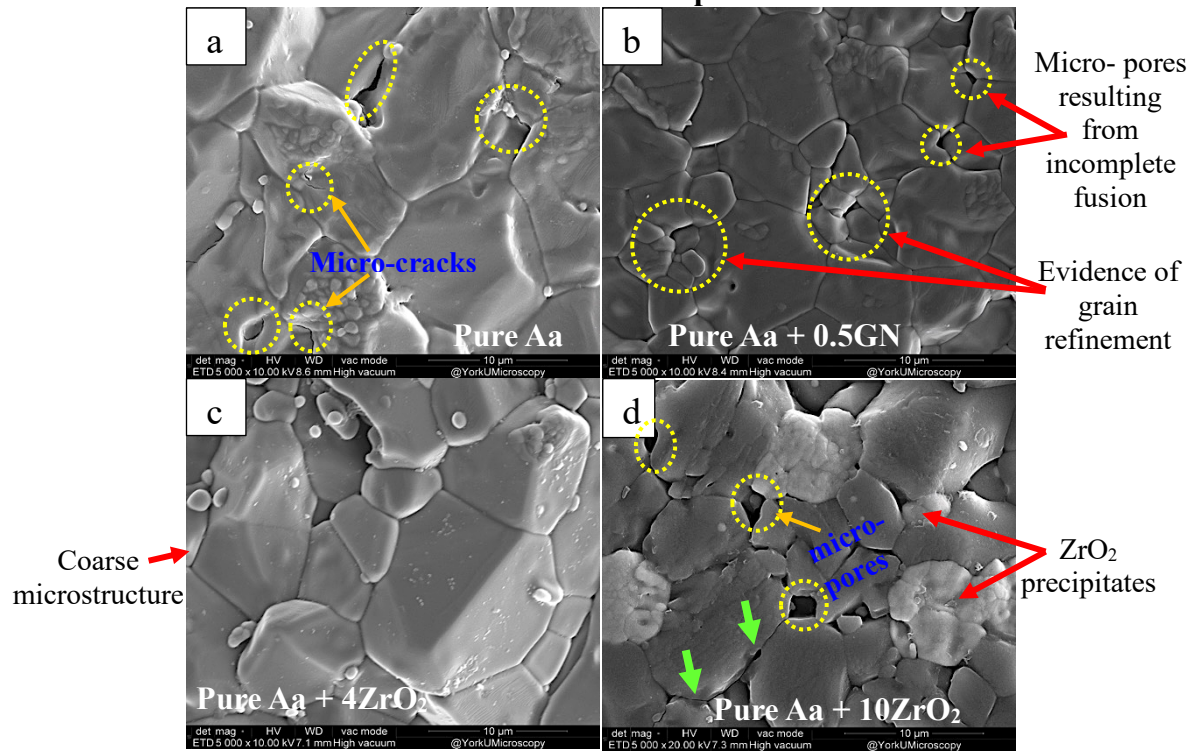
Figure 4.2: (A)-(a) 3D optical profile of full wear track using the optical profilometer (b) Graph of wear rate (mm³/N.m) variations of Al₂O₃ nanocomposites. (B) SEM micrographs showing peeling off within wear tracks (a) wear track of Pure Al₂O₃ with large and coarse peel-off and delamination areas (b) Al₂O₃ with 0.5wt%GN addition depicting small and very fine delamination areas within

wear track (c) Al_2O_3 -4wt% ZrO_2 with large delamination and peel-offs (d) Al_2O_3 -10wt% ZrO_2 with relatively uniform worn surface

In **Paper II**, we investigated the influence of the single additions on the microstructural evolution and mechanical properties of fabricated Al_2O_3 nanocomposites. This paper also addresses **Objective 2** of this study. The evolving microstructure including defects such as porosity, and mechanical properties of the hot-pressed Al_2O_3 -graphene (0.5wt%GN) and Al_2O_3 - ZrO_2 (4wt% and 10wt%) nanocomposites including, micro-hardness (H_v) and fracture toughness (K_{IC}) were studied (Figure 4.3A). For the Al_2O_3 - ZrO_2 nanocomposites, we observed that the addition of 10wt% ZrO_2 resulted in a notable 23% reduction in the grain size of the Al_2O_3 matrix. However, the inclusion of 4wt% ZrO_2 led to a surprising 14% increase in grain size compared to the parent Al_2O_3 matrix. X-ray diffraction (XRD) analysis indicated that the Al_2O_3 -4wt% ZrO_2 sample had an approximately 85% monoclinic (m) and 15% tetragonal (t), while the Al_2O_3 -10wt% ZrO_2 sample had about 93% monoclinic (m) and 7% tetragonal (t) contents. The high volume fraction of the monoclinic crystal structure in the Al_2O_3 -10wt% ZrO_2 sample explained the presence of numerous cracks, as the transition from the ductile tetragonal to brittle monoclinic phase is associated with the initiation and propagation of cracks.

One of the unique discoveries in this study is the mechanism of Al_2O_3 matrix grain refinement by the ZrO_2 particles via phase transformation during sintering. The interactions between the matrix grain and the phase transition mechanisms of ZrO_2 during sintering and cooling are essential to the final grain structure, as illustrated in (Figure 4.3B). The sintering process involves the heating and cooling of a material to create a cohesive structure. In this context, a reversible diffusionless shear-type martensitic phase transformation occurs, changing the crystal structure of ZrO_2 from monoclinic (m- ZrO_2) to tetragonal (t- ZrO_2) and vice versa. Initially, at room temperature, the dispersed nanocomposite contains a stable m- ZrO_2 structure (Figure 4.3B-a). As temperature increases during sintering, the transformation to t- ZrO_2 at approximately $\sim 1170^\circ\text{C}$ leads to a decrease in volume, creating room for matrix grain growth (Figure 4.3B-b). At this stage, the matrix can coalesce and form larger grains as high-temperature diffusion continues up to maximum sintering temperature of 1600°C , in the presence of the transformed t- ZrO_2 (Figure 4.3B-c).

(A) As-sintered microstructure before mechanical test showing micro-defects such as micro-pores



(B)

Effect of *t-m* ZrO₂ transformation on matrix grain growth during sintering and cooling

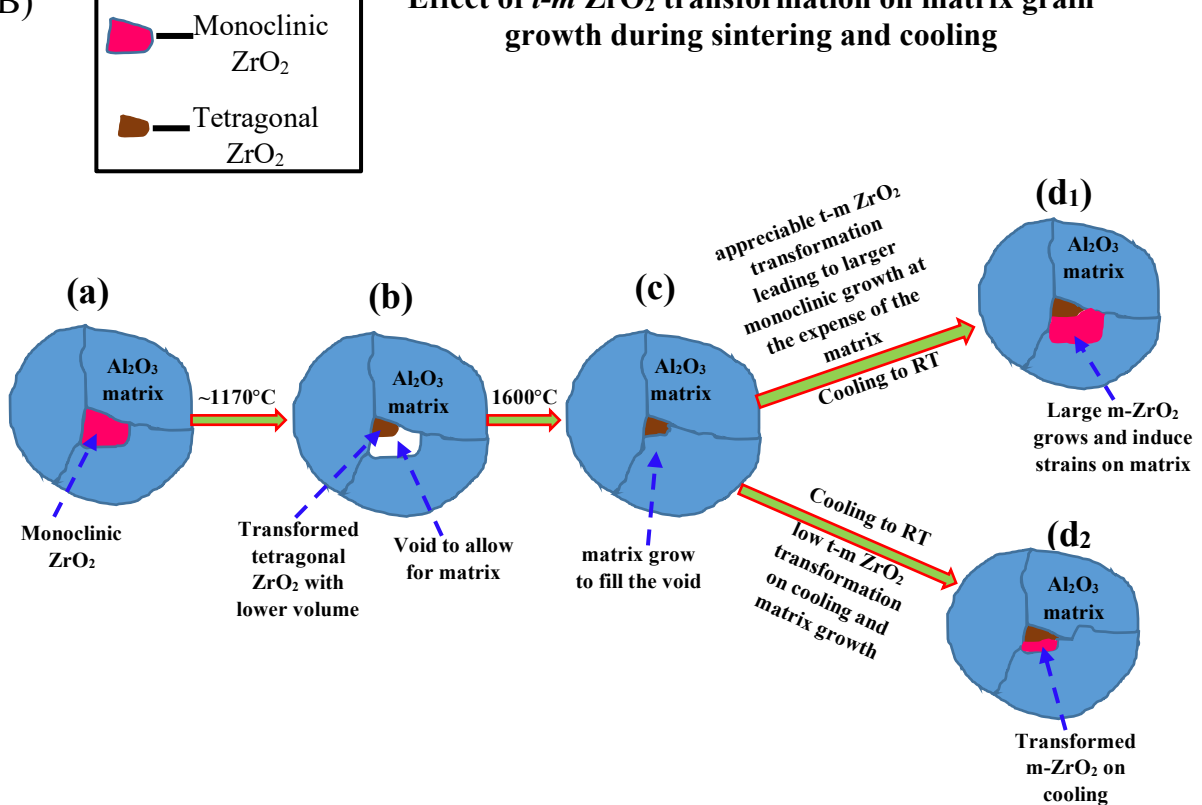


Figure 4.3: (A) FE-SEM micrographs of nanocomposites illustrating apparent microstructural defects (a) Pure Al_2O_3 showing large grains with micro-cracks (b) Al_2O_3 with 0.5wt% graphene depicting micro pores (c) Al_2O_3 with 4wt% ZrO_2 showing a coarse microstructure (d) Al_2O_3 with 10wt% ZrO_2 showing micro-pores and grain boundary cracking. (B) Schematics of the effect of tetragonal to monoclinic (*t-m* ZrO_2) transformation on matrix grain growth during sintering and cooling.

During cooling, a tetragonal to monoclinic phase transformation (*t-m* ZrO_2) occurs due to cooperative changes in short and long-range interactions. The extent of this transformation and the volume fraction of the transformed monoclinic phase (*m-ZrO*₂) at the matrix grain boundaries significantly impact the final grain structure of the Al_2O_3 matrix. Two scenarios are discussed regarding the cooling phase and its effect on Al_2O_3 matrix grain size:

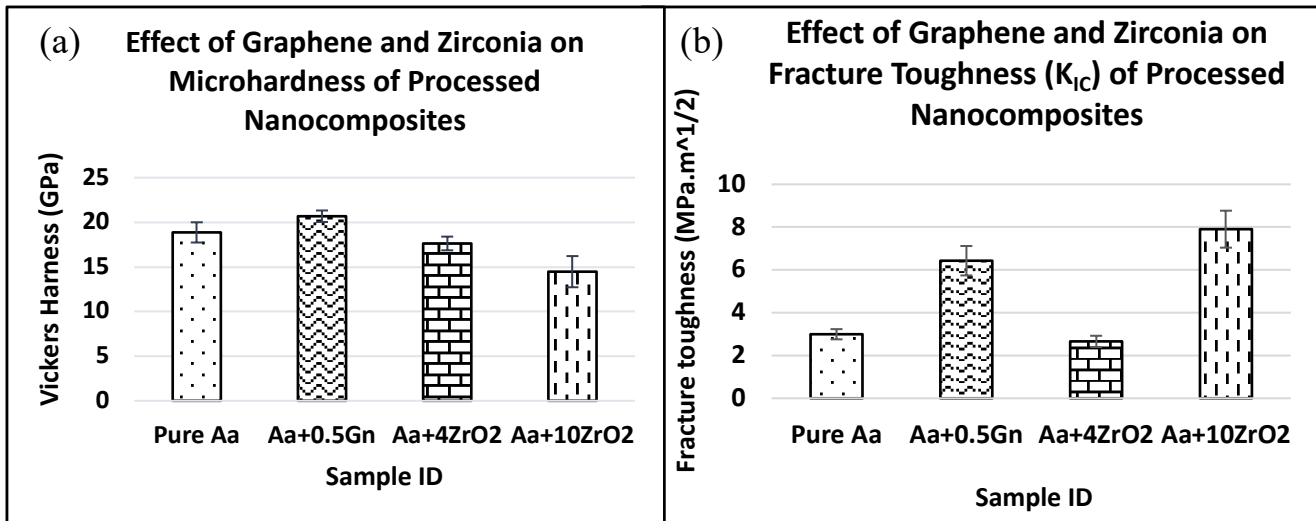
1. Scenario (d1): A high volume of monoclinic transformation during cooling causes expansion, inducing high stress on the matrix boundaries, leading to the refinement of Al_2O_3 grains as *m-ZrO*₂ expands. This explains the Al_2O_3 -10wt% ZrO_2 sample's behavior, where most of the *t-ZrO*₂ transforms to *m-ZrO*₂ (93% monoclinic vs. 7% tetragonal), resulting in higher induced stresses on the matrix grains and consequent reduction in grain size of the Al_2O_3 matrix.
2. Scenario (d2): In contrast, insufficient transformation of the monoclinic phase upon cooling allows the matrix grains to continue growing and increasing in size. As a result, more tetragonal phase is retained in the structure, leading to relatively lower inhibition of matrix grain growth. This explains the larger grain size in the Al_2O_3 -4wt% ZrO_2 sample, where there was a higher volume of *t-ZrO*₂ (85% monoclinic vs. 15% tetragonal) after cooling.

The study also suggests that the limitation to Al_2O_3 matrix grain growth during sintering is due to the increased grain boundary drag force caused by the added ZrO_2 particles (10wt%) on the matrix grain boundaries. Overall, the phase transition mechanisms of ZrO_2 play a crucial role in determining the grain growth behavior of the matrix materials during sintering, with different transformation patterns leading to varied grain sizes and structures.

On the other hand, the incorporation of 0.5wt% graphene (GN) in the Al_2O_3 matrix resulted in about a 37% reduction in the size of the alumina grains (Figure 4.3A-b). This addition also led to an approximately 10% increase in hardness due to the distribution of graphene along the grain

boundaries of the parent Al_2O_3 matrix, which effectively restricted grain coalescence and growth. Furthermore, the inclusion of 0.5wt%GN and 10wt% ZrO_2 contributed to significant improvements in the fracture toughness (K_{IC}). The fracture toughness increased up to 115% with the addition of 0.5wt% graphene and 164% with 10wt% ZrO_2 . These enhancements were primarily attributed to

(A) Effect of single additions on mechanical properties of processed nanocomposites



(B) Fractography characterization illustrating intergranular and transgranular fracture modes

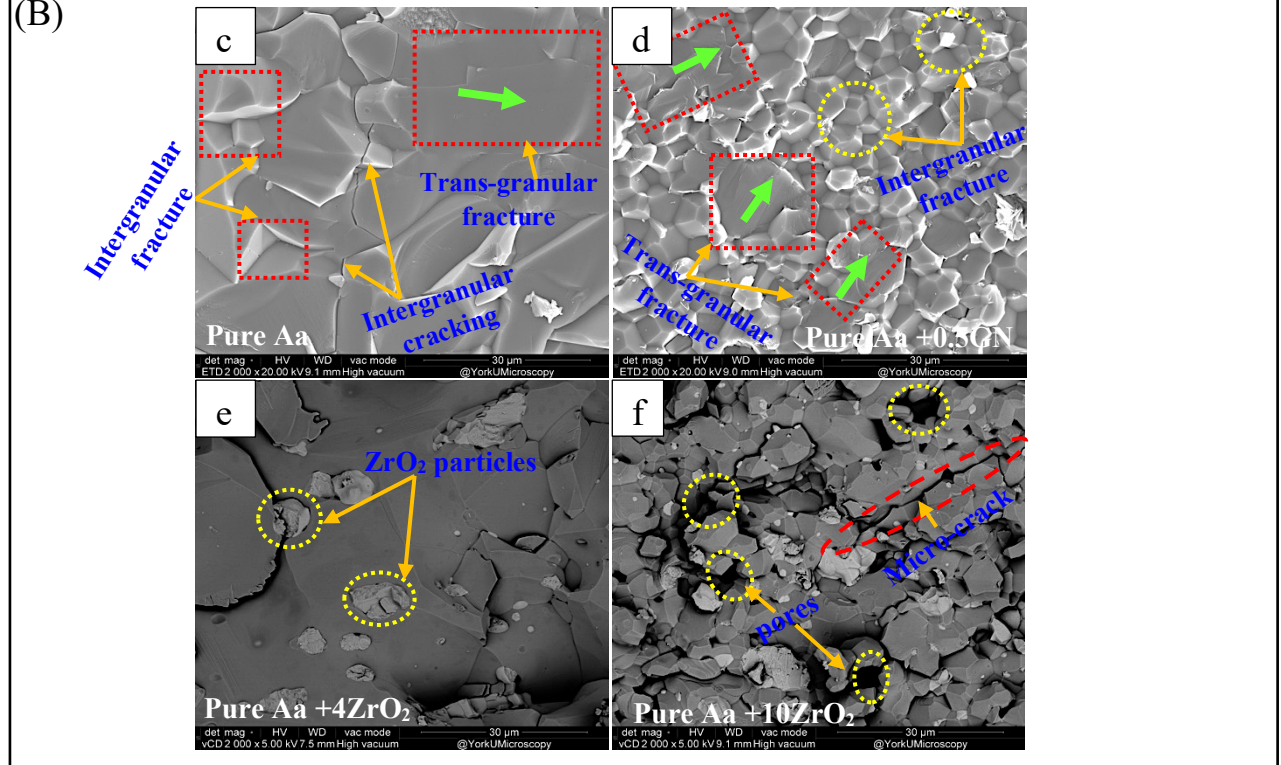


Figure 4.4: (A) Graph showing the (a) the effect of Graphene and ZrO_2 on the Vickers micro-hardness of fabricated nanocomposites (b) the effect of Graphene and ZrO_2 on the Fracture toughness (K_{IC}) of fabricated nanocomposites (B) FE-SEM micrographs of fractured surface of (a) pure Al_2O_3 matrix sample showing both intergranular and transgranular mode of fracture (b) Al_2O_3 -0.5wt% nanocomposite sample demonstrating both intergranular and transgranular fracture behaviour (c) Al_2O_3 -4wt% ZrO_2 depicting intergranular fracture and grain-boundary cracking, with ductile fracture of the ZrO_2 precipitates

the fine-grained microstructures and toughening mechanisms of the intergranular graphene and ZrO_2 particles. Notably, micro-crack toughening induced from ZrO_2 phase transition played a crucial role in toughening the nanocomposites as illustrated in the fractography studies (Figure 4.4B). Overall, our study revealed valuable insights into the structural and mechanical properties of Al_2O_3 -graphene and Al_2O_3 - ZrO_2 nanocomposites, highlighting the potential for tailoring these materials for various advanced structural applications.

Paper III focuses on **Objective 3** of this study, as identified in Chapter 1. In this study, we described the simultaneous dispersion of multiple reinforcement nanoparticles such as graphene, carbon nanotubes, and zirconia, within the alumina matrix. The article further delves into the collective impact of these multi-material additives on matrix grain refinement, friction, and wear behavior, as well as the synergistic mechanisms that arise from the simultaneous incorporation of graphene, carbon nanotubes, and zirconia. The Al_2O_3 matrix multi-material nanocomposites were developed and fabricated, reinforced with multiple nano-materials: zirconia (ZrO_2), graphene (GN), and carbon nanotubes (CNTs). The objective was to investigate the synergistic effect of these multi-materials on microstructural evolution, mechanical properties, and tribological behavior, particularly the wear mechanism. To prepare the samples, monolithic Al_2O_3 and Al_2O_3 -based nanocomposites with 10wt% ZrO_2 , 0.5wt%GN, and 2wt%CNTs were produced using the colloidal mixing process and similar sintering conditions described in Chapter 3. The results were then compared to the monolithic Al_2O_3 for benchmarking purposes.

The addition of 10wt% ZrO_2 alone led to about 25% decrease in matrix grain size, while the combination of ZrO_2 , GN and CNTs resulted in a remarkable reduction in both the matrix and

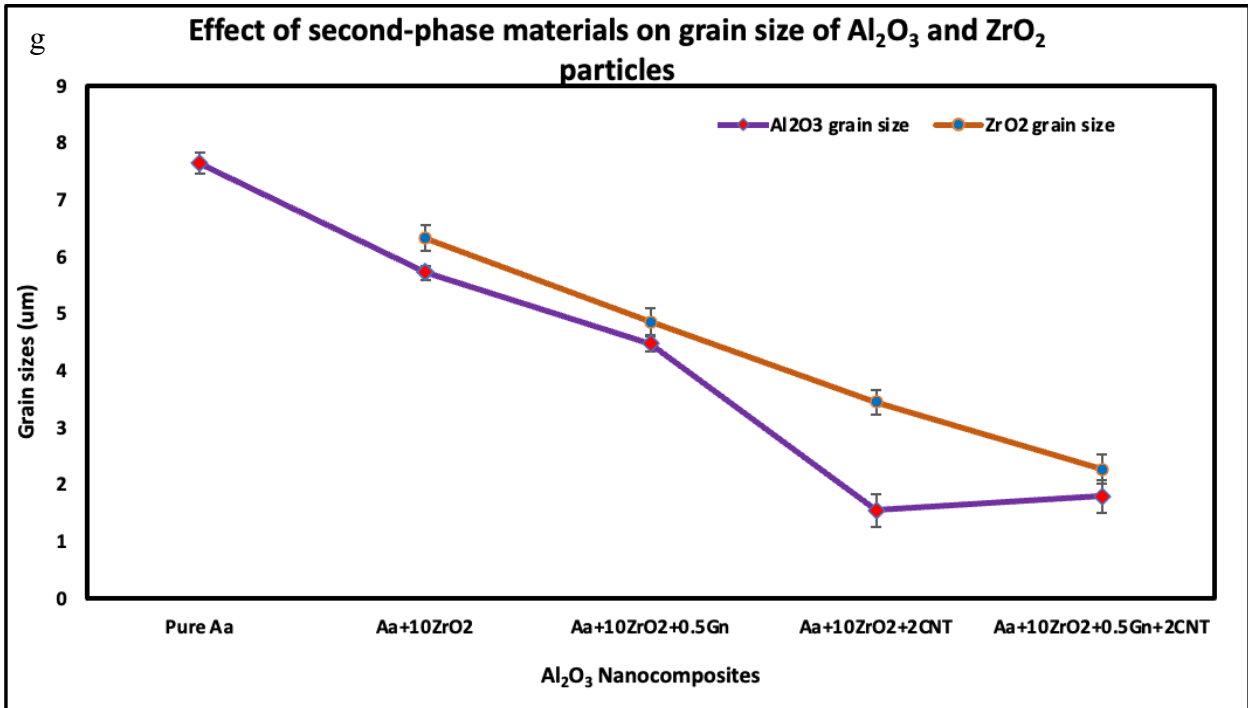
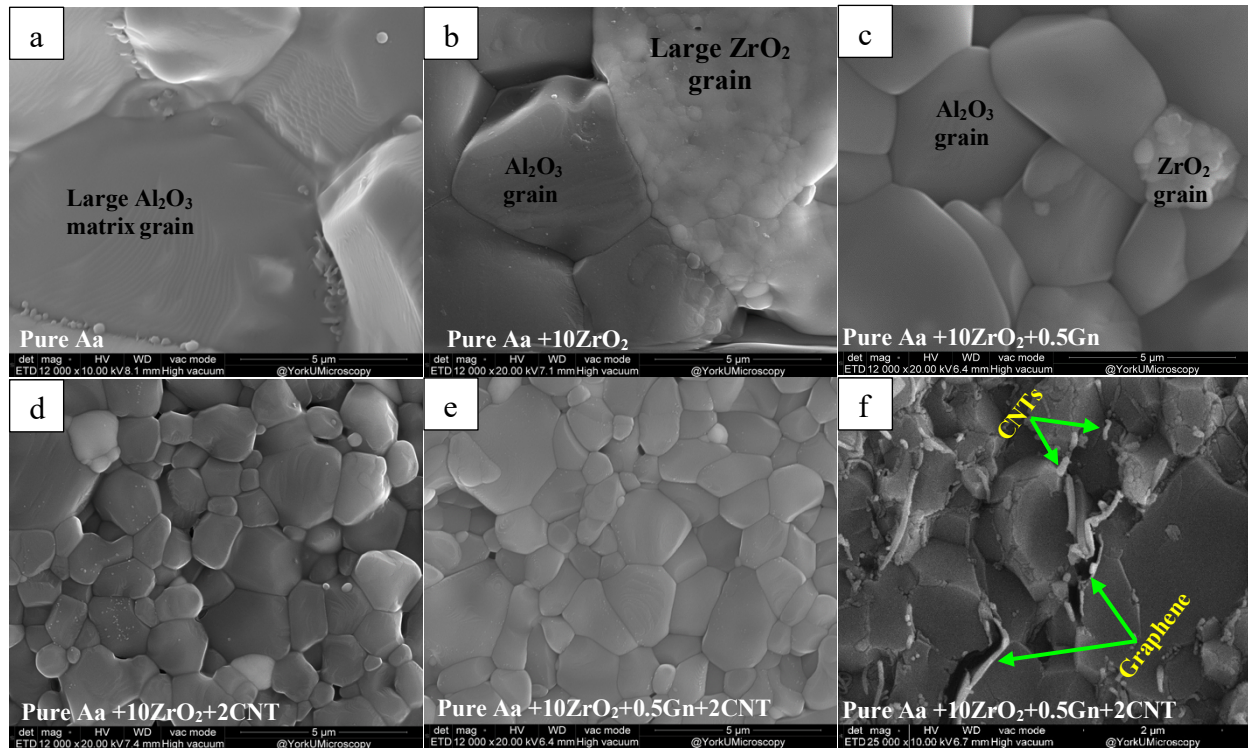


Figure 4.5: Microstructural evolution of multiple nano-reinforcement additions in Al₂O₃ matrix nanocomposites (a) Pure Al₂O₃ (b) Al₂O₃-10ZrO₂ (c) Al₂O₃-10ZrO₂-0.5GN (d) distribution of GN and CNT particles within matrix (e) Al₂O₃-10ZrO₂-2CNT (f) Al₂O₃-10ZrO₂-0.5GN-2CNT (g) Variation of the Al₂O₃ matrix and ZrO₂ grain size as a function of the second-phase materials

ZrO₂ grains, up to 88% and 46%, respectively (Figure 4.5). This reduction was attributed to the effective parallel pinning action of the matrix grains by the homogeneously dispersed multi-materials in the monolithic Al₂O₃.

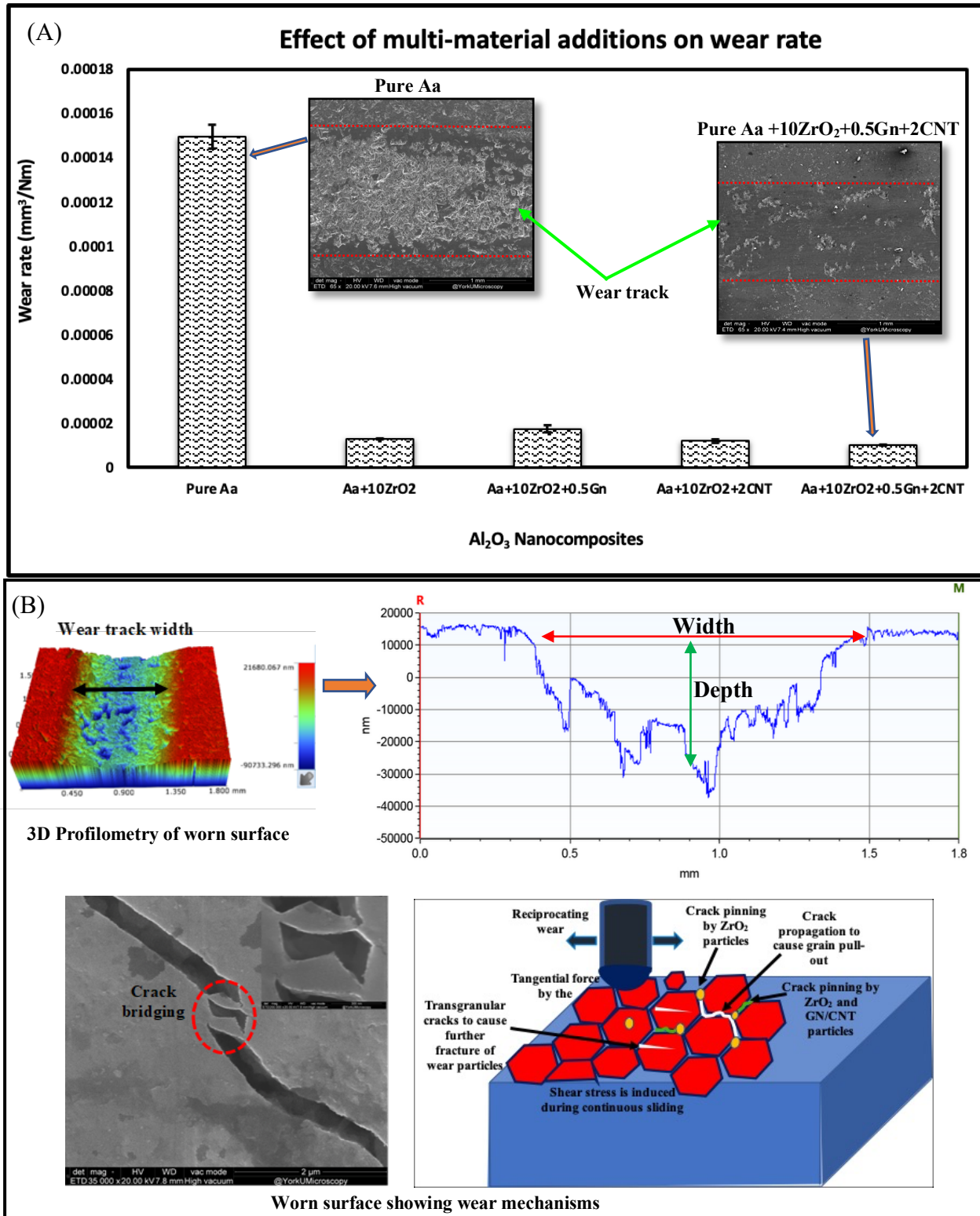


Figure 4.6: (A) Effect of multi-material reinforcement on the wear rate of Al_2O_3 nanocomposites (B) 3D optical profile of wear track and wear mechanisms during sliding wear on nanocomposite surface.

Moreover, the nanocomposite with only 10wt% ZrO_2 exhibited an 88% decrease in wear rate (Figure 4.6A). In contrast, the multiple additions of GN and CNTs demonstrated superior wear resistance, with up to 93% reduction in wear rate compared to the monolithic Al_2O_3 . This enhanced wear resistance was attributed to the micro-crack bridging and restriction to intergranular fracture, preventing pull-out of the matrix grains during sliding wear (Figure 4.6B). Additionally, the combined crack pinning by the finely dispersed ZrO_2 particles, along with the bridging action of GN and CNTs, contributed to the synergistic response of these multi-materials, resulting in improved wear performance of the fabricated nanocomposites.

In **Paper IV**, we investigated in detail the influence of multiple reinforcement additions on the mechanical properties of alumina (Al_2O_3) and elucidated various combined strengthening and toughening mechanisms by the nano-reinforcements within the Al_2O_3 matrix. This study also satisfies **Objective 3**, and addresses the trade-off in mechanical properties with the addition of selected nano-reinforcement amounts to the monolithic Al_2O_3 structure. A comprehensive understanding of the mechanical performance and deformation behavior resulting from various combinations of these nano-structured additives within advanced Al_2O_3 matrix structures was provided in this paper. The under-study Al_2O_3 -based nanocomposites reinforced with selected optimal amounts of ZrO_2 (10wt%), GN (0.5wt%), and CNTs (2wt%) were fabricated through a hot-pressing process at 1600°C according to the fabrication route discussed in Chapter 3. The mechanical properties, specifically fracture toughness (K_{IC}), and bending strength (σ_f), were measured using three-point bending techniques, including single-edge notched beam (SENB) tests and direct crack measurement (DCM) methods. These measurements were compared against the monolithic Al_2O_3 matrix material under similar experimental conditions. Vickers hardness showed a 48% increase with the combined additions of ZrO_2 , GN and CNTs, in contrast to the 25% decrease observed with the single addition of ZrO_2 in comparison to the monolithic Al_2O_3 (Figure 4.7a). This improvement was attributed to the refined grain structures and effective load transfer capabilities of the combined multi-phase materials.

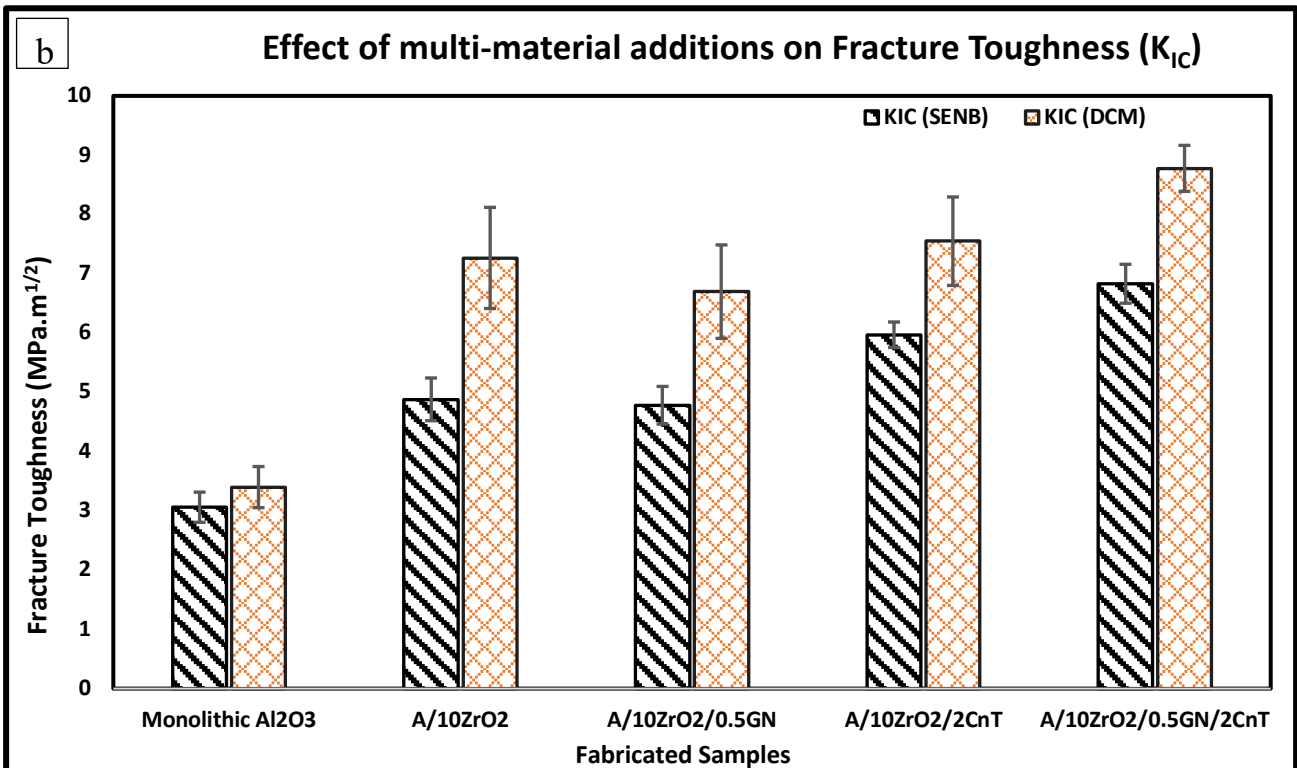
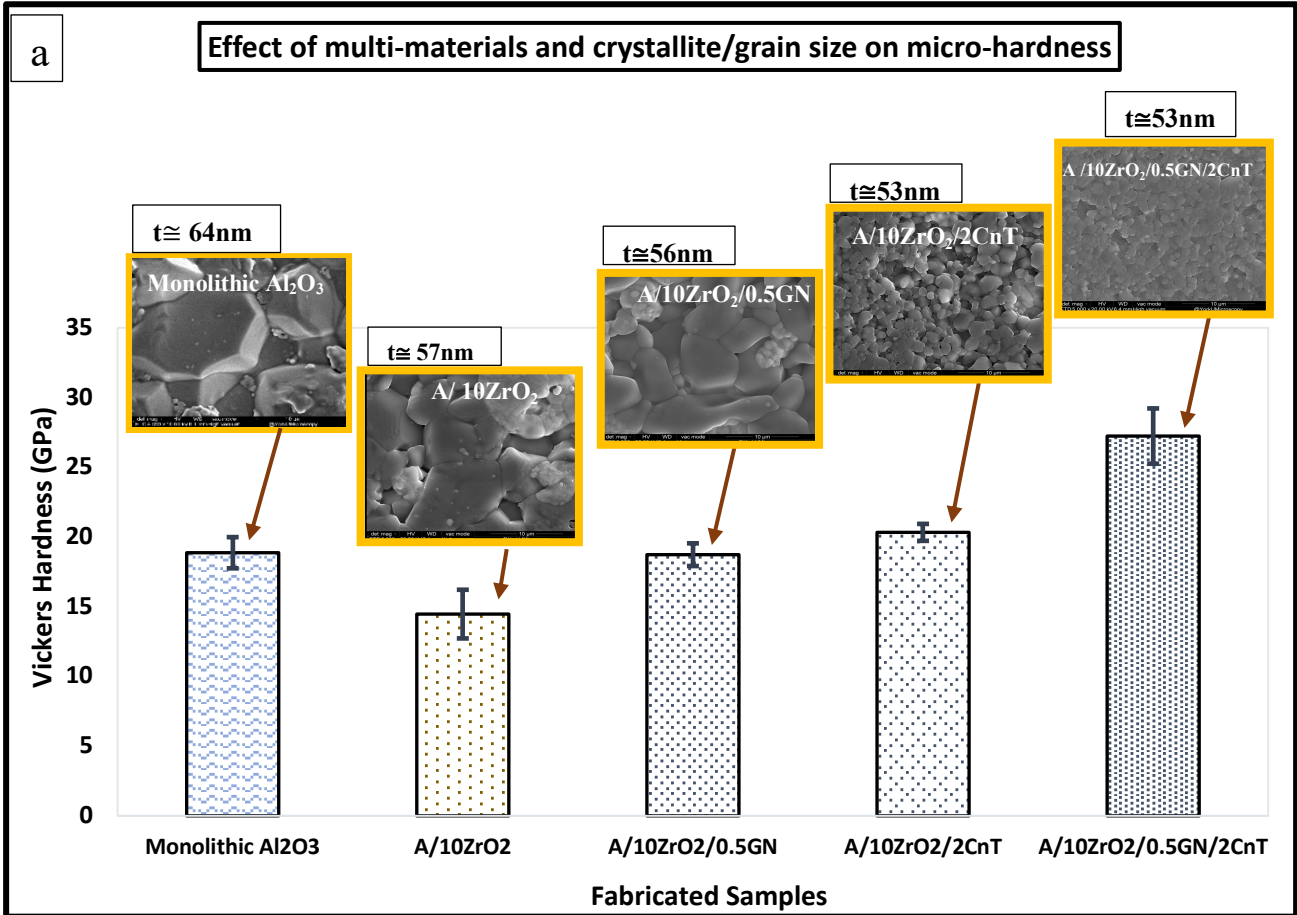


Figure 4.7: (a) Effect of multi-materials and grain size/crystallite size on micro-hardness of fabricated nanocomposites (b) Effect of multi-material addition on fracture toughness (K_{IC}) of nanocomposites as measured by SENB and DCM methods.

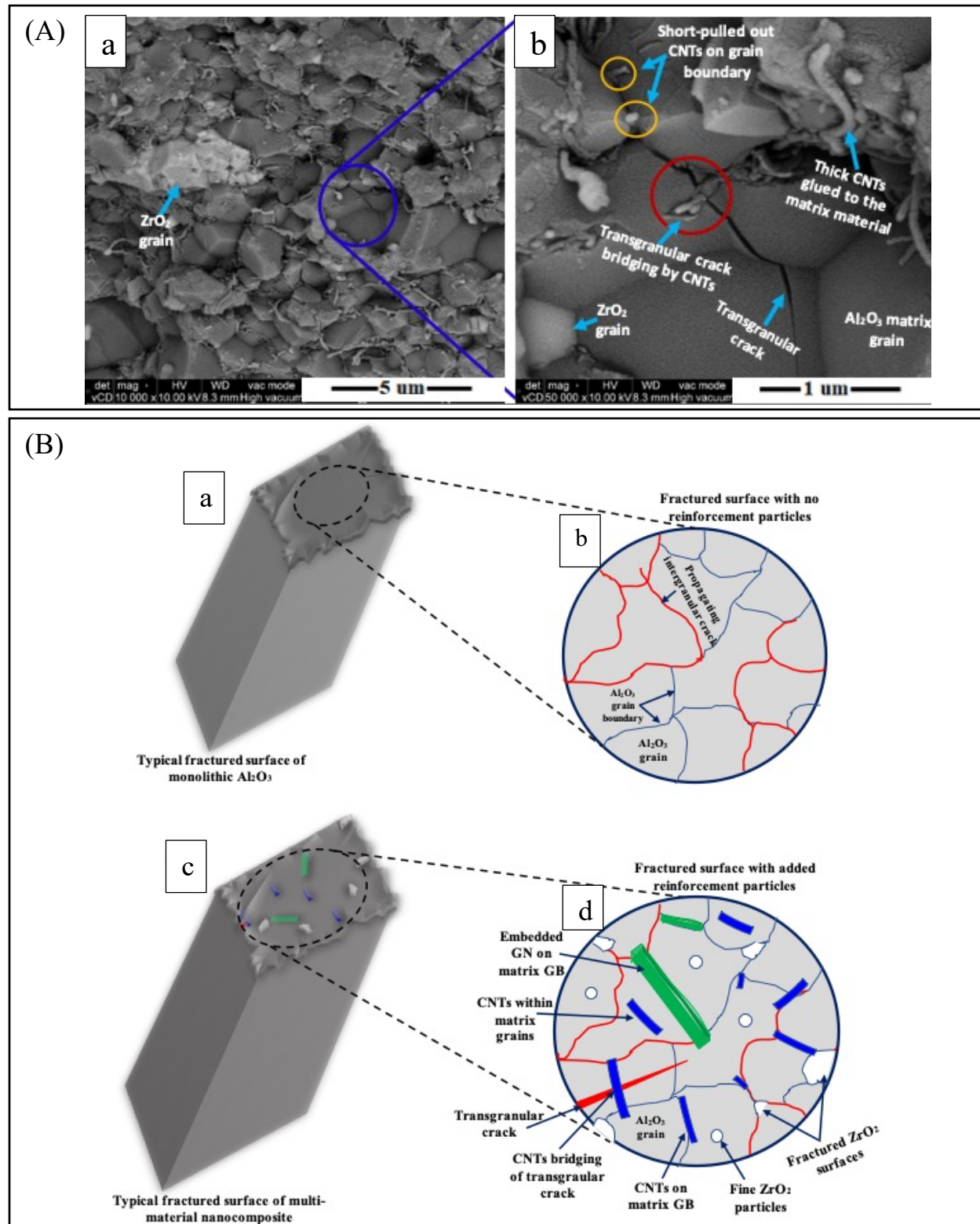


Figure 4.8: (A) (a)-(b) FE-SEM fractographs demonstrating toughening mechanisms within multi-material nanocomposites (B) Schematics of toughening mechanisms by fabricated monolithic Al_2O_3 and nanocomposites (a)-(b) fractured surface of monolithic Al_2O_3 without any reinforcement particles (c)-(d) fractured surface of nanocomposites reinforced with ZrO_2 , GN and CNTs

From the conventional SENB tests, we observed a substantial 60% increase in fracture toughness with the addition of only 10wt% ZrO_2 to the monolithic Al_2O_3 . Remarkably, the incorporation of both GN and CNTs within the Al_2O_3 - ZrO_2 structure led to a drastic 159% increase in fracture toughness compared to the monolithic Al_2O_3 . While K_{IC} values obtained from SENB tests were slightly lower than those from the DCM method, the overall trend in toughness behavior remained consistent (Figure 7b). Moreover, the bending strength of the prepared monolithic Al_2O_3 increased by up to 46% when combined with ZrO_2 , GN, and CNTs. Our investigation identified various toughening and strengthening mechanisms, including pull-outs by GN and CNTs, crack arrest, and crack bridging, as the primary sources of enhancement in the mechanical properties of the multi-material nanocomposites (Figure 4.8). Additionally, the incorporation of carbon additives influenced monoclinic and tetragonal ZrO_2 phase transformations, further contributing to the overall mechanical behavior of the Al_2O_3 -10wt% ZrO_2 nanocomposites.

Paper V presents a comparative study of hybrid reinforcement additions of ZrO_2 (4wt%) and GN (0.5wt%), as well as ZrO_2 (4wt%) and CNTs (2wt%), in the alumina (Al_2O_3) matrix, which also satisfies **Objectives 3**. The incorporation of higher ZrO_2 amounts ($\geq 20\text{wt}\%$) in $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite systems can improve fracture toughness. However, this improvement often comes at the cost of reduced hardness, wear resistance, and strength performances. To address this property trade-off, a novel approach involves adding a third-phase carbon nanostructure, such as CNTs and GN to $\text{Al}_2\text{O}_3/\text{ZrO}_2$ reinforced with low ZrO_2 content ($\leq 5\text{wt}\%$). This hybrid nanocomposite system allows us to explore the remarkable mechanical properties of these materials while overcoming the limitations of high ZrO_2 content. In this study, we utilized a colloidal mixing process followed by hot pressing at 1600°C to consolidate four different nanocomposite structures: monolithic Al_2O_3 , $\text{Al}_2\text{O}_3/\text{ZrO}_2$, $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{CNTs}$, and $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{GN}$. We used low ZrO_2 content (4wt%)

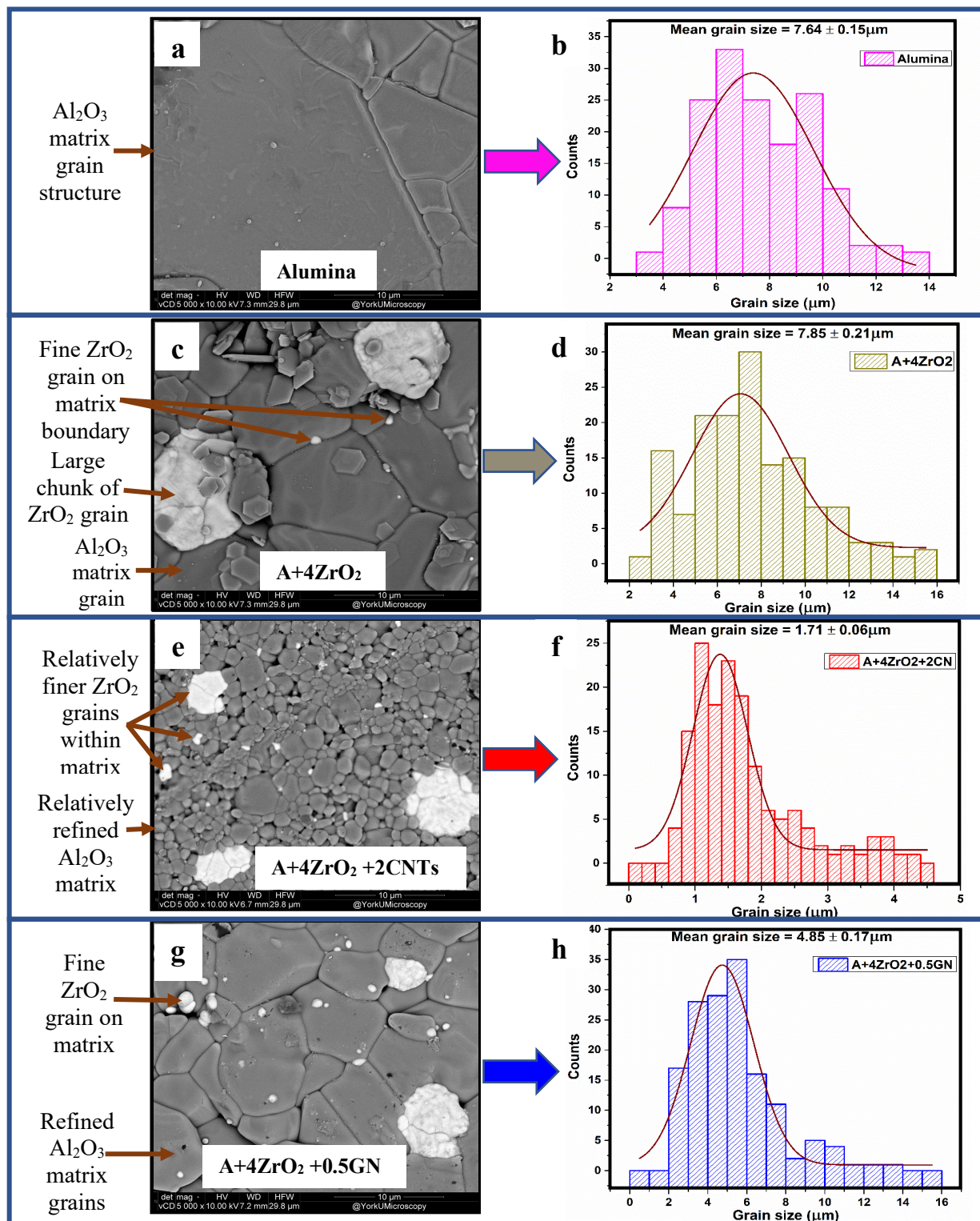


Figure 4.9: FE-SEM micrographs and grain size distributions of sintered hybrid nanocomposites (a) monolith Al_2O_3 (b) Al_2O_3 -4ZrO₂ (c) Al_2O_3 -4ZrO₂-2CNTs (d) Al_2O_3 -4ZrO₂-0.5GN

and optimum amounts of CNTs (2wt%) and GN (0.5wt%) as hybrid reinforcement phases. The addition of ZrO_2/CNTs and ZrO_2/GN hybrids to the monolithic Al_2O_3 resulted in notable matrix grain refinement (up to 78% reduction in matrix grain size), as illustrated in Figure 4.9.

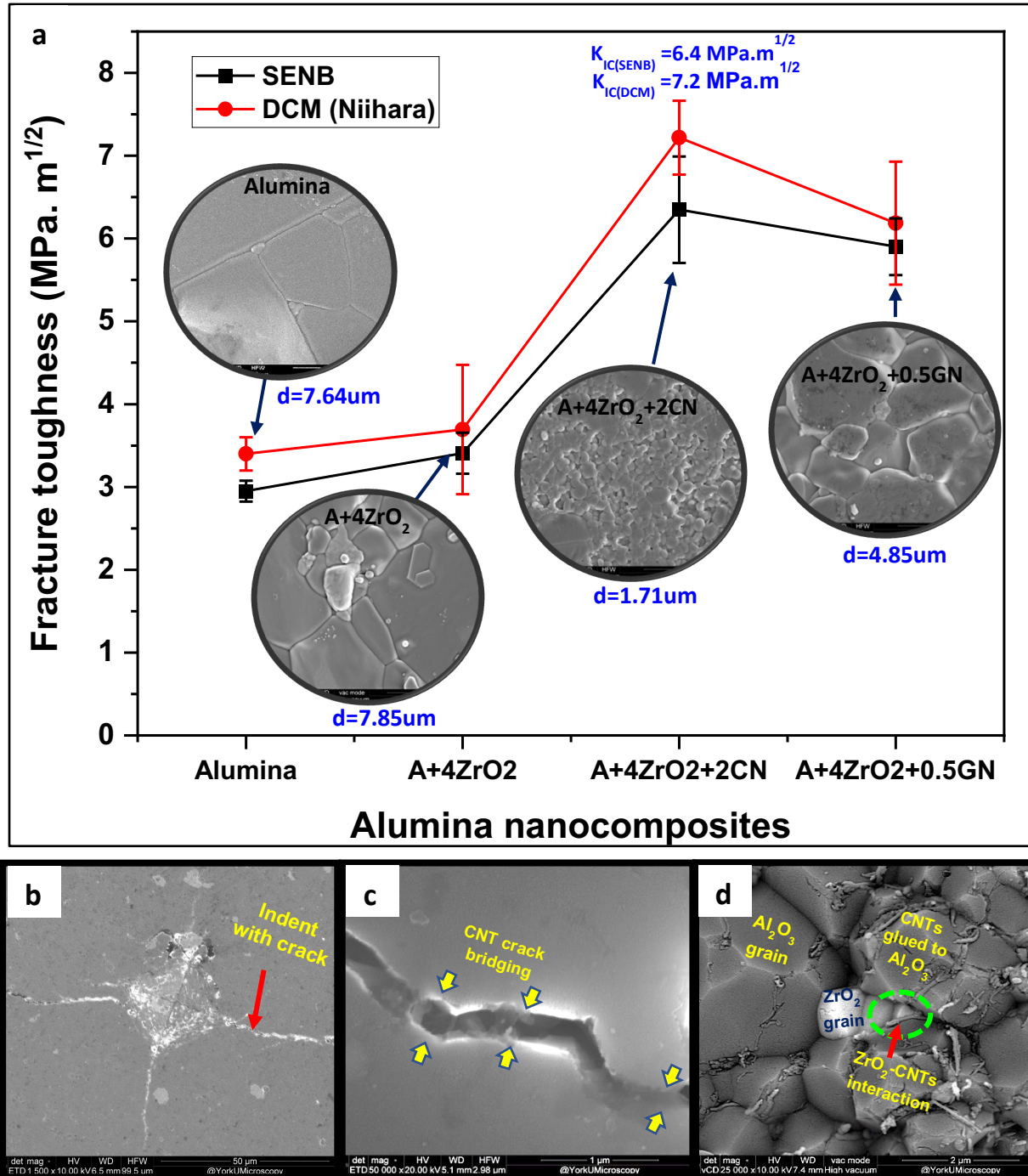
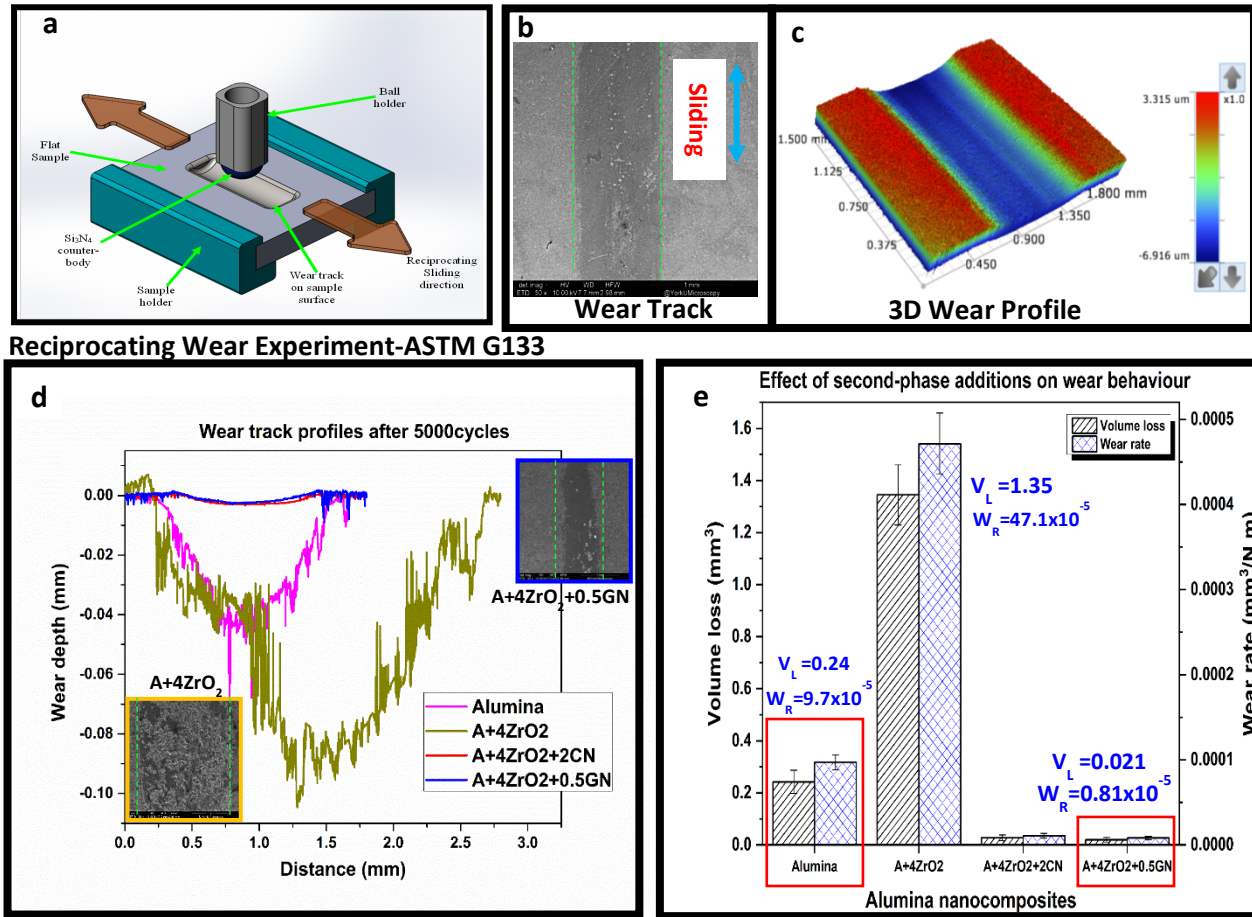


Figure 4.10: (a) Effect of hybrid nano-reinforcement additions on fracture toughness (K_{IC}) properties of Al_2O_3 nanocomposites (b) indent with emanating cracks (c)-(d) toughening mechanisms of hybrid nano-reinforcements.

(A) Effect of hybrid nano-reinforcements on tribological properties



(B) Grain refinement and wear resistant mechanisms in hybrid nanocomposites

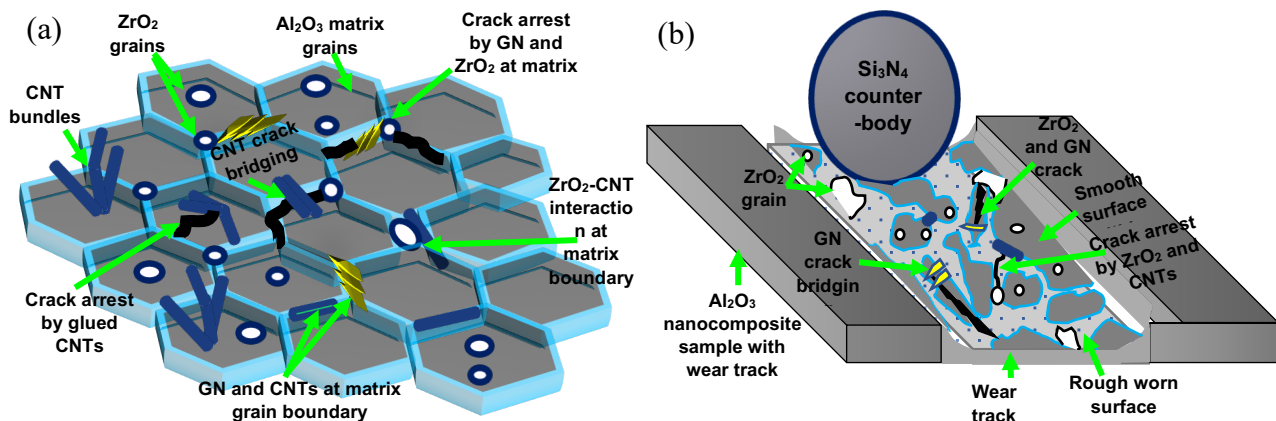


Figure 4.11: (A) Tribological performance of Al₂O₃ nanocomposites (a) reciprocating wear test configuration(b)-(c) worn surface of sample with 3D wear track profile after wear test (d) Wear width and depth variations obtained from worn grooves of nanocomposites after 5000 sliding cycles. (B) Schematic illustrations of (a) interaction of ZrO₂, CNTs and GN within matrix structure (b) wear resistant mechanisms in wear grooves.

Significant improvements in microhardness, fracture toughness, and flexural strength were also demonstrated by the hybrid inclusion. The microhardness increased from 19 GPa to 24 GPa, the fracture toughness improved from $\sim 3 \text{ MPa}\cdot\text{m}^{1/2}$ to $\sim 7 \text{ MPa}\cdot\text{m}^{1/2}$, and the flexural strength rose from 260 MPa to 374 MPa. These enhancements were primarily attributed to the reduction in the matrix and ZrO_2 grain sizes, the favorable interaction between the reinforcement phases, and the combined mechanisms of crack bridging and deflection, matrix grain wrapping, and grain gluing facilitated by CNTs and GN (Figure 4.10).

Furthermore, the wear rate of the monolithic Al_2O_3 material was significantly improved from $9.71 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ to $0.81 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$, representing a $\sim 92\%$ decrease, with the inclusion of ZrO_2/CNTs and ZrO_2/GN hybrid nano-reinforcements (Figure 4.11A). This improvement was attributed to the overall enhanced mechanical properties and wear-resistant mechanisms during dry sliding (Figure 4.11B).

Paper VI (*manuscript in-preparation*) investigates the nature of interfacial bonding between the alumina (Al_2O_3) matrix and the nano-reinforcement phases. We also assessed the roles of the multiple additions of carbon nanostructures such as graphene and carbon nanotubes (CNTs) on the functional performance of the fabricated advanced Al_2O_3 multi-material nanocomposites such as electrical properties. This study satisfies **Objective 4** of this research. The mechanical properties of the fabricated nanocomposites are influenced by the interfacial structures and interfacial barriers. Our previous studies in Paper I-V demonstrated a drastic refinement in matrix grain size with consequent enhancement in hardness, fracture toughness, bending strength and tribological performance. This stems from the nature of the interface which dictates mechanisms such as load carrying capacity of the nanocomposite in the presence of applied stress. Figure 4.12(a)-(b) shows a transmission electron micrograph (TEM) which illustrates good adherence of the Al_2O_3 matrix with the carbon nanostructures such as GN and firm connection at the interface. The high nanoscale roughness on the GN surface is known to improve interfacial bonding with ceramic matrix, enhancing physical bonding and inducing high frictional forces at the matrix-GN boundary. This in turn produces high energy for the system during pull-out activities resulting in the high mechanical properties demonstrated in Papers II-V. Figure 4.12 (c)-(d) illustrates the high-resolution transmission electron micrograph (HRTEM) images of the nanocomposites illustrating

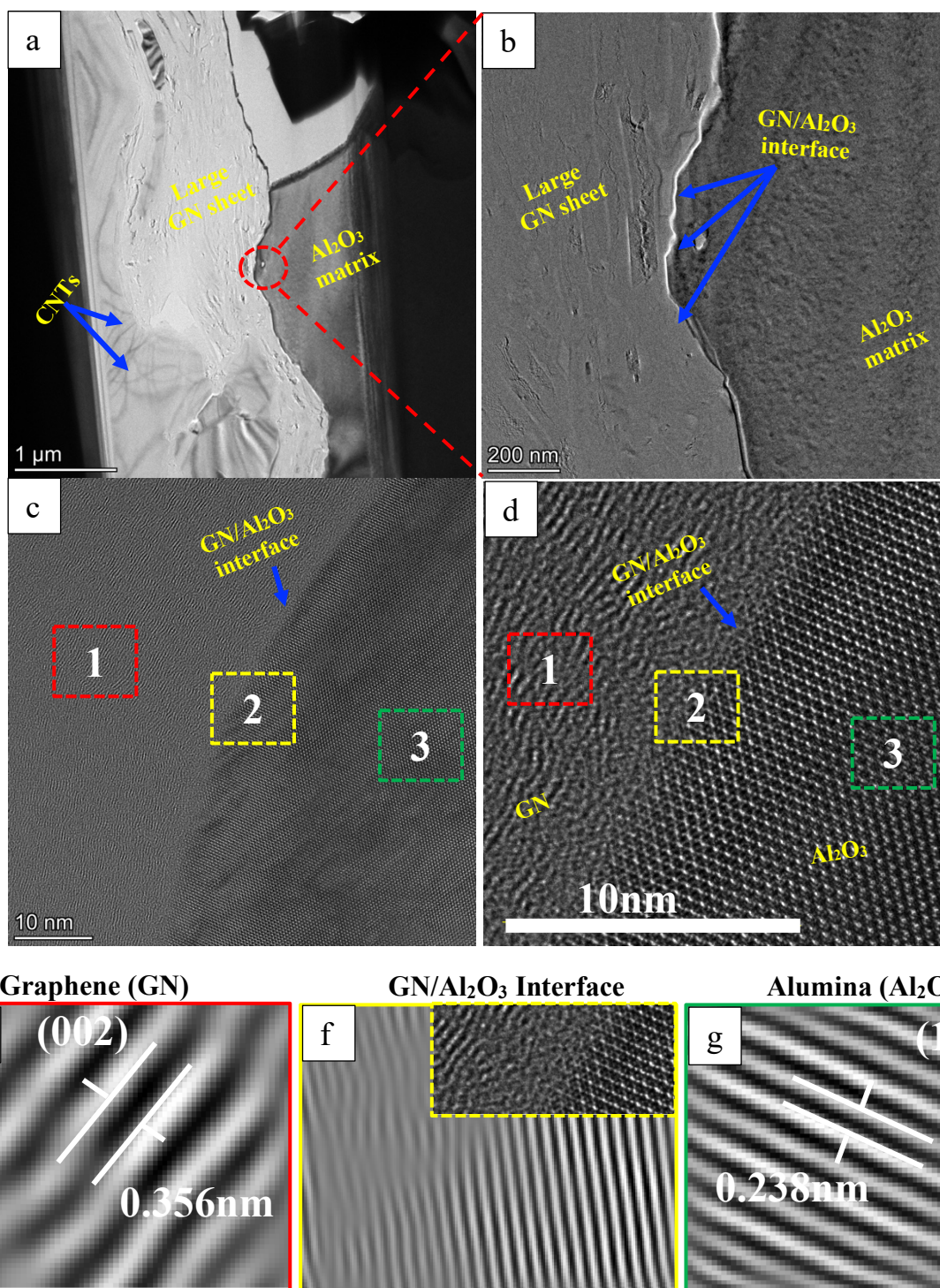


Figure 4.12: (a)-(b) TEM micrograph showing the bonding and the interface of the carbon nanostructures with the Al_2O_3 matrix (c)-(d) HRTEM of the two distinct crystalline regions oriented in different directions (e)-(g) IFFT image of the graphene (GN), interface and the Al_2O_3 matrix.

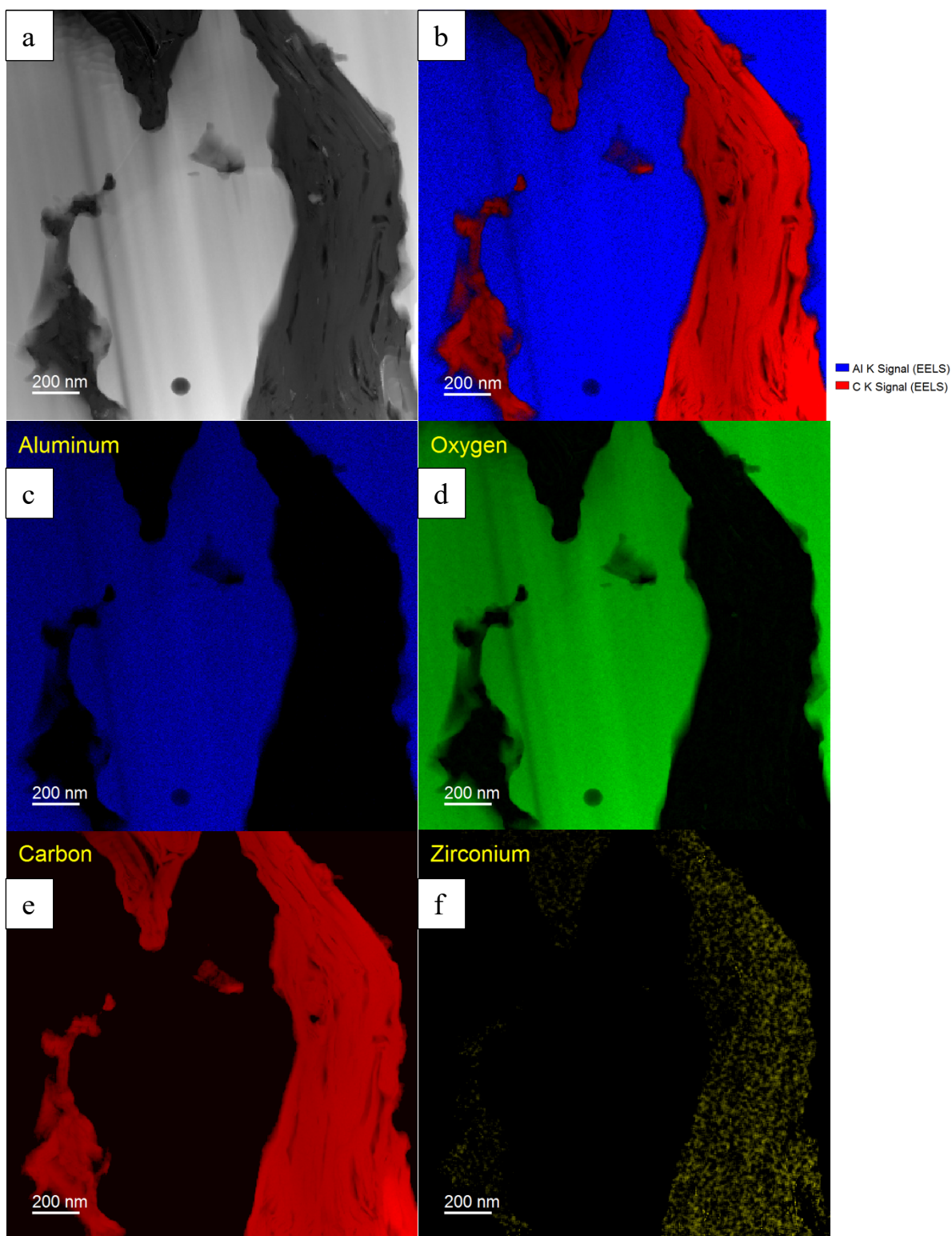


Figure 4.13: (a) High angle annular dark field (HAADF) image showing wrapping of Al_2O_3 matrix grain by large GN sheet (b)-(f) Elemental distribution maps of Al_2O_3 -GN interaction obtained from electron energy loss (EELS) signals.

two distinct layers with different orientations and crystalline appearance. Detailed image processing using the Gatan digital micrograph software were used to analyse these regions including the interface. The Inverse Fast Fourier Transformation (FFT) technique was used to analyse each region separately (Figure 4.12e-g). The IFFT image confirms that the d-spacing of $\sim 0.356\text{nm}$ belongs to the GN nanostructure at (002) plane (Figure 4.12-e). The (002) plane is one of the major peaks observed for carbon according to the XRD analysis from Paper IV, as seen in

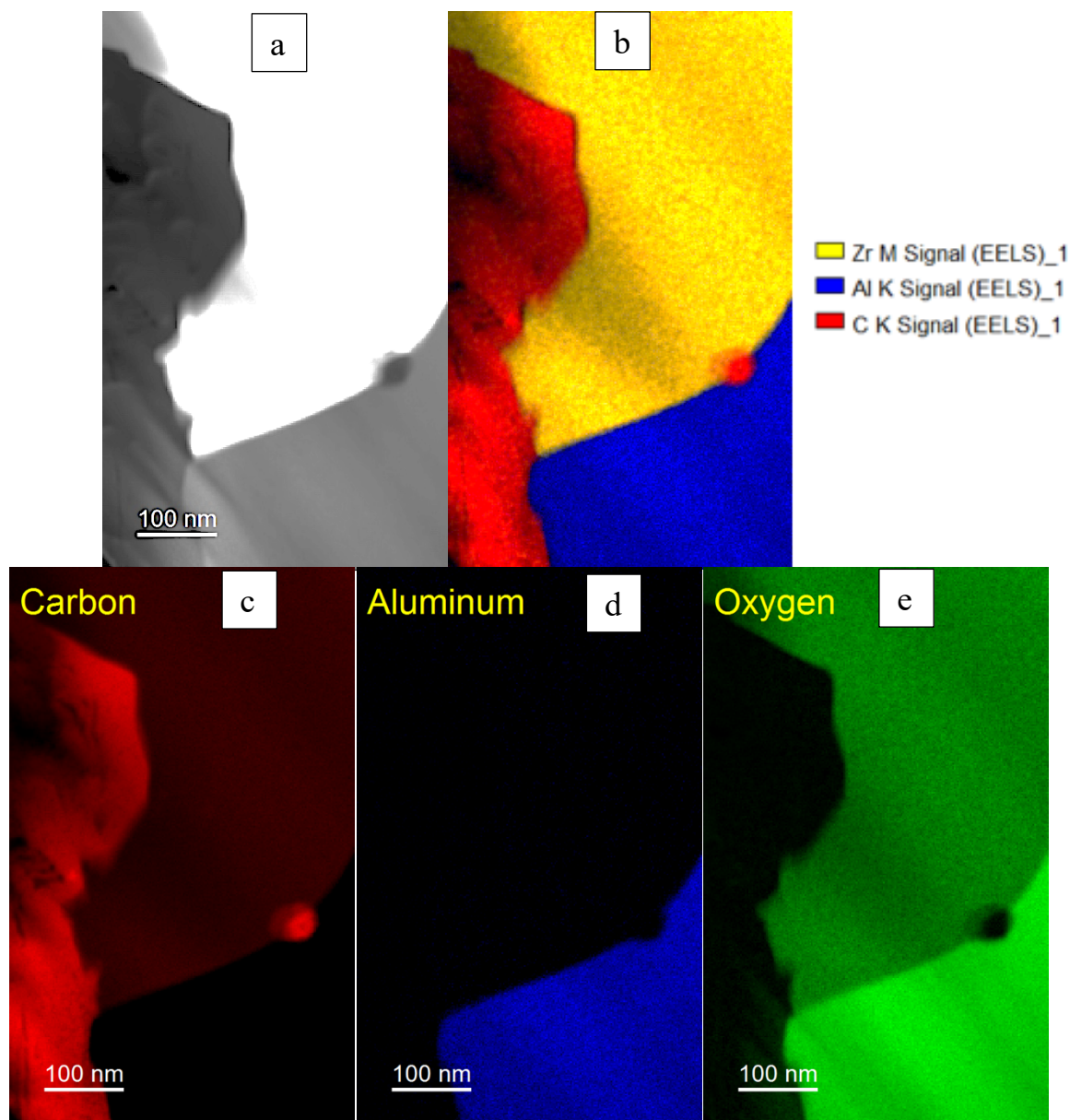


Figure 4.14: (a) High angle annular dark field (HAADF) image depicting the interaction of Al_2O_3 with ZrO_2 and carbon nanostructures (b)-(e) Elemental distribution maps of Al_2O_3 - ZrO_2 -GN interactions obtained from electron energy loss (EELS) signals.

the Appendix section of this thesis. In addition, the IFFT image in Figure 4.12-g d-spacing of $\sim 0.238\text{nm}$ was observed for the Al_2O_3 matrix at the (104) plane. This plane corresponds to a major intensity in the XRD peaks according to Paper II-V. A clean interface was demonstrated by the IFFT image of the interface in Figure 4.12-f, which depicts no reaction or products were formed at the interface. This is essential for the load-transfer capability at the interface of the Al_2O_3 matrix and the carbon nanostructures especially during bending. Furthermore, the mechanism of grain refinement is evidently demonstrated with the wrapping action of the carbon nanostructure on surrounding Al_2O_3 matrix grains, as demonstrated by the high angle annular dark field (HAADF) image in Figure 4.13. The growth of the trapped Al_2O_3 grains between the GN sheets are restricted and compressive forces are exerted on the matrix grains during consolidation and sintering. Figure 4.14 also shows the interaction of Al_2O_3 matrix with ZrO_2 and the carbon nanostructures (specifically CNTs) sandwiched between the matrix and ZrO_2 grains. This is also evident of the affinity of the carbon nanostructures to the matrix grain boundary to hinder diffusion process across the matrix boundary during sintering, leading to finer grain structure and improved load distribution by the reinforcements.

This study also explored electrical conductivity as the functional attribute of the nanocomposites. Figure 4.15 shows the variation of the electrical conductivity with the addition of carbon nanostructures to the ceramic Al_2O_3 matrix. Due to high resistance, the conductivity of the purely ceramic structures such as Al_2O_3 matrix, $\text{Al}_2\text{O}_3\text{-4wt\%ZrO}_2$ and $\text{Al}_2\text{O}_3\text{-10wt\%ZrO}_2$ nanocomposites registered overflow, due to the range limitation of the source meters. Hence, $10^{13}\ \Omega\cdot\text{cm}$ was approximated as the measured bulk resistivity, with corresponding conductivity values estimated as $10^{-13}\ \text{S/m}$ [92][108]. Several literature studies establishes that most ceramics are categorized as insulators, characterized by their high electrical resistivity values exceeding $10^{12}\ \Omega\cdot\text{cm}$, and minimal electrical conductivity, typically falling below $10^{-12}\ \text{S/m}$ [92][108] [109][201]. Figure 4.15 illustrates the variation of the electrical conductivity of the nanocomposites with the addition of various nano-reinforcement phases. The graph clearly illustrates that the incorporation of GN and CNTs led to a substantial enhancement in electrical conductivity, increasing from $10^{-13}\ \text{S/m}$ to $10^2\ \text{S/m}$. This remarkable improvement signifies an increase of up to 15 orders of magnitude. This improvement is due to many factors including the intrinsic electrical properties of CNTs and GN, percolation effect, as well as the refined grain structure of the nanocomposite. High aspect ratio of CNTs due to its one-dimensional (1D) structure increases electron mobility by

Table 4.1: Electrical properties of alumina (Al_2O_3) matrix multi-material nanocomposites

Fabricated Hot-Pressed Alumina (Al_2O_3) Matrix Nanocomposite Samples	Sample ID	Electrical Resistivity ($\Omega\cdot\text{cm}$)	Electrical Conductivity (S/m)
1. Monolithic/Pure Al_2O_3 (Aa)	Aa	10^{13}	10^{-13}
2. Aa+4wt% ZrO_2	A4Z	10^{13}	10^{-13}
3. Aa+10wt% ZrO_2	A10Z	10^{13}	10^{-13}
4. Aa+0.5wt%GN	AG	10.4×10^{-1}	9.6×10^1
5. Aa+4wt% ZrO_2 +0.5wt%GN	A4ZG	11.92×10^{-1}	8.4×10^1
6. Aa+4wt% ZrO_2 +2wt%CNTs	A4ZC	9.89×10^{-1}	1.06×10^2
7. Aa+10wt% ZrO_2 +0.5wt%GN	A10ZG	9.49×10^{-1}	1.05×10^2
8. Aa+10wt% ZrO_2 +2wt%CNTs	A10ZC	7.03×10^{-1}	1.49×10^2
9. Aa+10wt% ZrO_2 +0.5wt%GN+2wt%CNTs	A10ZGC	9.15×10^{-1}	1.09×10^2

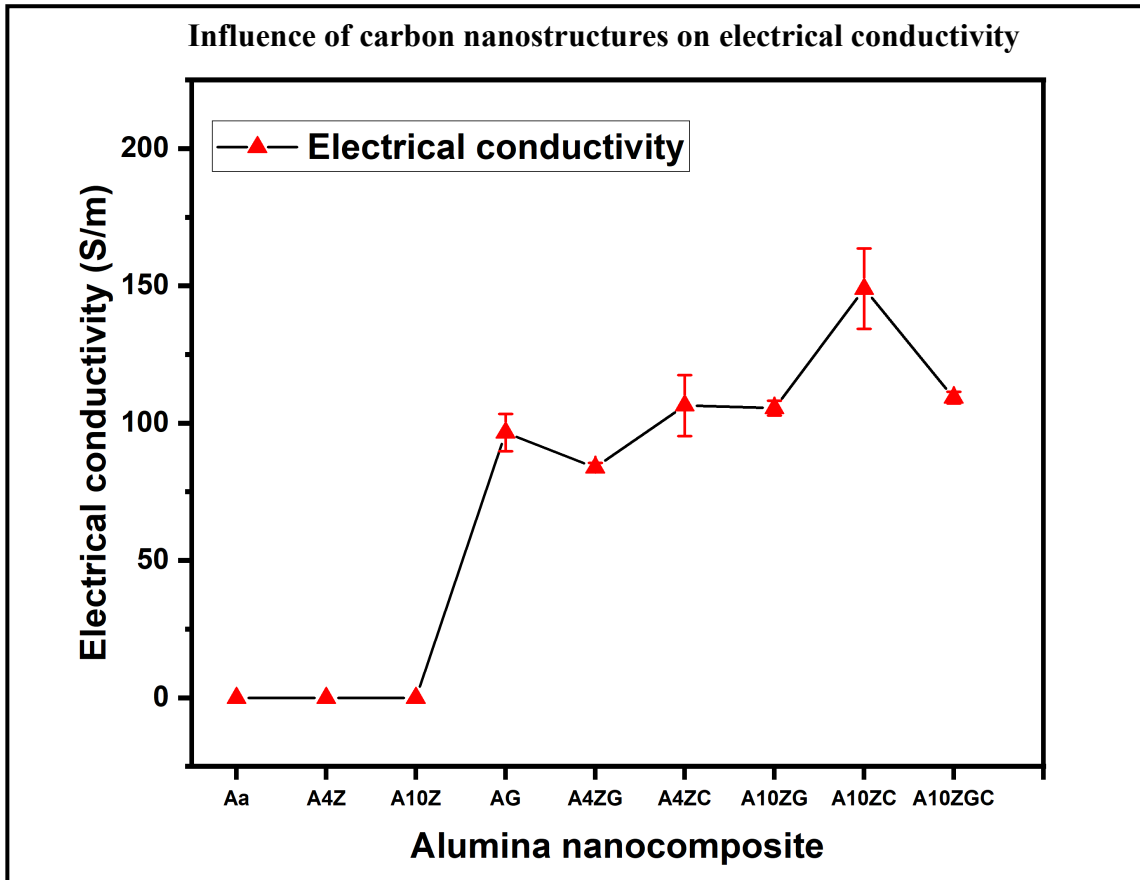


Figure 4.15: Graph showing the effect of carbon nanostructures on electrical conductivity of Al_2O_3 multi-material nanocomposites.

creating continuous pathway and networks within the Al_2O_3 matrix. The incorporation of two dimensional (2D) GN with relatively large GN- Al_2O_3 matrix contact area, as seen from Figures 4.12-4.14, also enhances conductivity of the nanocomposite by creating large interface to promote electron transport. The formation of the continuous network structure by CNTs and GN is known as the percolation effect. This phenomenon enhances the bulk and macroscopic electrical properties of the CNTs and GN reinforced nanocomposites by reaching a critical percolation threshold as optimal amounts of CNTs and GN are distributed within the Al_2O_3 ceramic matrix [202].

Numerous studies have supported the influence of a refined grain structure on the enhanced electrical properties observed in nanocomposites reinforced with CNTs and GN [203][204]. For ceramic structures such as Al_2O_3 , the introduction of these carbon nanostructures has been found to minimize grain boundary resistance. This, in turn, establishes a conductive network at the matrix boundaries due to the strong affinity of CNTs and GN for these grain boundaries. The arrangement of CNTs and GN along the grain boundaries is further illustrated through fractography studies in Papers IV-V, as outlined in the Appendix. This, combined with a well-defined interface between the matrix and the nanostructures, ensures minimal impedance to electron transfer within the nanocomposites. Consequently, the incorporation of selected optimal amounts carbon nanostructures into the Al_2O_3 matrix holds the potential to enhance the mechanical and multifunctional attributes of Al_2O_3 ceramics. Such advancements position these novel materials for prospective high-performance applications, even in challenging environmental conditions.

CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 Summary of Thesis

In summary, the quest for robust structural materials capable of withstanding extreme conditions has led to a critical demand for advanced technologies. The need for lightweight materials possessing exceptional mechanical attributes, especially in challenging environments, underscores the significance of advanced ceramics such as alumina (Al_2O_3). However, the intrinsic limitations of monolithic alumina, particularly its relatively low fracture toughness, have hindered its potential for critical applications.

In response, microstructural design and tailoring emerged as a solution, involving the dispersion of sub-micron and nano-phase reinforcements within the alumina matrix to form nanocomposite structures. This research systematically investigates the influence of individual and combined additives: zirconia (ZrO_2), graphene (GN), and carbon nanotubes (CNTs), on microstructure, mechanical, tribological and functional properties. In the current studies, the alumina (Al_2O_3)-based multi-material nanocomposites were prepared by dispersing multiple nano-reinforcement particles such as graphene (0.5wt%), carbon nanotubes (2wt%) and zirconia (4wt% and 10wt%) within monolithic Al_2O_3 matrix via colloidal mixing of the nano-reinforcements and alumina matrix. This was instantly followed by hot-pressing sintering at 1600°C , with a constant applied pressure of 60MPa for 1 hour. The fabrication process yielded dense sintered Al_2O_3 - ZrO_2 -GN-CNTs nanocomposites with densities around 3.98 g/cm^3 .

Microstructural analysis using advanced characterization techniques such as SEM and TEM revealed the role of the nano-reinforcements in the evolving microstructure of the nanocomposite. Various mechanical, tribological and functional properties including microhardness, fracture toughness (K_{IC}), bending strength (σ_f), sliding wear performance and electrical conductivity were also assessed in this study. Compared to the monolithic Al_2O_3 , the mechanical properties, tribological performances and functional properties of the fabricated multi-material nanocomposites were improved with the incorporation of ZrO_2 , GN and CNTs due to the significant grain size reduction, and various strengthening and toughening mechanisms occurring simultaneously. The grain refinement, coupled with load transfer capabilities of the nano-phase

reinforcements and various mechanisms, resulted in notable enhancement in the bulk properties of the fabricated nanocomposites. In this study, the multi-material additions of selected optimal amounts of the nano-reinforcements to the Al_2O_3 matrix limited the issue with the trade-off in properties such as fracture toughness and strength, by simultaneously yielding improved combined mechanical properties. A summary of the major findings and conclusions from this research are presented below:

1. The microstructure of the hot-pressed monolithic Al_2O_3 displayed a coarse-grained structure following the sintering process. This coarse-grained microstructure contributed to the comparatively diminished mechanical properties, including fracture toughness (K_{IC}), bending strength (σ_f), and an elevated wear rate. The existence of micro-cracks within this structure substantiates the derived value for the original Al_2O_3 sample. In addition, the monolithic Al_2O_3 exhibited typical intergranular fracture mode along the grain boundaries with a measured fracture toughness (K_{IC}) (up to $\sim 3.1 \text{ MPa}\cdot\text{m}^{1/2}$ for SENB and $\sim 3.4 \text{ MPa}\cdot\text{m}^{1/2}$ for DCM), and bending strength of 259 MPa.
2. With the single addition of 0.5wt%GN to Al_2O_3 , a fine-grained structure with reduced grain size produced higher mechanical properties and wear resistance. This was mainly due to the homogeneous distribution of the GN nano-phase, making the load-transfer effective within the Al_2O_3 matrix. The fracture toughness (K_{IC}) was also increased up to $6 \text{ MPa}\cdot\text{m}^{1/2}$.
3. The addition of 4wt% ZrO_2 to Al_2O_3 resulted in a coarser microstructure comparable to that of Al_2O_3 . The microhardness and fracture toughness (K_{IC}) behaviour with added 4wt% ZrO_2 was also related to the structure and distribution of limited amount of ZrO_2 particles. A comparative the toughness (K_{IC}) value (up to $3.7 \text{ MPa}\cdot\text{m}^{1/2}$) suggests that an insufficient load-bearing activity of the added ZrO_2 due to the limited tetragonal to monoclinic (*t-m*) ZrO_2 transformation. Though the addition of only 4wt% ZrO_2 yielded comparable grain sizes to the Al_2O_3 matrix, there was however a significant refinement of the matrix grains with the hybrid inclusion of ZrO_2 -CNTs and ZrO_2 -GN within the matrix, with up to 78% and 38% grain size reduction observed for the Al_2O_3 -4wt% ZrO_2 -2wt%CNTs and Al_2O_3 -4wt% ZrO_2 -0.5wt%GN hybrid nanocomposites respectively. The ZrO_2 grains were also refined up to 69% and 27% with the respective additions of ZrO_2 -CNTs and ZrO_2 -GN hybrid reinforcements to the Al_2O_3

matrix. Hybrid additions of ZrO₂-CNTs and ZrO₂-GN also increased the fracture toughness and flexural strength of the parent Al₂O₃ from $\sim 3\text{MPa}\cdot\text{m}^{1/2}$ and $\sim 7\text{MPa}$ up to $\sim 260\text{MPa}\cdot\text{m}^{1/2}$ and $\sim 374\text{MPa}$ respectively. This was due to the finer grain structure, and the combined presence and interaction of the reinforcement nanostructures precipitating within the matrix grains and grain boundaries, simultaneous toughening and strengthening mechanisms including crack bridging and deflection by GN and CNTs, GN grain wrapping, CNT pull-outs and grain gluing which illustrated good CNT-matrix bonding. The wear resistance also improved from $9.71 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ up to $0.81 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ with the additions of ZrO₂-GN and ZrO₂-CNTs, which was accustomed to the enhanced mechanical properties and the wear resistant mechanisms such as crack arrest, bridging and deflection by the reinforcement phases.

4. The incorporation of both 10wt%ZrO₂ and 0.5wt%GN caused a relatively finer grain structure in the Al₂O₃ matrix. Even though hardness value was comparable to the monolithic Al₂O₃, the wear resistance was highly increased. ZrO₂ pinning effect and bridging by the added GN restricted microcrack propagation to cause high volume loss and wear rate. The fracture mode changed from intergranular with few transgranular fracture of the matrix and the ZrO₂ grains, with a slight 4% decrease in K_{IC} against the Al₂O₃-10wt%ZrO₂ but up to 56% increase when compared to that of the monolithic Al₂O₃. The presence of micro-pores could hinder the anticipated rise in toughness value (up to $8.78\text{MPa}\cdot\text{m}^{1/2}$) even though GN pull-outs action were operative. However, the dissipated energy during GN pull-out was responsible for the increase in the bending strength ($\sim 325\text{MPa}$) with the addition of the 0.5wt%GN. Meanwhile, the immense enhancement in the mechanical properties such as fracture toughness (up to $7.55\text{MPa}\cdot\text{m}^{1/2}$) with the addition of both 10wt%ZrO₂ and 2wt%CNTs to the Al₂O₃ matrix is ascribed to the homogeneous dispersion, fine-grained structure, as well as the toughening and strengthening mechanisms including crack bridging, crack arrest and pull-out activities of the CNTs. The fusion of the CNTs to the matrix material also depicts good interfacial bonding which accounts for the high strength in the nanocomposite up to 460MPa.
5. The synergy effect of the simultaneous additions of 10wt%ZrO₂, 2wt%CNTs and 0.5wt%GN reinforcement phases is also revealed in the Al₂O₃ matrix structure, as well as the hardness

and wear properties. Relative to the monolithic Al_2O_3 , the refined grain structure, the complementary roles and toughening mechanisms of the combined ZrO_2 , GN and CNTs within the Al_2O_3 multi-material nanocomposite reached an improved fracture toughness (K_{IC}) value by up to 123% and 159%, as measured from the SENB and DCM respectively. This therefore displays a good coordination of the carbon nanostructures which also demonstrated the highest value in the bending strength ($\sim 483\text{MPa}$). The effectiveness of this addition on the overall mechanical properties of the multi-material nanocomposites is attributed to the uniform dispersion of these nanophase structures in the Al_2O_3 matrix. Excellent coordination between the homogeneously dispersed second-phase particles yielded a higher wear resistance (93% reduction in the wear rate) through the pinning and bridging effect of the embedded ZrO_2 and carbon-based nano-reinforcements.

6. Interfacial studies showed a clean interface between matrix and nano-reinforcements. Advanced TEM characterization depicts the favorable adherence of Al_2O_3 matrix to carbon nanostructures, contributing to high mechanical properties through improved interfacial bonding. A clean interface is vital for load-transfer at the Al_2O_3 matrix-carbon nanostructures interface during bending. Grain refinement mechanism is demonstrated using high angle annular dark field (HAADF) images which showed restricted growth of Al_2O_3 grains due to the wrapping action of carbon nanostructures. The interaction of Al_2O_3 matrix with ZrO_2 and carbon nanostructures (CNTs) was also evident, highlighting their affinity to matrix grain boundaries to hinder diffusion during sintering, resulting in finer grain structure and improved load distribution.
7. This study further investigated the electrical properties including electrical resistivity conductivity as a functional attribute of the fabricated nanocomposites. The enhancement in electrical conductivity with the incorporation of GN and CNTs, elevating it from 10^{-13} S/m to 10^2 S/m , an increase of up to 15 orders of magnitude. Factors contributing to this enhancement include the intrinsic electrical properties of CNTs and GN, the percolation effect, and the refined grain structure of the nanocomposite. CNTs and GN, with their 1D and 2D structures respectively promote electron mobility within the Al_2O_3 matrix by creating substantial contact area and forming continuous networks and pathways. This network formation is known as the

percolation effect, Additionally, the incorporation of the carbon nanostructures minimizes grain boundary resistance and establishes a conductive network at the matrix boundaries.

In conclusion, this study showcases the promise of microstructural design in enhancing advanced ceramic materials for demanding engineering applications. By strategically integrating these nano-phase reinforcements in their optimal contents, mechanical properties, wear resistance and functional performance of ceramic alumina (Al_2O_3)-based nanocomposites can be remarkably improved. These findings offer practical solutions for diverse industries, addressing challenges in harsh environments and lightweight structural demands.

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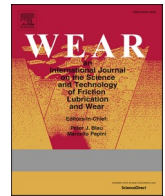
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APPENDIX

PUBLISHED RESEARCH PAPERS RELATED TO CHAPTER 4

Paper I: Effect of graphene and zirconia on microstructure and tribological behaviour of alumina matrix nanocomposites

S. H. Duntu, I. Ahmad, M. Islam, S. Boakye-Yiadom (2019) Effect of Graphene and Zirconia on Microstructure and Tribological Behaviour of Alumina Matrix Nanocomposites, *Wear*, 438-439, (<https://doi.org/10.1016/j.wear.2019.203067>).



Effect of graphene and zirconia on microstructure and tribological behaviour of alumina matrix nanocomposites

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ABSTRACT

The inherent brittleness of monolithic alumina (Al_2O_3) has consistently limited its potential for several high-performance structural applications such as engine turbine parts and high temperature space materials. The fracture toughness and wear properties of alumina can be improved by the uniform dispersion of sub-micron and nano-phase particles in the alumina parent matrix. In the current study, alumina-based nanocomposites were fabricated by homogeneous dispersion of zirconia (4 wt% and 10 wt%) and graphene (0.5 wt%) using colloidal mixing followed by hot-pressing at 1600 °C for 1 h. The microstructure of the processed composite was extensively observed under high-resolution electron microscopes. The effects of zirconia and graphene on the mechanical and tribological properties were also investigated. The final microstructures depict extensive grain-refinement by the uniform dispersion of 0.5 wt%Gn and 10 wt%ZrO₂ in the parent alumina matrix. A coarse-grain microstructure was observed with the addition of the 4 wt%ZrO₂ due to insufficient inhibition of alumina grain growth during sintering. The coefficient of friction results from the wear test using a UMT Tribolab equipment with constant normal load of 25 N, 100 mm/s sliding velocity for 1000s, under ASTM G133-05 illustrates a steep increase for the 0.4 wt% ZrO₂ addition but a significant decrease for the 10 wt%ZrO₂ addition. Consequently, the addition of 10 wt% ZrO₂ resulted in ~98% decrease in the wear rate which was attributed to its refined microstructure and effective load-bearing activities of the uniformly dispersed ZrO₂ precipitates. Meanwhile, the addition of 0.5 wt%Gn revealed a fine-grained microstructure and consequent lower wear rate (~90.5%), but there was a relative increase in the coefficient of friction, which suggested that there is a direct relationship between the microstructure and wear behaviour than the coefficient of friction.

1. Introduction

Advanced ceramics such as alumina, zirconia, silicon carbide and boron carbide have wide range of potential in the aerospace, automotive, defence and biomedical industries due to their attractive and suitable physical, mechanical and chemical properties [1–3]. In recent years, alumina as a lightweight structural ceramic, has gained much attention in various engineering and material research fields. Current extensive applications of advanced alumina include high speed cutting tools, high temperature bearings, wear resistant coatings, armour plates and electrical and thermal insulators. These are attributed to their excellent properties such as high hardness, wear resistance, high temperature strength, good oxidation and corrosion resistance [4–7]. Also, the chemical stability coupled with good compatibility with the physiological and biological environment makes it suitable for biomedical

applications such as joint prosthesis and dental inserts [8]. In addition to its high scratch resistance, alumina as a bioceramic, tends to provide a very good lubricating action between interfaces in the body due to its high ability to adsorb polar molecules such as water and body fluid on its surface [9].

Indeed, alumina and many other advanced structural ceramics present numerous possibilities in various engineering applications. However, several high-performance structural applications of advanced ceramic materials such as their use in gas turbines for power plants, rocket and jet engines, heat shields for space vehicles, fusion reactor first wall, heat treatment furnaces, aircraft brakes and turbine engines are restricted due to their inherent brittleness, low fracture toughness and mechanical resistance [10–13]. Generally, the low fracture toughness of monolithic alumina and most engineering ceramics is due to their atomic bonding, crystal structure and microstructure after processing

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[14]. Atomic bonds in ceramics are usually ionic and covalent, which have a tendency to limit dislocation movement and the amount of plastic deformation within the structure [15,16]. In addition, technical ceramics are developed by consolidating ultrafine microscopic powders at high temperatures ($>1300^{\circ}\text{C}$) to produce near dense and most times coarse microstructures [17]. Typically, the manufacturing processes of advanced ceramics are major sources of initial micro-flaws in the final microstructure. The sensitivity of these materials to these inherent flaws such as microcracks, voids and inclusions results in their low fracture toughness especially under high performance structural applications [18,19].

Studies have shown that microstructural design can be used to improve the fracture toughness and mechanical properties of monolithic ceramics. This microstructural modification involves deliberate and effective tailoring of the microstructure by the distribution of other materials within the material to achieve maximized performance [17, 20,21]. Marshall reported that the toughness of ceramics can be improved by refining the polycrystalline grain size and shape [22]. This is achieved by embedding second-phase sub-micron or nanoparticles within the ceramic matrix phase to form a composite or a nanocomposite. Ceramic matrix nanocomposites consists of a monolithic ceramic matrix system with homogeneously dispersed nano-scale second-phase particles such as carbon nanotubes, graphene, SiC, Si_3N_4 , etc [23,24]. Several research works have attempted to incorporate suitable second-phase particles into alumina matrix with the aim to improve the fracture toughness and wear resistance. Most common additives such as zirconia (ZrO_2), silicon carbide SiC, carbon-based inclusions (Graphene and CNT) and silicon nitride (Si_3N_4) have been used coupled with several processing routes and sintering techniques such as spark plasma sintering (SPS), stir casting, hot isostatic pressing (HIP) [25]. The challenge is to successfully disperse these particles on the grain boundaries of alumina matrix to impede matrix grain growth and obtain a refined microstructure with improved mechanical properties [26].

Although there have been several reports in literature showing the success of these processing routes to achieve improved properties, other investigations have considerably shown that the mechanical properties of the final composite are not necessarily improved by the addition of these second-phase particles. In some cases, the additions of certain amounts of ZrO_2 , graphene, carbon nanotubes and SiC tend to deplete the fracture toughness and compromise the desired low-density attributes of the final nanocomposites [27]. The variation of mechanical properties are mainly attributed to the effectiveness of the fabrication process to uniformly distribute particles within matrix and weak interfacial bonding after sintering [28]. Studies on Al_2O_3 matrix reinforced with graphene and carbon nanotubes have shown that the superior properties of the manufactured composites depend on the homogeneous dispersion of the graphene particles on the matrix phase, overall densification of composites, the retention of the structure during high temperature sintering process and the concentration of the particles in the matrix phase [1,29–32].

Zirconia (ZrO_2) is an attractive structural ceramic which is commonly used to improve the fracture toughness of structural alumina. Past studies have revealed that the fracture toughness of Al_2O_3 ($\sim 3 \text{ MPa m}^{1/2}$) can be significantly improved (above $8 \text{ MPa m}^{1/2}$) when ZrO_2 phase is uniformly dispersed within the matrix [19]. The predominant toughening mechanism which involves the transformation of the metastable tetragonal structure to a voluminous (from 3% to 5% volume expansion) monoclinic structural phase in the presence of an induced stress improves the toughness and mechanical properties of alumina by impeding crack propagation [33,34]. In addition, grain refinement by the addition of ZrO_2 is possible when there is sufficient self-diffusion of ZrO_2 particles within the alumina 4-grain junction to inhibit abnormal grain growth during sintering [35–37]. Desired toughening effect of zirconia is observed when there is uniform distribution of ZrO_2 phase within the ceramic matrix. It is also reported that huge variation in mechanical properties is observed in alumina-zirconia

composites due to variation of ZrO_2 amount, porosity, grain size and conditions for the final sintering process [38–41]. Several researchers have also concluded that an improved toughness and mechanical properties is experienced when an optimum amount of ZrO_2 , from 8 to 20 vol% is utilized as a homogeneous phase within Al_2O_3 matrix [35,37, 42–44]. Naglieri et al. used wet chemical method to prepare $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites by varying the ZrO_2 content from 5 vol%–20 vol% and reported that maximum fracture toughness and hardness was exhibited by the 10 vol% ZrO_2 addition due to significant tetragonal to monoclinic transformation at tip of crack. In their work, the 5 vol% ZrO_2 recorded lowest fracture toughness which was typically ascribed to poor dispersion and agglomeration of ZrO_2 particles within Al_2O_3 matrix [45]. Khoshkalam et al. also adapted gel casting method to prepare $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites with up to 20 vol% ZrO_2 content and recorded optimum fracture toughness, finer microstructure and higher flexural strength with the 10 vol% ZrO_2 inclusion [46].

Since its discovery, two-dimensional graphene has been adapted as a possible means to produce tougher structural ceramic material by incorporating it as a second phase within the ceramic matrix [24,47]. The combination of superior mechanical and physical properties such as high strength, stiffness and flexibility, large surface area and good electrical and thermal conductivity makes it very effective in a matrix phase [48–50]. These additives are known to refine the ceramic matrix phase and improve their fracture toughness when they are homogeneously distributed within the matrix phase after sintering. Iftikhar et al. suggested that the presence of graphene at the Al_2O_3 grain boundary restricts boundary movement during sintering which suppresses further grain growth and yield refined microstructures [51–53]. Various studies have also shown that small amounts of graphene (0.1–1.0 vol%) within Al_2O_3 matrix offer superior mechanical properties [26,48]. Higher graphene content during processing have been reported to cause extreme carbon agglomeration (due to their van der Waals forces) which causes incomplete sintering, poor densification and consequentially lower mechanical properties [52]. Gallardo-Lopez and her group used spark plasma sintering to produce zirconia matrix composites reinforced with nanostructure graphene and reported a high electrical conductivity but poor densification with the addition of 20 vol% graphene [54]. In addition, Iftikhar et al. reported 45% improvement in fracture toughness with 0.75 wt%graphene nanoplatelets (GNP) inclusion within Al_2O_3 matrix, whilst the 1.25 wt% gave poor properties as a result of GNP agglomeration [51]. Several works have also revealed that the major toughening mechanisms demonstrated by these graphene phases within a ceramic matrix material include crack deflection, pinning and graphene pull-out [25–26,51–53]. This effect is fully experienced in the composite material when there is phase homogeneity and good interfacial bonding between the graphene phase and the matrix after sintering [24,25,47,53].

Even though single additions of graphene and ZrO_2 on the microstructural evolution and properties of alumina are widely studied, the synergistic effect resulting from multiple combinations of graphene and ZrO_2 and metal oxides are still not well understood. To study and understand the synergistic effects of multiple additions of graphene and ZrO_2 to Al_2O_3 matrix, the tribological behaviour and the microstructural evolution resulting from the single additions of graphene and ZrO_2 would have to be systematically characterized and studied. Thus, we first need to analyse and understand the individual effect of these reinforced particles on the microstructure and mechanical properties of the Al_2O_3 matrix before multiple combinations of these particles to the alumina matrix. This study aims to systematically process and characterize Al_2O_3 matrix nanocomposite incorporated with different concentrations of ZrO_2 and graphene as a baseline for multiple combinations of these particles to the alumina matrix.

2. Experimental procedure

2.1. Sample preparation

The as-received α -alumina powder (Sigma Aldrich, UK), having an average particle size of <50 nm and purity of 99.96% was uniformly dispersed in distilled water to form an alumina suspension. The graphene was prepared from graphite oxide (GO), which was obtained from fine graphite flakes using the Hummers' method discussed elsewhere [55]. The as-received surface enhanced graphite flakes (Grade-3775, Asbury Graphite Mills Inc., NJ, USA) were first chemically modified to graphite oxide (GO) followed by thermal exfoliation upon heating to 1600 °C at 1000 °C/min and 4.5×10^2 Torr pressure in an induction-heat furnace. Detailed characterization of the processed graphene is discussed in other work [51].

Concentrations of 4 wt% and 10 wt% of zirconia (<80 nm in diameter, Sigma Aldrich, UK), and 0.5 wt% graphene were separately dispersed in distilled water. A surfactant was used together with ultrasonic vibrations to enhance uniform dispersion of the graphene by decreasing the van der Waals's attractive forces. The alumina slurry was added to both zirconia and graphene suspensions whilst continuously stirred using a probe sonicator to obtain a homogeneous mixture. The slurry formed were then dried on a hot plate at temperatures between 120–150 °C under sonication to obtain the powder mixture. Dried powder mixture was constantly milled in a mortar to obtain very fine and uniform nanocomposite powders. Consolidation was then carried out by hot-pressing in a graphite die at 1600 °C at a constant 60 MPa pressures for 1 h holding time. The final processed nanocomposites which are rectangular shaped with dimensions of about 50 mm $\times$ 40 mm $\times$ 2 mm were then subjected to mechanical and microstructural characterization.

The density of the processed alumina nanocomposite with different composition of zirconia (4 wt% and 10 wt%) and 0.5 wt% graphene as shown on Table 1 were determined using the helium gas pycnometer (AccuPyc II 1340 Pycnometer) and a high precision weighing balance with an accuracy of 0.0001 g. Table 1 below shows the summary of the fabricated composites. The final rectangular shaped sintered nanocomposites with average dimensions 50 $\times$ 40 $\times$ 2 mm were sectioned using a diamond wire-saw to smaller rectangular sizes (15 $\times$ 10 $\times$ 2 mm) for microstructural analysis. The sectioned samples were cold mounted in epoxy resin. The mounted samples were then ground progressively from coarse to fine finish using different grits of SiC grinding paper (400, 600, 800 and 1200), and then polished to a mirror finish up to 0.05 μ m using a diamond suspension.

The microstructures of the polished consolidated nanocomposites were characterized using a High-Resolution Field Emission Scanning Electron Microscope (Quanta 3D, Thermofisher) with emission gun operating at 20 KV. The samples' surfaces were coated with a thin layer of platinum charging on the sample surface in the SEM chamber. Backscattered electron (BSE) micrographs and chemical composition analysis of the nanocomposites were carried out using a thermionic emission gun SEM equipment (TESCAN VEGA 3) coupled with an energy dispersive spectroscopy (EDS). Further microstructural analysis was also carried out using phase contrast information and the distribution of second-phase particles within the nanocomposites.

Table 1
Summary of fabricated samples.

Sample	Description	Density (g/cm ³)	Surface roughness (Sa, nm) of polished samples
Pure Al ₂ O ₃	Pure Alumina (Aa)	4.05	61.818 $\pm$ 8.18
AG0.5	Aa+0.5Gn	3.96	63.392 $\pm$ 5.65
AZ4	Aa+4ZrO ₂	4.01	66.205 $\pm$ 7.92
AZ10	Aa+10ZrO ₂	4.03	76.158 $\pm$ 4.29

An X-ray Micro-Computed Tomography (Micro-CT) system (240 kV, GE Phoenix v|tome|x m compact micro CT) coupled with GE DXR detector array was adapted to analyse the internal microstructural features of the prepared samples after sintering. Optimised X-ray scan parameters were chosen to achieve the best contrast and penetration of X-ray. A better visual contrast between the matrix and inclusions were obtained using an acceleration voltage of 100 kV and beam current of 100 μ A. A Volume Graphics Software (VGStudio Max) was used to process the raw image data after each scanning. The presence of void and inclusions of each sample within the detection limit of the Micro-CT system (≥ 20 μ m) were critically assessed.

2.2. Surface roughness measurement

Prior to wear test, surface roughness of the polished composites was measured by a Non-contact White Light Interferometry using a Bruker Contour GT Optical profilometer system. The surface roughness of each specimen was investigated using the ISO 25178, which utilizes a high pass and low pass filter to reveal the asperities of the polished composite surface. Ten separate measurements were made on each sample surface over an area of 961 $\times$ 721 μ m² and the average 3D surface roughness value (Sa) was calculated.

2.3. Wear test

A ball-on-flat configuration (Fig. 1) was used to conduct a dry sliding wear test on a flat polished specimen using the UMT tribolab (Bruker Tribometer, Canada). The specimens were prepared for the test in accordance with the conditions described in ASTM G133-10. A 9.525 mm diameter spherical Si₃N₄ ball with purity of 99.9% and surface roughness (Sa) of 5.11 $\pm$ 0.25 nm was used as the counter body during the experiment. Si₃N₄ against Al₂O₃ is one of the ceramic on ceramic material combinations proposed for artificial joint or joint replacement [56]. We chose the Si₃N₄ counter ball against Al₂O₃ because it is a proposed ceramic-ceramic system to be used for artificial implants [56].

The counter ball was cleaned in an ethanol ultrasonic bath for about 5 min prior to the wear test as prescribed by the standard. The ball was then secured in an appropriate customized holder which was suspended normally to the specimen stage. The tip of the ball was closely examined to prevent ball movements in the holder during the test. The finely polished alumina specimens with dimensions (15 mm $\times$ 10 mm $\times$ 2 mm) was also cleaned ultrasonically and secured on the reciprocating stage using a pair of rectangular holders (Fig. 1) to limit vibrations. A preload of 5 N was applied to the Si₃N₄ ball at the initiation of each test for 5s, to ensure smooth engagement of the contact surfaces before the sliding and to ensure safe condition of the sensitive loading force sensor. A constant normal load of 25 N was applied to the stationary ball immediately after the pre-load sequence for 1000s, using a to and fro sliding velocity of 100 mm/s of the sample stage, which represents the testing frequency of 5 Hz according to the ASTM standard. The stroke length used was 10 mm which gave a total sliding distance of 100 m equivalent to 5000 cycles which was calculated according to equations (1) and (2) below;

$$\text{Total sliding distance(m)} = 0.002 \times t \times f \times L \quad (1)$$

$$\text{Total number of cycles} = t \times f \quad (2)$$

where t is test time, f is oscillating frequency and L is stroke length [57].

The experiment was repeated three times on each sample surface by changing the position of the counterball and moving to an unworn area on the sample surface. The test was conducted in a dry sliding condition at room temperature of 22 ± 3 °C and relative humidity of 40–60%.

The worn samples were analysed using the optical microscope (ZEISS M2 Imaging System, Canada) and SEM (TESCAN VEGA 3) to observe the morphological changes within the wear track region. The optical

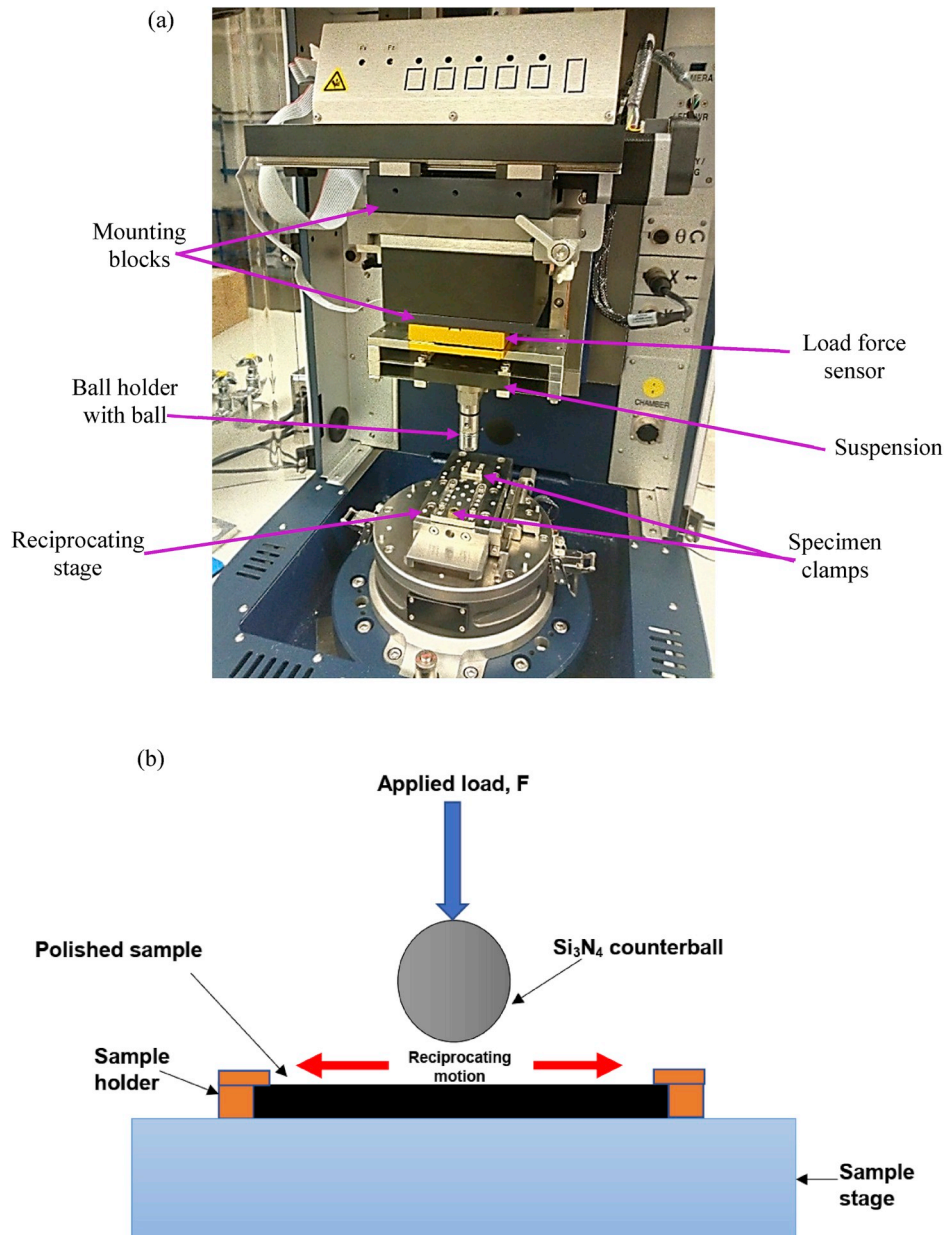


Fig. 1. (a) Major parts of the UMT Tribolab Wear Testing Equipment (b) Illustration of ball-on-flat reciprocating wear test.

profilometer was used to generate the 2D and 3D profile of each worn surface after the wear test. The acquired profile was used to determine accurately the wear depth and wear width of the wear tracks. These were used to estimate the volume of wear and the corresponding wear rate of the samples.

3. Results

3.1. Microstructure of as-sintered alumina nanocomposites before wear tests

3.1.1. Structure of as-sintered Al_2O_3 and Al_2O_3 -0.5 wt% graphene samples

The as-sintered samples were characterized to understand the effect of the temperature (1600 °C) and pressure (50 MPa) on the evolved microstructure after sintering. Similar sintering conditions were used to prepare all the samples. The fabricated nanocomposites were rectangular shaped with typical dimensions of about 50 mm by 40 mm by 2 mm. All the prepared nanocomposites were almost fully dense with no

observable macro-cracks and macro-defects. The bulk densities of the sintered samples are presented in Table 1.

Microstructural characterization of the polished samples using the FE-SEM reveal that the addition 0.5 wt% graphene refined the microstructure of pure Al_2O_3 . Fig. 2 shows the micrographs of the finely polished pure Al_2O_3 and Al_2O_3 -0.5 wt%Gn (from here on referred to as the pure Al_2O_3 and AG0.5) samples. It was observed that the pure Al_2O_3 revealed coarser matrix after sintering (Fig. 2(a)) when compared with the matrix of the AG0.5 sample (Fig. 2(b)). The addition of 0.5 wt% graphene shows a relatively more refined Al_2O_3 matrix which demonstrates that the presence of graphene resulted in grain refinement of the Al_2O_3 matrix. In addition, Fig. 2(b) demonstrates that not only did the addition of 0.5 wt% graphene cause grain refinement, but the grains also appear to be more equiaxed. There were no observable second phase precipitates in the Al_2O_3 -0.5 wt% graphene sample.

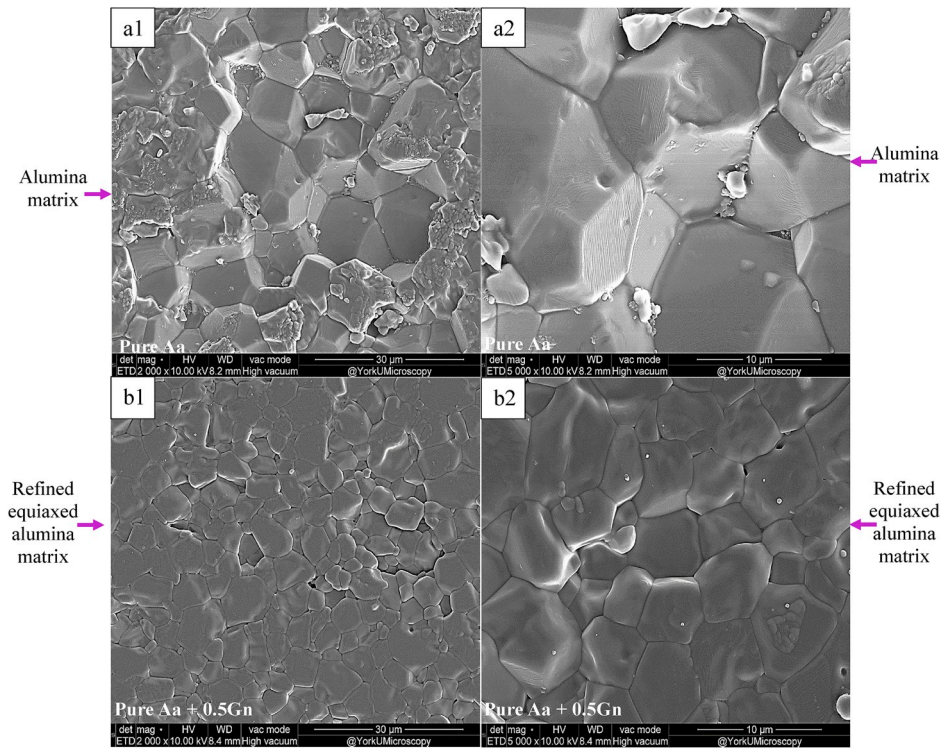


Fig. 2. SEM micrographs of as-sintered samples under the same magnifications illustrating Al_2O_3 matrix refinement (a) Pure Al_2O_3 with relatively coarse microstructure (b) Al_2O_3 with 0.5 wt% graphene addition showing grain-refinement of Al_2O_3 matrix.

3.1.2. Structure of as-sintered Al_2O_3 -4wt% ZrO_2 and Al_2O_3 -10 wt% ZrO_2 samples

The micrographs in Fig. 3 show the microstructures of the as-sintered Al_2O_3 -4wt% ZrO_2 and Al_2O_3 -10 wt% ZrO_2 samples (from here on referred

to as the AZ4 and AZ10 samples) after fine polishing up to 0.25 μm using diamond suspension. Generally, a refined Al_2O_3 matrix is observed with the addition of 10 wt% ZrO_2 whilst the addition of 4 wt% ZrO_2 showed a coarser matrix. Fig. 3(b) demonstrates the relatively finer Al_2O_3 matrix

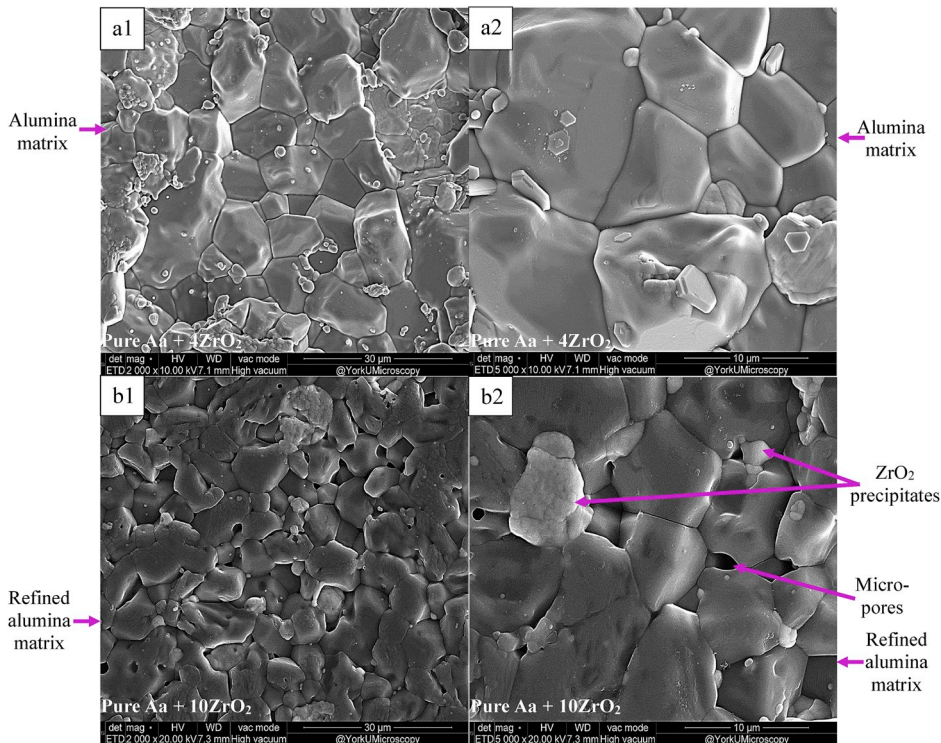


Fig. 3. SEM micrographs of as-sintered samples under the same magnifications revealing the effect of ZrO_2 addition on Al_2O_3 matrix (a) Al_2O_3 with 4 wt% ZrO_2 with relatively coarse-grain structure (b) Al_2O_3 with 10 wt% ZrO_2 showing a refined Al_2O_3 matrix.

with the addition of 10 wt%ZrO₂ in the AZ10 sample when compared with both the pure Al₂O₃ and AZ4 samples. However, the addition of 4 wt%ZrO₂ depicted a relatively coarser matrix in the AZ4 sample when compared with AZ10 (Fig. 3(a)). The coarser matrix in the AZ4 sample is comparable to that of the pure Al₂O₃ matrix.

To observe the structure and morphology of the precipitates formed in the AZ4 and AZ10 samples, the samples were studied using the backscattered electron (BSE) mode in the SEM. The BSE micrographs revealed the dispersion and spatial distribution of relatively spherical ZrO₂ precipitates in the AZ4 and AZ10 specimens. Fig. 4 shows the BSE micrographs revealing the large z-contrast between the Al₂O₃ matrix and the zirconia precipitates (grey spherical precipitates) in the AZ4 and AZ10 samples. There were large and relatively small dispersions of the ZrO₂ precipitates in both the AZ4 and AZ10 samples (Fig. 4(b) and (c)). However, there were larger ZrO₂ precipitates in the AZ4 samples among very tiny ZrO₂ precipitates creating a significant size gradient between the ZrO₂ precipitates. However, there was a relatively smaller size gradient of the ZrO₂ precipitates in the AZ10 samples when compared with the AZ4 samples. Also, a coarser morphology of the parent Al₂O₃ matrix with the dispersed ZrO₂ particles was observed with the 4 wt% ZrO₂ precipitates in the AZ4 sample. There was uniform distribution of ZrO₂ precipitates in the AZ10 samples with relatively higher quantities of ZrO₂ precipitates within the Al₂O₃ matrix due to the higher concentration of ZrO₂ used. The Al₂O₃ matrix in the AZ10 is significantly finer than in AZ4 which further illustrates the refining effect of the 10 wt%

ZrO₂ addition.

Energy Dispersive Spectroscopy (EDS) was used to qualitatively verify the individual elemental distributions and components within the samples. The EDS mapping in Figs. 5 and 6 show the surface topography of the mapped regions of AZ4 and AZ10 samples respectively with the various constituent elements demonstrating that ZrO₂ precipitates are distributed within the Al₂O₃ matrix. A uniform spatial distribution of dense and ultra-fine ZrO₂ precipitates were more apparent in the mapped AZ10 sample relative to the sparsely dispersed precipitates in the AZ4 sample. Fig. 5 shows the EDS maps of the AZ4 sample illustrating the dispersion of both the bigger and fine ZrO₂ precipitates. In Fig. 5(c), a detailed distribution of very fine ZrO₂ precipitates sparsely dispersed within the matrix is also revealed in the AZ4 sample. Fig. 6 shows the EDS mapping of AZ10 which demonstrates an even distribution of highly dense ZrO₂ precipitates within the Al₂O₃ matrix. Tiny precipitates which were otherwise not revealed in the previous micrographs (Fig. 5(c)) have been detailed in Fig. 6(c), reinforcing the fact that AZ10 sample has a more uniform dispersion of ZrO₂ precipitates within its microstructure. Tables 2 and 3 displays the quantitative results from the EDS mapping of the AZ4 and AZ10 samples respectively.

3D scans of the as-sintered samples using a non-destructive X-ray Computed Tomography (CT) revealed the internal microstructure of the fabricated samples. Generally, no voids and inclusion were detected in the pure Al₂O₃ and Al₂O₃-0.5Gn samples under similar scanning conditions. However, higher volume of inclusion was detected in the

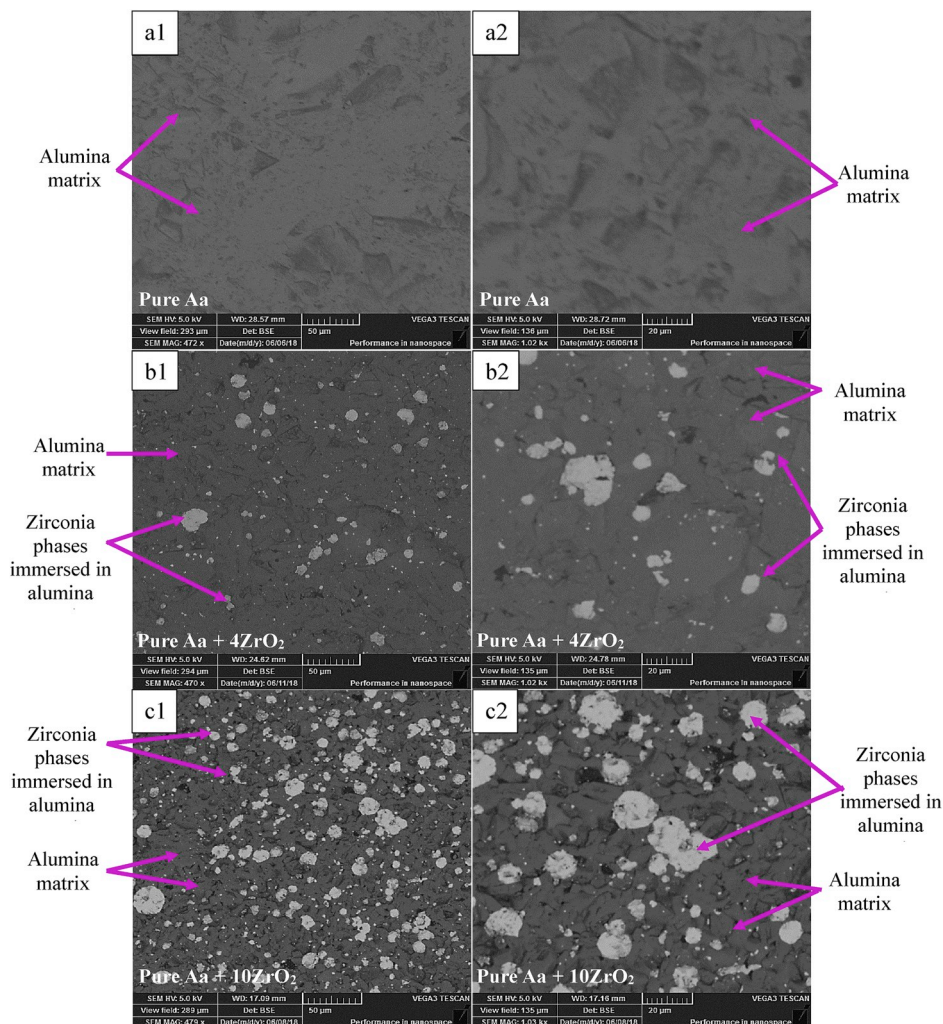


Fig. 4. Backscattered Electron SEM micrographs showing ZrO₂ phase distribution within Al₂O₃ matrix (a) Pure Al₂O₃ without ZrO₂ (b) Al₂O₃ with 4 wt% ZrO₂ (c) Al₂O₃ with 10 wt%ZrO₂ showing a relatively refined alumina matrix.

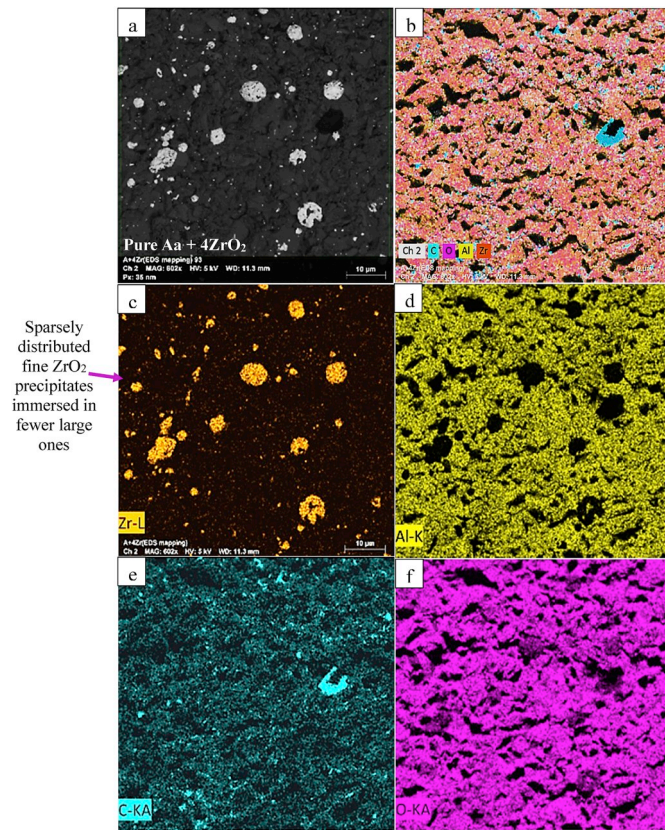


Fig. 5. EDS mapping of elements in Al_2O_3 -4wt% ZrO_2 sample (a) BSE image of AZ4 sample (b) Overall mapped data (c) EDS mapping showing Zr elements and ZrO_2 distribution within the Al_2O_3 matrix (d) EDS mapping of element Al (e)–(f) EDS mapping of elements O and C.

Al_2O_3 -10 ZrO_2 than the Al_2O_3 -4wt% ZrO_2 sample which also showed no void present. Fig. 7(a) and (b) shows the 3D scan images of pure Al_2O_3 and AG0.5 sample demonstrating no apparent inclusions and voids within the detecting limit of the system. The detection limit of the Micro-CT system used was between 50 μm -70 μm and therefore was able to register the inclusions within this range. This might also explain the absence of porosity in all the scanned samples, since micro-porosity below the system resolution will not be accounted for. Within this detection range, some inclusions were detected in the AZ4 and AZ10 samples as shown in Fig. 7(c) and (d). The volume of inclusion detected for the AZ10 sample scanned was about 10.59 mm^3 and that of AZ4 was about 0.055 mm^3 . Typically, there were no observable microcracks or defects detected in all the scanned samples within the detection limit of the Micro-CT scan system.

3.2. Surface roughness and wear test

Prior to wear tests, the polished samples were studied using an optical profiler to document the surface roughness. Fig. 8 shows the 3D topography of the polished samples measuring the surface roughness before wear test and Table 1 shows the various surface roughness values.

The coefficient of friction (COF) data was continuously recorded by the UMT Tribolab system over a sliding distance of 700 m and time intervals of 0.01s during the test. Table 4 shows the mean COF values for all nanocomposites after wear test. From Table 4, it is observed that the addition of 10 wt% ZrO_2 yielded the least COF value which is about 74% lower than pure Al_2O_3 . Thus, the AZ10 sample had the lowest COF value relative to pure Al_2O_3 . Meanwhile, the addition of 4 wt% ZrO_2 did not lower the COF of Al_2O_3 and relatively registered the highest COF value. Also, there was approximately 27% increase in the COF when 0.5 wt%

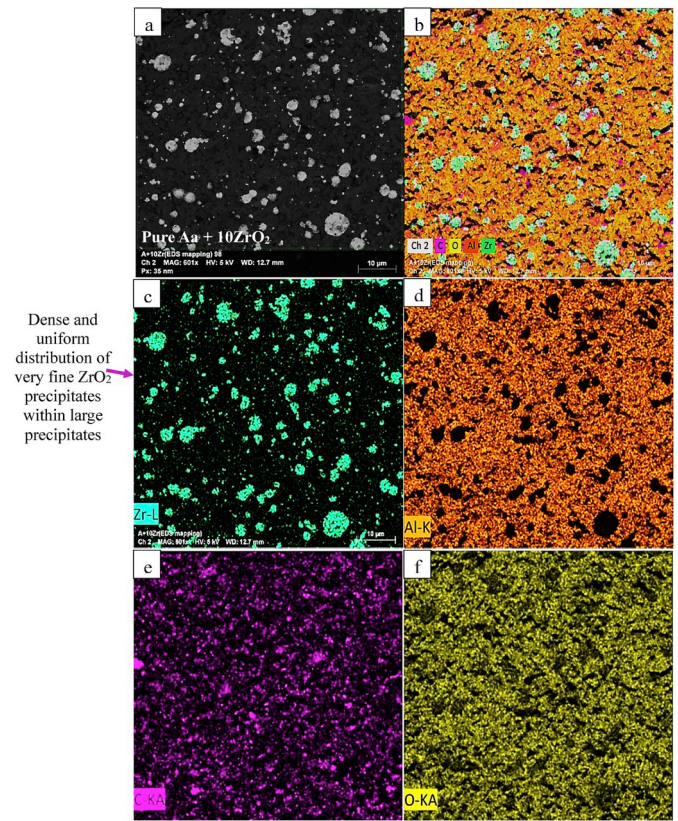


Fig. 6. EDS mapping of elements in Al_2O_3 -10 wt% ZrO_2 sample (a) BSE image of AZ10 sample (b) Overall mapped data (c) EDS mapping showing Zr elements and ZrO_2 distribution within the Al_2O_3 matrix (d) EDS mapping of element Al (e)–(f) EDS mapping of elements O and C.

Table 2

EDS mapping results for Al_2O_3 -4wt% ZrO_2 .

Element	Mass [%]	Mass Norm. [%]	Atom [%]	Abs. error [%] (1 Sigma)
Carbon	4.92	6.97	12.08	0.61
Oxygen	26.09	36.99	48.13	2.81
Aluminum	35.05	49.71	38.35	1.69
Zirconium	4.46	6.32	1.44	0.24
Sum	70.52	100.00	100.00	

Table 3

EDS mapping results for Al_2O_3 -10 wt% ZrO_2 .

Element	Mass [%]	Mass Norm. [%]	Atom [%]	Abs. error [%] (1 Sigma)
Carbon	4.65	6.25	11.34	0.61
Oxygen	26.90	36.20	49.28	2.96
Aluminum	33.51	45.10	36.41	1.62
Zirconium	9.26	12.46	2.97	0.47
Sum	74.31	100.00	100.00	

graphene was added to pure Al_2O_3 , as well as the 4 wt% addition.

The wear rate was reported in terms volume loss per sliding distance and applied load (mm^3/Nm). The volume loss was estimated by the product of the wear track width, track length and wear track depth (mm^3), as shown in Table 4. The optical profilometer was used to calculate the wear depth and width by scanning the track region to generate a 3D and 2D wear track profile as shown in Fig. 9. The calculated specific wear rate of the nanocomposites under the same test conditions are also displayed in Table 4. Generally, a higher volume loss

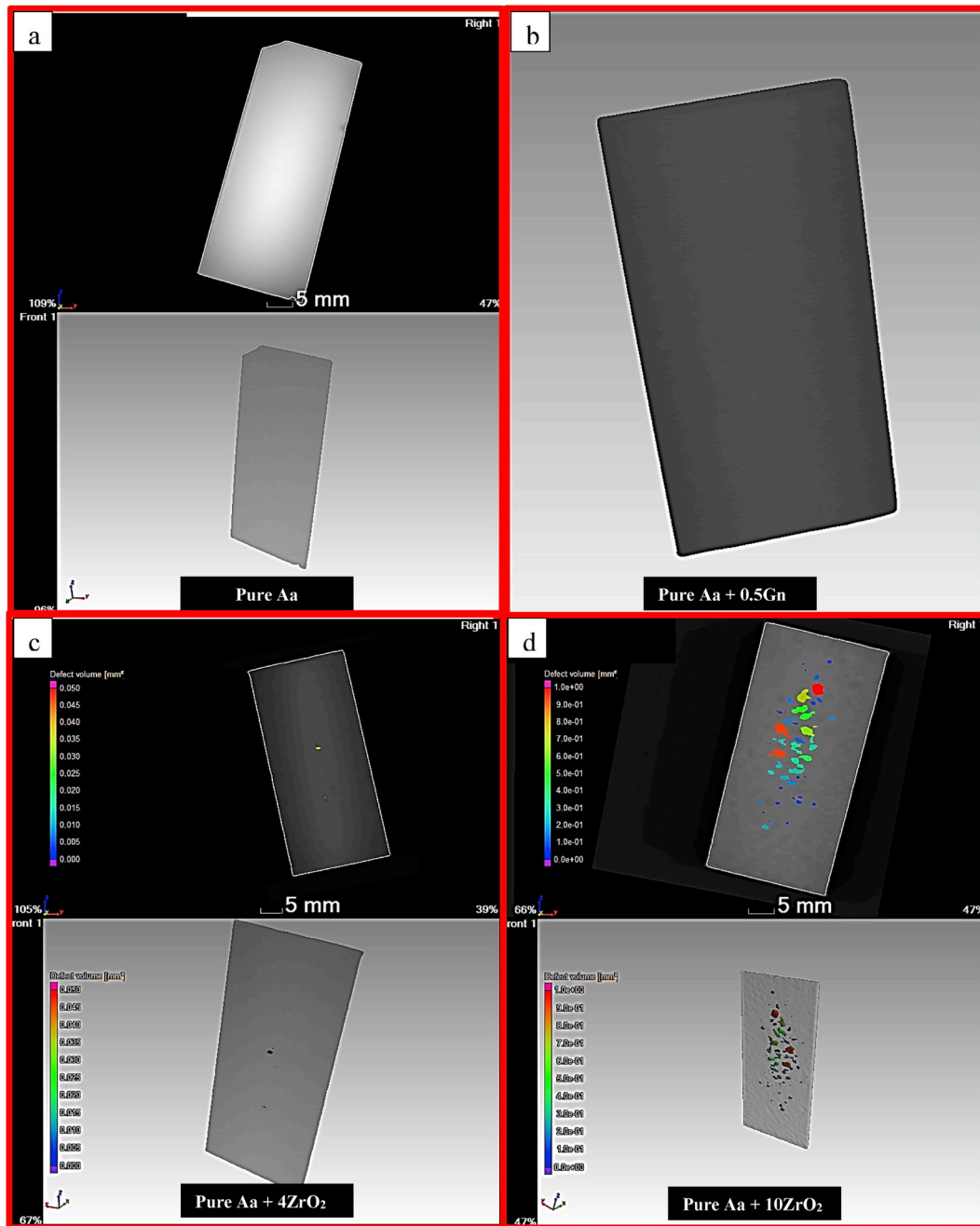


Figure 7. 3D Computed Tomography (CT) of fabricated nanocomposites showing volume fractions of inclusions (a) Pure Al_2O_3 (b) Al_2O_3 -0.5 wt% graphene (c) Al_2O_3 -4 vol% ZrO_2 (d) Al_2O_3 -10 vol% ZrO_2 .

and wear rate were illustrated by the AZ4 sample relative to the pure Al_2O_3 . The addition of 0.5 wt% graphene and 10 wt% ZrO_2 to Al_2O_3 however gave a lower wear rate and volume loss. Fig. 9(a) and (b) illustrates the volume loss of the pure Al_2O_3 and AG0.5 sample. It is also observed from Table 4 that even though the addition of 0.5 wt% graphene to parent Al_2O_3 did not necessarily yield a low COF relative to that of pure Al_2O_3 , its wear rate and volume loss decreased drastically. The wear rate and volume loss demonstrated by the AG0.5 sample were approximately 90.5% lower than that of pure Al_2O_3 . The results from Table 4 also illustrates that a relatively large volume of material was worn from the AZ4 sample surface during the sliding test, which also had the highest wear rate as shown in Fig. 9(c). The amount of material loss from the AZ4 sample was more than that of pure Al_2O_3 sample ($\sim 1261\%$ higher), which indicates that the addition of 4 wt% ZrO_2 decreased the

wear resistance of the parent Al_2O_3 material. The AZ10 specimen which has 10 wt% ZrO_2 had the least volume loss with the least wear rate ($\sim 98\%$ lower than pure Al_2O_3) as shown in Table 4 and Fig. 9(d). This illustrates that the wear characteristics of pure Al_2O_3 is extensively improved with 10 wt% ZrO_2 addition. The graphs in Fig. 10(a) and (b) shows the trend and variation of the COF and wear rate as a function of ZrO_2 and graphene content. The 3D profile image in Fig. 11 also illustrates the full wear track profile of the pure Al_2O_3 and AZ4 sample showing a relatively larger wear track for the AZ4 sample.

3.3. Microstructure after wear

After the wear tests, regions within and away from the wear tracks were studied to understand the type and mechanism of wear of the

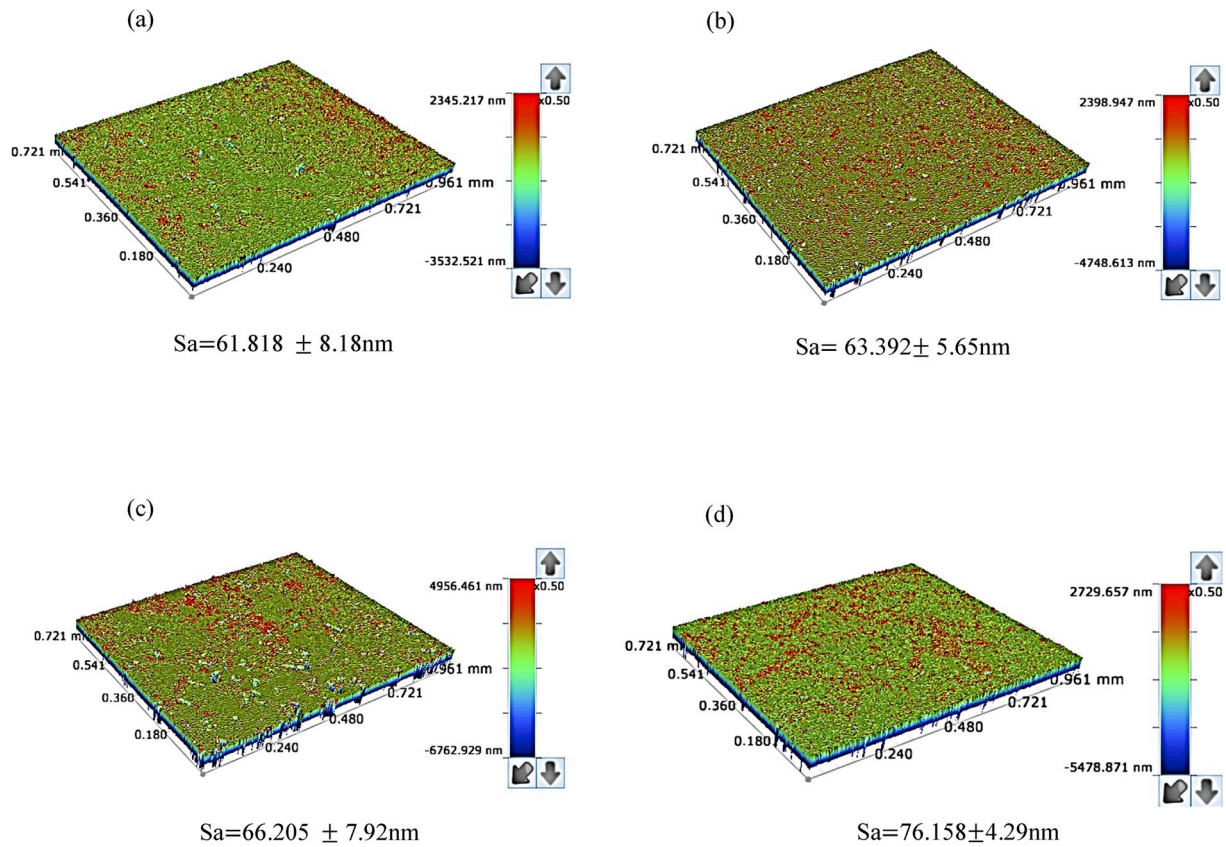


Fig. 8. Optical profilometer surface roughness measurements of finely polished (a) Pure Al_2O_3 (b) Al_2O_3 -0.5 wt%graphene (c) Al_2O_3 -4wt% ZrO_2 (d) Al_2O_3 -10 wt % ZrO_2 .

Table 4
Summary of Wear results.

Sample ID	COF	Wear depth (mm)	Wear width (mm)	Wear volume (mm^3)	Wear rate (mm^3/Nm)
Pure Al_2O_3	0.5874	0.0150	0.7399	0.1110	4.4408×10^{-5}
AG0.5	0.7460	0.0012	0.8783	0.0106	4.2270×10^{-6}
AZ4	0.7478	0.0609	2.4808	1.5107	6.0426×10^{-4}
AZ10	0.1499	0.0005	0.5141	0.0025	1.0127×10^{-6}

samples. Generally, it was observed that the samples had both coarser and finer peel-offs within the matrix of the wear tracks as well as grain and precipitate refinements. The addition of 0.5 wt%graphene and 10 wt % ZrO_2 both gave a refined wear track with less peel-offs in the direction of the sliding. Meanwhile, the 4 wt% ZrO_2 addition illustrated fairly larger material peel-offs and a coarser wear track, with unrefined ZrO_2 precipitates within the wear track.

Fig. 12 shows the micrographs of the worn surfaces of pure Al_2O_3 and AG0.5 samples after the wear test under constant load of 25 N and duration of 1000s. These micrographs demonstrate the large delaminations within the pure Al_2O_3 sample when compared with the AG0.5 sample. These large delamination areas result from Al_2O_3 matrix grain pull-out and peel-off actions during the continuous counter-body sliding. The optical micrograph in Fig. 12(a) shows a smooth wear track of pure Al_2O_3 . The structure within the wear track indicates relatively large peel-off sites with very smooth areas and surfaces covered with debris in the sliding direction. However, in the case of AG0.5 sample, the wear track appears to be very fine with no apparent large

worn regions as compared to the pure Al_2O_3 (Fig. 12(b)). The worn regions are also covered with very fine debris in the direction of the sliding.

The smaller and finer peel-off regions are more distinct in Fig. 13 clearly depicting the wear behaviour of the samples which is attributed to the constant sliding interaction between the samples and the Si_3N_4 counter ball. A non-uniform peel-off of surfaces is evident in the pure Al_2O_3 (Fig. 13(a)). The wear track path is characterized with large worn regions of materials in the direction of sliding. The AG0.5 sample experienced a continuous finer wear with a relatively uniform and smaller delamination sites within track region (Fig. 13(b)). Fig. 13(c) and (d) shows a more distinct BSE images of the wear surface detailing the large worn areas for pure Al_2O_3 compared with the smooth worn regions within the wear track of the AG0.5 sample.

Detailed microstructural analysis within wear tracks of the ZrO_2 doped samples show that the addition of 10 wt% ZrO_2 led to finer worn surface with less peel-off regions. Meanwhile, the addition of 4 wt% ZrO_2 led to a rather larger peel-offs within the wear track demonstrating the high amount of wear has occurred. Fig. 14 shows the micrographs of regions within the wear tracks of the pure Al_2O_3 and Al_2O_3 - ZrO_2 samples. It was observed that the AZ4 sample had significantly large peel-offs compared with the pure Al_2O_3 and AZ10 samples. A relatively larger and wider wear track was observed on the surface of AZ4 sample as shown in Figs. 14(b) and 15(a). There were also large observable peel-offs of matrix grains leading to larger delamination regions within the pure Al_2O_3 sample compared with the AZ10 sample. However, they were relatively smaller than those observed in the AZ4 samples. In the case of AZ10 sample, a mild wear is indicated, with relatively smoother worn surface and very fine peel-offs as shown in Fig. 15(b). The smaller and finer peel-off regions are more distinct in Fig. 15(b2) clearly depicting the wear behaviour of the AZ10 sample.

The distribution of the ZrO_2 precipitates within the wear track after

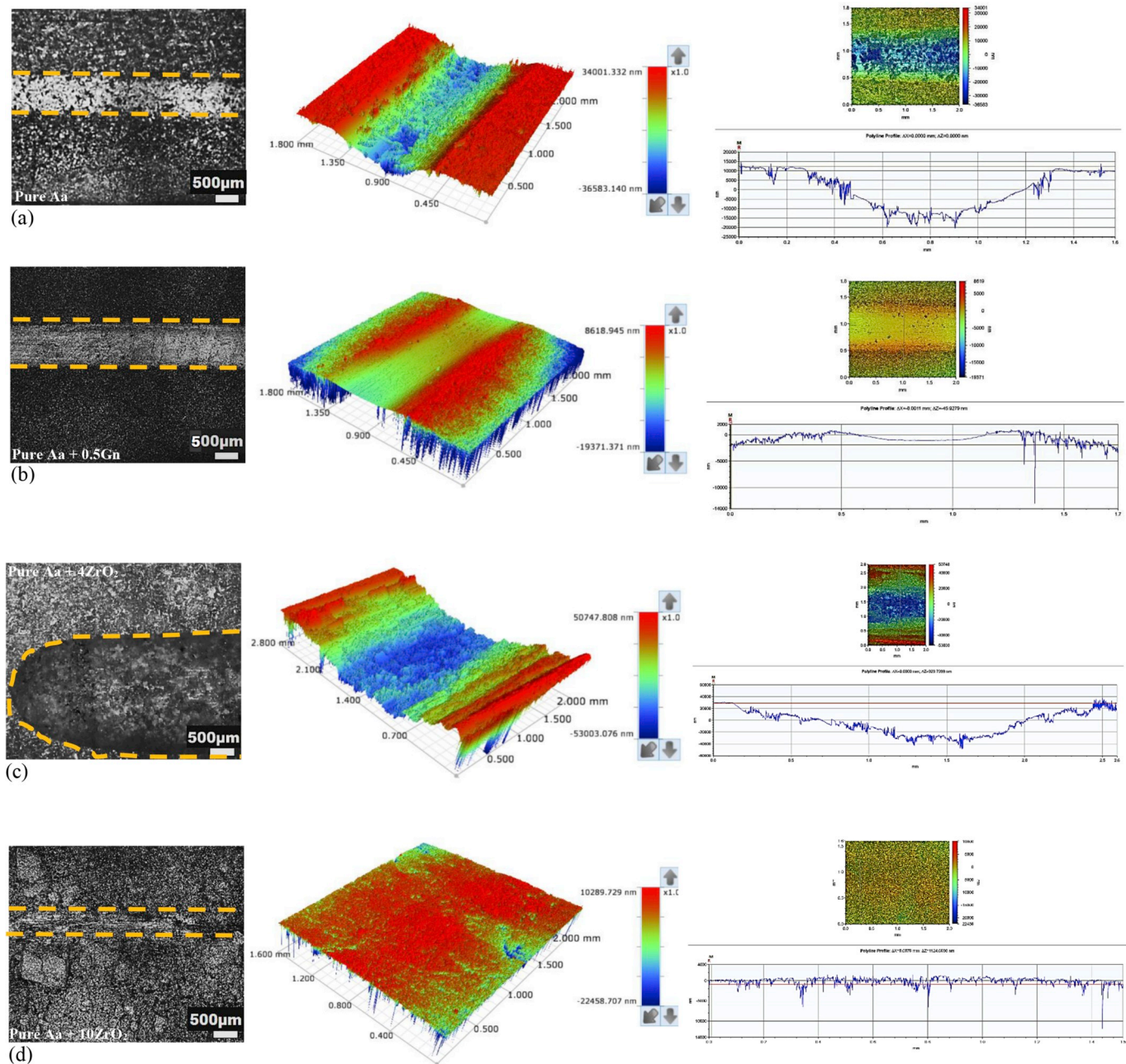


Fig. 9. 2D and 3D wear track profiles showing depth measurements of wear tracks.

the sliding wear test on the Al_2O_3 – ZrO_2 samples suggest that there is an extensive refinement of the ZrO_2 precipitates during continuous sliding in the AZ10 sample than the AZ4 sample which demonstrated unrefined precipitates within its wear track. The BSE micrographs in Fig. 15(c) and (d) shows the ZrO_2 precipitates in the worn region AZ10 sample appears to be more refined than that of AZ4 sample. The non-uniform worn region of the AZ4 is further shown in Fig. 15(c). In addition, there are large regions within the wear track of the AZ4 sample with almost no ZrO_2 precipitates. These regions appear to have larger peel-offs than other areas within the sample (Fig. 15(c)). Meanwhile, in Fig. 15(d) a uniform worn surface is clearly observed in the AZ10 with finer precipitates of ZrO_2 within wear track. These finer ZrO_2 precipitates are well refined and evenly dispersed within the entire wear track.

3.3.1. Wear debris analysis

Debris from the worn regions were collected after the test using a

carbon tape and extensively characterized to analyse critically the nature of the particles removed. It is shown that the debris contains both finer and larger chunks of materials removed from the worn surface. It is also evident that particles are pulled-out from the sample's surface as sliding continues which creates the peel-off regions. Generally, the wear debris of pure Al_2O_3 sample present bigger worn-out particles immersed smaller ones as compared to the very fine debris demonstrated by the AG0.5 sample. Meanwhile, finer particles are observed with the addition of 10 wt% ZrO_2 in contrast to the larger pulled-out particles presented by the addition of 4 wt% ZrO_2 , which demonstrates that larger volume of materials have been worn from the surface of the AZ4 sample.

Figs. 16–20 gives the general overview of wear debris from the worn surface of each sample. Figs. 16–17 illustrates the general finer nature of the worn particles from each sample surface. Wear debris of AG0.5 sample are relatively finer with smaller embedded particles than pure Al_2O_3 which has coarse debris with larger particles (Fig. 16). The worn-

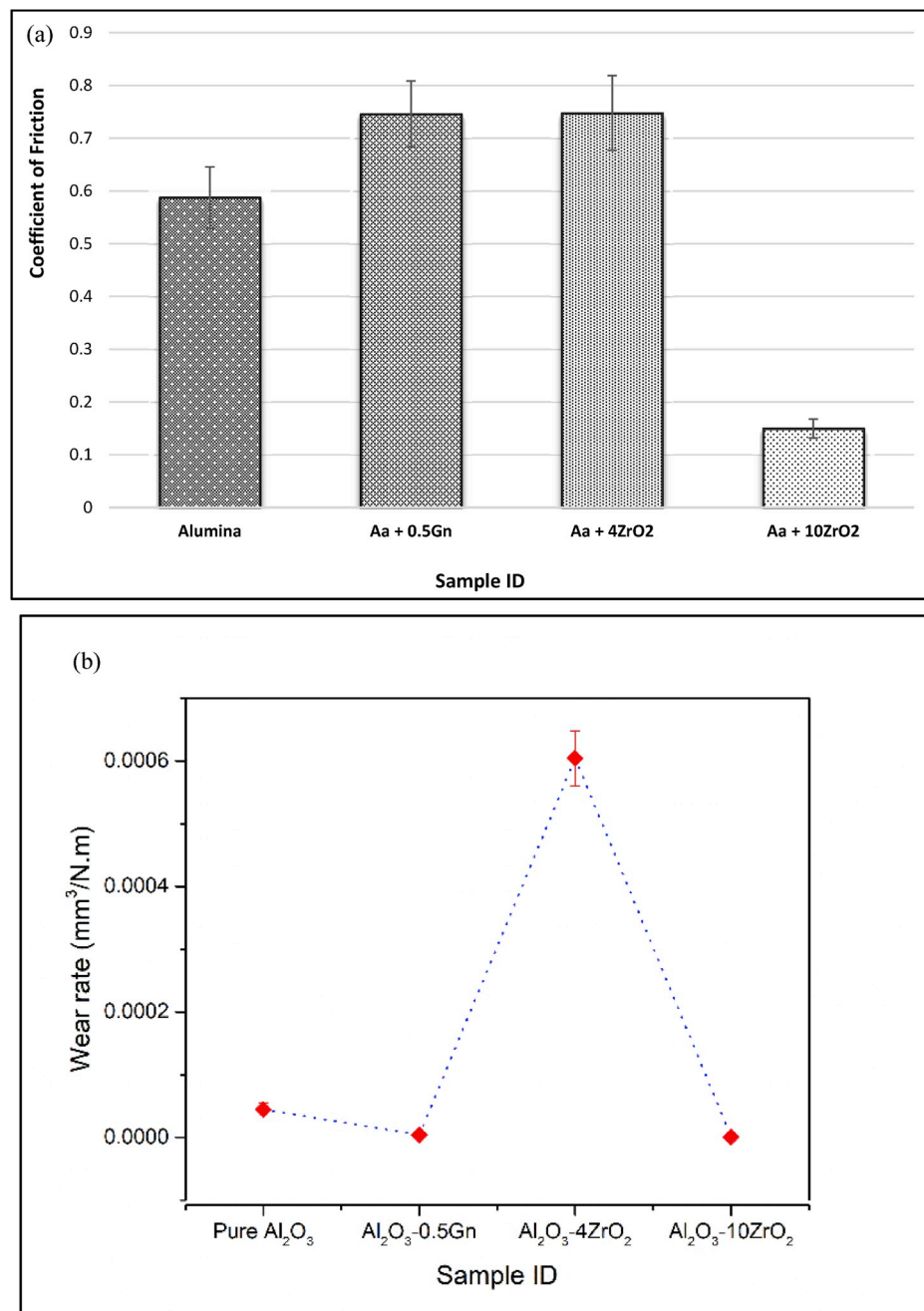


Fig. 10. (a) Graph of coefficient of friction after wear test (b)Wear rate (mm³/N.m) of Al₂O₃ nanocomposites.

out particles of Al₂O₃–ZrO₂ samples as shown in Fig. 17 indicate larger and coarse wear debris from the wear track surface of AZ4 sample (Fig. 17(a)). The debris from AZ10 wear track are generally very fine with much smaller worn particles embedded in a fine debris.

The micrographs in Fig. 18 present distinct features of the wear debris which also confirms that bigger chunks of materials are removed from the pure Al₂O₃ surface in the direction of sliding as shown in Fig. 18(a), thus the large delamination sites within the wear track. The AG0.5 sample experienced a continuous finer and relatively uniform peel-offs within the wear track region. This is characterized by the smaller and relatively more refined wear debris and smaller chunks of Al₂O₃ particles removed (Fig. 18(b)). EDS mapping on the wear debris (Fig. 19) indicates the Al₂O₃ particles pull-out from the worn surfaces in pure Al₂O₃. The mapping also shows very small concentration of Si₃N₄ counter-ball particles which reveals that the ball material hardly wears

during the test.

Detailed characterization of the debris from the Al₂O₃–ZrO₂ samples illustrates the distribution of the ZrO₂ precipitates within the debris. In general terms, very fine ZrO₂ precipitates are immersed in the debris of the AZ10 sample which illustrates and reinforces that the precipitates are continuously refined during sliding. On the other hand, the debris from AZ4 present rather larger ZrO₂ precipitates mainly settling on larger pulled-out Al₂O₃ matrix particle which deduces that the addition of 4 wt%ZrO₂ did not lead to any precipitate refinement during the sliding.

Fig. 20 shows the distribution of ZrO₂ precipitates in the wear debris of AZ4 and AZ10 samples. In both samples, deposits of individual ZrO₂ particles are traced on the surface of debris and within the finer wear residues. However, relatively large deposits of ZrO₂ precipitates are found on bigger chunks of Al₂O₃ particles in the AZ4 debris (Fig. 20(a)).

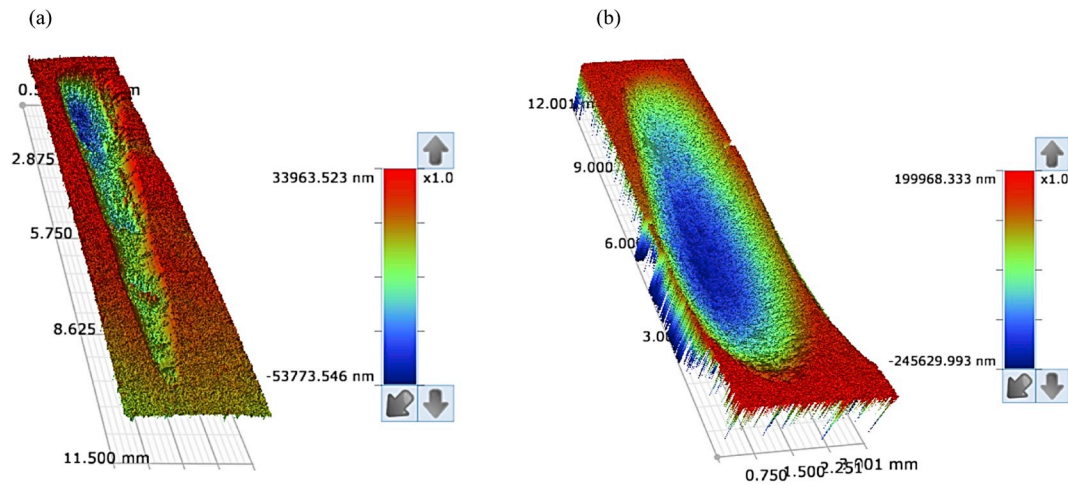


Fig. 11. 3D optical profile of full wear track using the Optical Profilometer (a) Pure Al_2O_3 (b) Al_2O_3 -4wt% ZrO_2 .

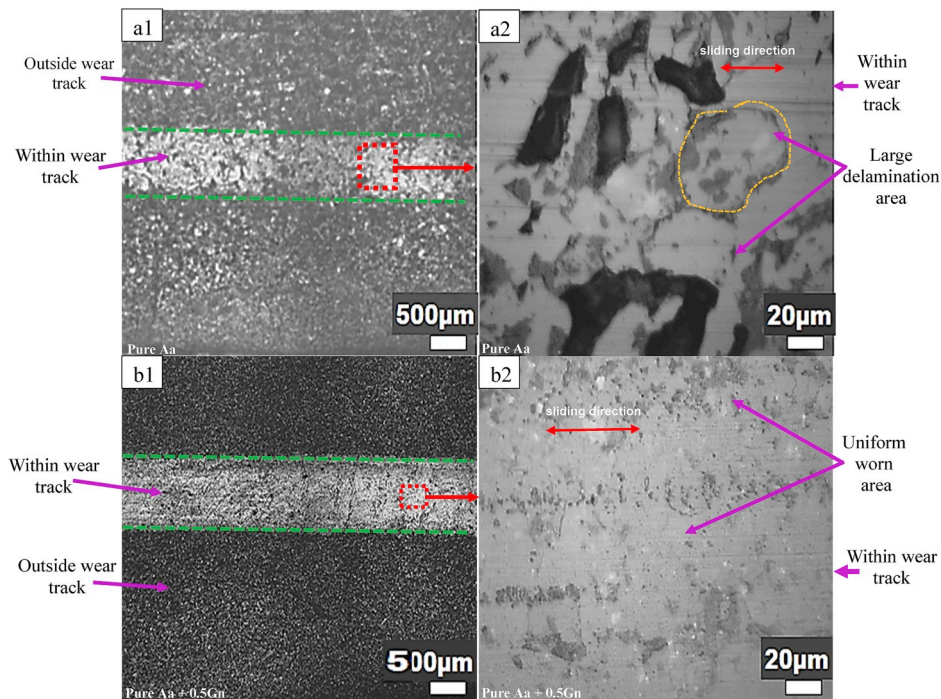


Fig. 12. Optical images of wear tracks on sample surface after wear test showing delamination regions and peel-offs within wear track (a) Pure Al_2O_3 with large delamination and peel-offs (b) Al_2O_3 with 0.5 wt% graphene illustrating a relatively uniform worn region and fine peel-offs in wear track.

There are also fine ZrO_2 precipitates on both the larger and smaller pulled-out Al_2O_3 particles within the wear debris of AZ4. Generally, there are relatively very few tiny ZrO_2 precipitates within the debris of the AZ4 sample as shown in Fig. 20(a) and this confirms the EDS mapping results which illustrates the sparse distribution of very small ZrO_2 precipitates within the Al_2O_3 matrix (Fig. 5(c)). Meanwhile, a finer and uniform dispersion of ZrO_2 precipitates are indicated within the worn particles of AZ10 (Fig. 20(b)). The wear debris are generally characterized with smaller and finer Al_2O_3 particles removed from sample surface during sliding test, hence the uniform peel-off sites within the wear track of AZ10. In addition, it is observed that more ZrO_2 precipitates are refined and uniformly dispersed within the debris of the AZ10 sample as shown in Fig. 20(b). The debris results clearly collaborate with the EDS mapping results which demonstrates that very fine and dense ZrO_2 precipitates are evenly dispersed within the Al_2O_3 matrix as shown in Fig. 6(c). These precipitates are otherwise refined and

further shows that the addition of 10 wt% ZrO_2 improves the wear resistant properties of monolithic Al_2O_3 .

4. Discussions

4.1. Influence of graphene and ZrO_2 on microstructure of nanocomposite

It is shown in the results that consolidation of pure Al_2O_3 at high sintering temperature of 1600 °C resulted in a relatively coarser microstructure. The addition of 0.5 wt% graphene to Al_2O_3 led to refined microstructure of the matrix as compared to pure Al_2O_3 sample. In addition, Al_2O_3 with 10 wt% ZrO_2 also led to significant amount of refinement of the matrix relative to the coarse-grained microstructure produced with the addition of 4 wt% ZrO_2 .

Generally, Al_2O_3 powders used for sintering possess large surface areas and large volume fractions of atoms at Al_2O_3 grain boundary

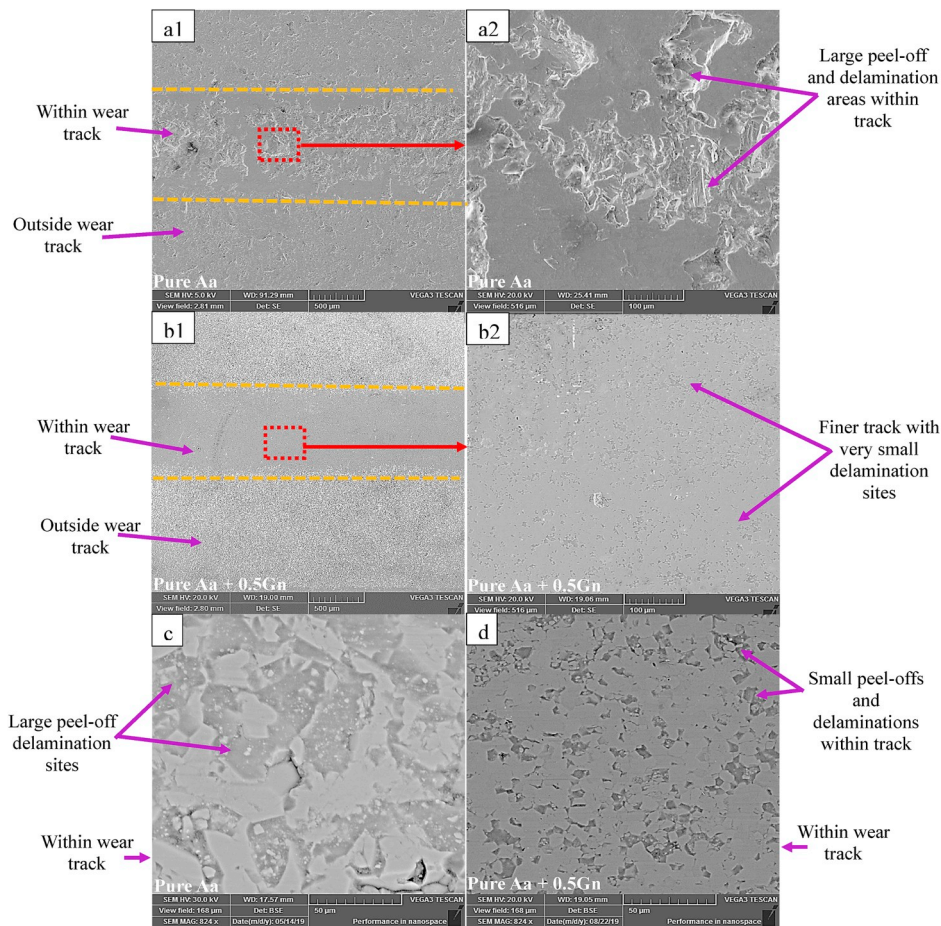


Fig. 13. SEM micrographs showing peeling off within wear tracks (a) Wear track of Pure Al₂O₃ with large and coarse peel-off and delamination areas (b) Al₂O₃ with 0.5 wt%Gn addition depicting small and very fine delamination areas within wear track(c) BSE image showing large worn regions within track of pure Al₂O₃ (d) BSE image showing smooth wear track and smaller delaminations of Al₂O₃ -0.5 wt%Gn sample.

interfaces which generates high number of diffusion paths during sintering [58]. These paths are favourable for increased mass flow and diffusivity of Al₂O₃ which leads to increase in size of grain boundaries and eventual grain growth during densification and sintering [58–60]. It has been shown that the resultant coarse microstructure in ceramic Al₂O₃ can be prevented if there are second phase particles that can inhibit grain boundary diffusion by acting as pinning sites or occupying junction sites at interfaces to restrict grain growth during sintering [61]. The reported refined Al₂O₃ matrix with the addition of 0.5 wt% graphene as demonstrated in Fig. 2(b) might be credited to the deposition of graphene nanoparticles preferentially at Al₂O₃ grain boundaries during consolidation and sintering. It has been reported in several studies that addition of graphene to a matrix can cause grain refinement of the matrix as a result of interfacial interactions and pinning action by the intergranular graphene phases when homogeneously distributed within the matrix [29,53,62–64]. Wang et al. reported similar grain refinement of hot-pressed Al₂O₃ with the addition of graphene nanosheets. He accounted the grain refinement to the inhibition of Al₂O₃ grain diffusion by the presence of graphene nanosheets at the grain boundaries during hot pressing [65]. Ifthikhar et al. also attributed the refined microstructure of prepared Al₂O₃-GNP composites restriction of boundary movement by the intergranular graphene nanoparticles during sintering which suppresses grain growth and yield refined microstructures [51].

The addition of 10 wt%ZrO₂ to Al₂O₃ also led to extensive refinement of the Al₂O₃ matrix as shown in Fig. 3. This is mainly attributed to the homogeneous dispersion of both fine and large ZrO₂ precipitates within the matrix. The EDS mapping results in Fig. 6(c) further confirms that the microstructure of the AZ10 sample consists of several tiny ZrO₂

precipitates uniformly dispersed in the entire matrix and thus resulting in higher refinement of the matrix grains. Several literature studies have reported that the addition of optimum amounts (up to 10 vol% and above) of sub-micron ZrO₂ particles to Al₂O₃ matrix can reduce grain growth and cause refinement of the matrix [35,45–46,66–68]. Lange et al. concluded in his work that the grain refinement of Al₂O₃ matrix by ZrO₂ precipitates is possible when there is sufficient self-diffusion of ZrO₂ particles within the Al₂O₃ 4-grain junction to exert significant dragging force on the matrix grain and thus inhibit abnormal grain growth during sintering [35]. French et al. also observed similar grain refinement in the Al₂O₃ matrix with higher volume fractions of ZrO₂ particles as a result of restriction in matrix grain growth and attributed it to the minimum matter transfer caused by the limited mutual solid solubility and physical constraints between Al₂O₃ matrix and the ZrO₂ particles [66]. Casellas et al. also reported that grain refinement of Al₂O₃ matrix is possible when large amount of ZrO₂ particles are used to restrict the microstructure from developing grain growth. He suggested that the formation of large ZrO₂ agglomerates as a result of higher ZrO₂ amounts hinders the mobility of the matrix grain boundary [67]. Khoshkalam et al. also concluded in their studies that increasing the ZrO₂ content causes refinement of Al₂O₃ matrix through grain boundary pinning effect by the ZrO₂ particles [46].

Meanwhile, the coarse microstructure with the addition of 4 wt% ZrO₂ as illustrated in Fig. 3 was anticipated since several studies reported similar trend with the addition of small amounts of ZrO₂ [45,68]. Generally, the final microstructure of the AZ4 sample was characterized with somewhat uniform distribution of few larger and fine ZrO₂ precipitates which were also sparingly dispersed within the Al₂O₃ matrix.

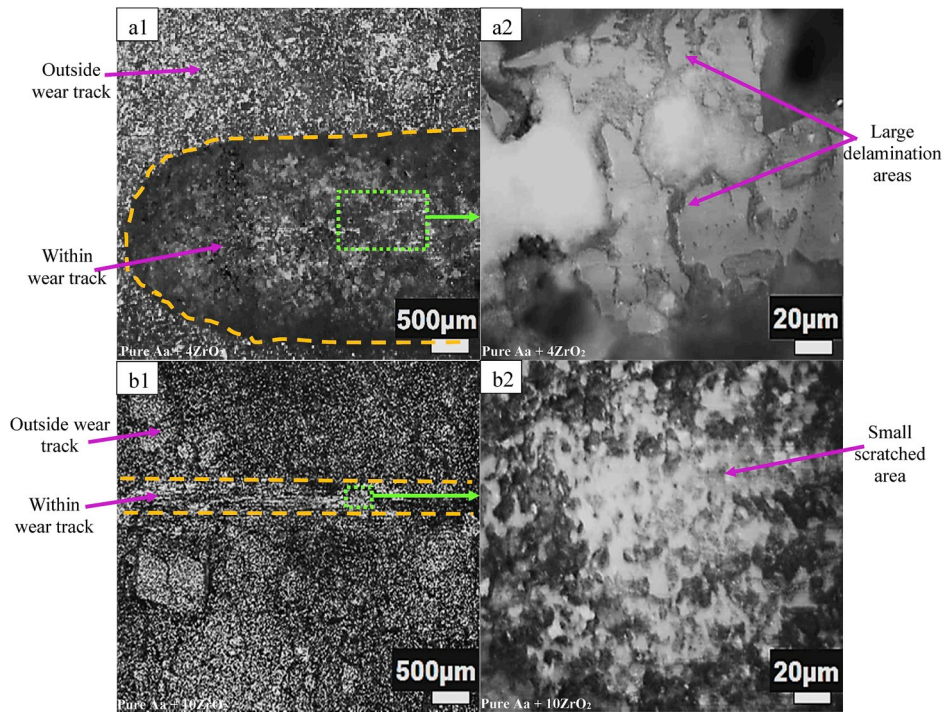


Fig. 14. Optical micrographs showing peeling off in wear tracks of Al_2O_3 - ZrO_2 nanocomposites (a) Al_2O_3 -4wt% ZrO_2 exhibiting larger delamination regions (b) Al_2O_3 -10wt% ZrO_2 depicting small and very fine peel-of areas within wear track.

The scanty dispersion of the very fine precipitates was also demonstrated in the detailed EDS mapping results in Fig. 5(c). Also, the addition of 4 wt% ZrO_2 were not sufficiently dispersed throughout the matrix resulting in several regions with less or no ZrO_2 precipitates. In these regions however, the Al_2O_3 matrix is coarser which shows that there was abnormal grain growth in these areas during sintering. In the literature, it has been reported that the inability of the 4 wt% ZrO_2 to cause a refined microstructure is directly linked with their insufficiency in restricting the abnormal grain growth of Al_2O_3 during sintering [35,45,46,66,67,68]. Lange et al. suggested in his studies that inclusions up to 5 vol% ZrO_2 is not sufficient to occupy the intergranular sites of the Al_2O_3 matrix to impede grain growth [35]. Casellas also reported coarse-grained microstructure in Al_2O_3 matrix doped with 5 vol% ZrO_2 and attributed this structure to the exaggerated grain growth of the matrix [67]. Naglieri et al. attributed the poor microstructure of Al_2O_3 doped with 5 vol% ZrO_2 to the agglomeration of the ZrO_2 particles and inhomogeneous distribution of ZrO_2 phases within the Al_2O_3 matrix [45].

4.2. Effect of microstructural features on wear properties

Final microstructure of nanocomposites prior to the wear test also contributed to the wear response of the fabricated nanocomposites. The addition of 0.5 wt% graphene resulted in the refinement of the Al_2O_3 matrix and led to a lower wear rate of the AG0.5 sample as shown in Figs 2(b), 9(b), 12(b) and 13(b) and (d) and Table 4. However, the coefficient of friction was not necessarily decreased with the addition of 0.5 wt% graphene relative to pure Al_2O_3 . This suggests that there is direct relationship between the microstructure and the wear response of the nanocomposite rather than the COF. As reported in various studies, the coefficient of friction is not a material property, but it is dependent on the surface interaction phenomena such as physical, chemical and temperature response of the contact surfaces during the constant sliding [69–72]. Rutkowski et al. reported similar trend in hot-pressed Al_2O_3 -graphene composites. He concluded that the sintered composites having up to 2 wt%Gn demonstrated good wear resistance but

higher coefficient of friction relative to the parent Al_2O_3 sample [73]. Tapasztó et al. also added 3 wt% graphene nanoplatelets to Si_3N_4 and reported tremendous decrease in wear rate but a comparable coefficient of friction value with the monolithic Si_3N_4 sample [74]. Reginfo et al. also reinforced aluminum matrix with graphene nanoplatelets and reported a low coefficient of friction but poor wear resistance of the nanocomposites [52].

The reported decreased wear rate of the prepared AG0.5 sample is attributed to its fine-grained microstructure with the addition of graphene. Typically, during the wear test, the sliding motion of the counterball with the specific applied nominal stress interact continuously with the sample surface. During this surface interaction, energy is transferred from the ball to the sample surface which is accommodated by the sample's microstructural features and load-bearing phases within the material. The interaction of pure Al_2O_3 sample with the Si_3N_4 counterball led to considerable removal of large grain particles from the surface as shown within wear track (Figs. 12(a) and 13(a)) and debris (Fig. 18(a)). The removal of large particles shows that there are no significant load-bearing structures or reinforcements in the pure Al_2O_3 sample to transfer sufficient applied load during the test. Therefore, the energy transmitted by the counterball is accommodated by the parent microstructure which is further used to cause the peeling-off within the structure. The peeling-off in the pure Al_2O_3 sample is possible since it is a brittle structure and cannot undergo any form of refinement in the presence of mechanical applied load. Also, as more energy is applied through the continuous sliding, the peeling-off becomes more evident with large Al_2O_3 grain pull-outs as seen in the wear debris in Fig. 18(a). In the case of the AG0.5 sample, the addition of 0.5 wt% graphene had great influence on the microstructure and its wear response. The fine wear track with low peel-offs suggest that the presence of tough graphene deposits at the grain boundary due to homogeneous dispersion clearly maintained their structural integrity during sliding wear and undoubtedly led to an effective transfer of mechanical load directly from the ball throughout the structure and caused refinement within the wear track with very small delamination sites.

The addition of 10 wt% ZrO_2 to Al_2O_3 also produced a refined-

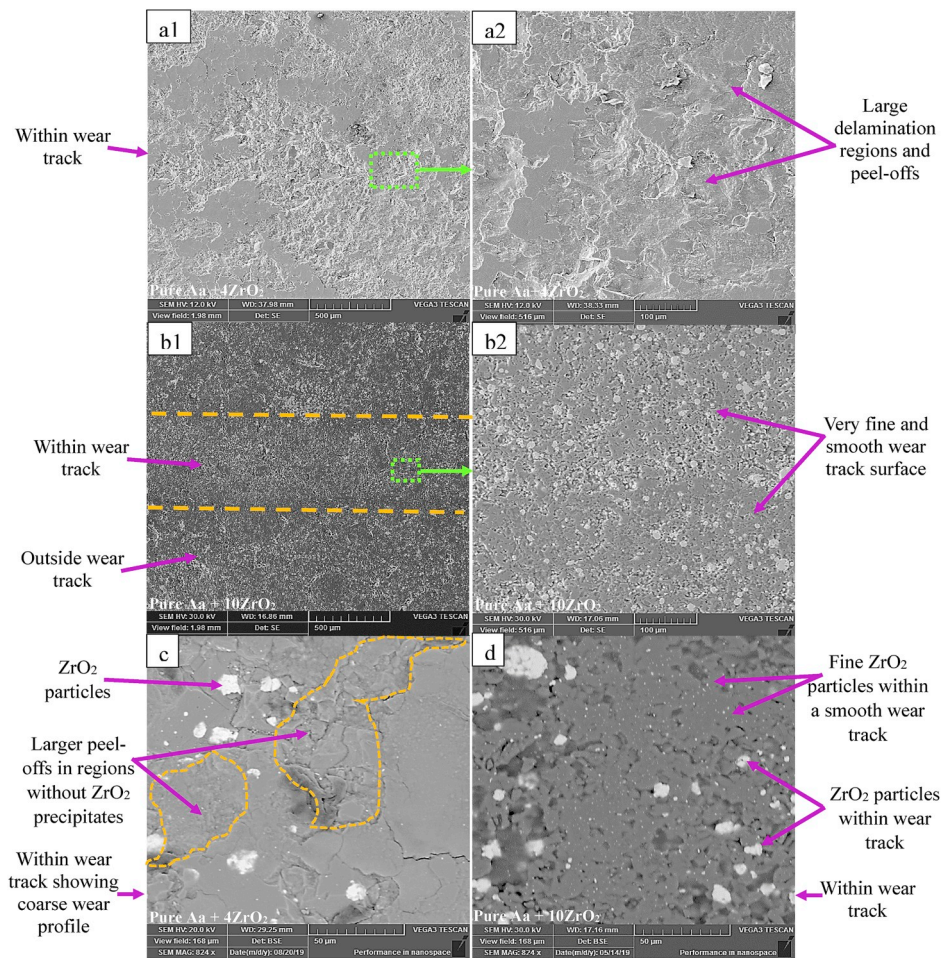


Fig. 15. SEM micrographs demonstrating peeling off in wear tracks of Al_2O_3 - ZrO_2 nanocomposites (a) Al_2O_3 -4wt% ZrO_2 with large delamination and peel-offs (b) Al_2O_3 -10wt% ZrO_2 with relatively uniform worn surface (c)–(d) BSE images showing the distribution of ZrO_2 within wear tracks of Al_2O_3 -4wt% ZrO_2 and Al_2O_3 -10wt% ZrO_2 samples respectively.

grained microstructure of the matrix and resulted in a relatively lower wear rate and lower coefficient of friction than the pure Al_2O_3 sample as illustrated in Figs 3(b), 15(b) and (d). The 4 wt% ZrO_2 addition to the Al_2O_3 gave a coarse-grained matrix microstructure and yielded extremely higher wear rate and higher coefficient of friction relative to pure Al_2O_3 . The microstructural features of the AZ10 sample such as the homogeneous dispersion of the very fine ZrO_2 precipitates within the matrix accounted for the decreased in both the wear rate and COF. The uniformly dispersed ZrO_2 precipitates are very efficient in the load-bearing activities of the structure during the wear test. A finer wear track observed in the AZ10 sample surface in Figs. 14(b), 15(b) and (d) suggest that the energy transferred by the counterball onto the sample surface during wear was absorbed by the finely distributed ZrO_2 precipitates which was used for extensive grain refinement and thus producing a refined wear track surface with minimum peel-offs. The refinement is also observed in the wear debris in Fig. 20(b) which demonstrates very fine worn-out particles of Al_2O_3 with finer ZrO_2 precipitates uniformly distributed within the worn-out Al_2O_3 particles. The closely compacted ZrO_2 precipitates in the AZ10 sample as demonstrated in the EDS results in Fig. 6(c) also explains the effective load-bearing capabilities and lower wear rate response of the AZ10 sample in the presence of an applied mechanical load.

On the other hand, the increase in wear rate and COF with the addition of 4 wt% ZrO_2 is directly linked to its coarse-grained microstructure as illustrated in Fig. 3. Generally, a coarse microstructure having larger grains demonstrates depleted mechanical properties as reported in various studies [75–77]. The wear of the AZ4 sample is

characterized with large peel-offs and delaminations of both Al_2O_3 particles and the second-phase ZrO_2 precipitates. This suggests that the addition of 4 wt% ZrO_2 was ineffective in performing its structural function as a load-bearing phase in the Al_2O_3 matrix and led to large pull-out of grain particles during continuous sliding. The peel-offs were relatively larger in the regions without ZrO_2 precipitates within the wear track of the same sample as shown in Fig. 15(c). These regions did not have significant reinforcements to support the applied load from the counterball and therefore the parent material pull-out in these areas due to its brittle nature. The scanty dispersion of the tiny ZrO_2 reinforcements within the matrix resulting in this phenomenon is all too clear in the micrographs and the EDS mapping result in Figs. 4(b) and 5 (c). Evidence of the large Al_2O_3 grain pull-out is clearly observed in the wear debris in Fig. 20(a). The bigger chunk of unrefined ZrO_2 precipitates deposited on the completely removed coarse Al_2O_3 particle suggests that there was no significant refinement of the ZrO_2 precipitates within the wear track which explains the high amount of wear in the AZ4 sample.

5. Conclusion

In this study, an attempt has been made to fabricate a homogenous structural Al_2O_3 matrix nanocomposite by incorporating it with ZrO_2 and graphene to understand the effect of the processing route and addition of ZrO_2 /graphene on the microstructural integrity and properties of the processed material. The effect of graphene and ZrO_2 additions on the evolution of the alumina matrix during processing including

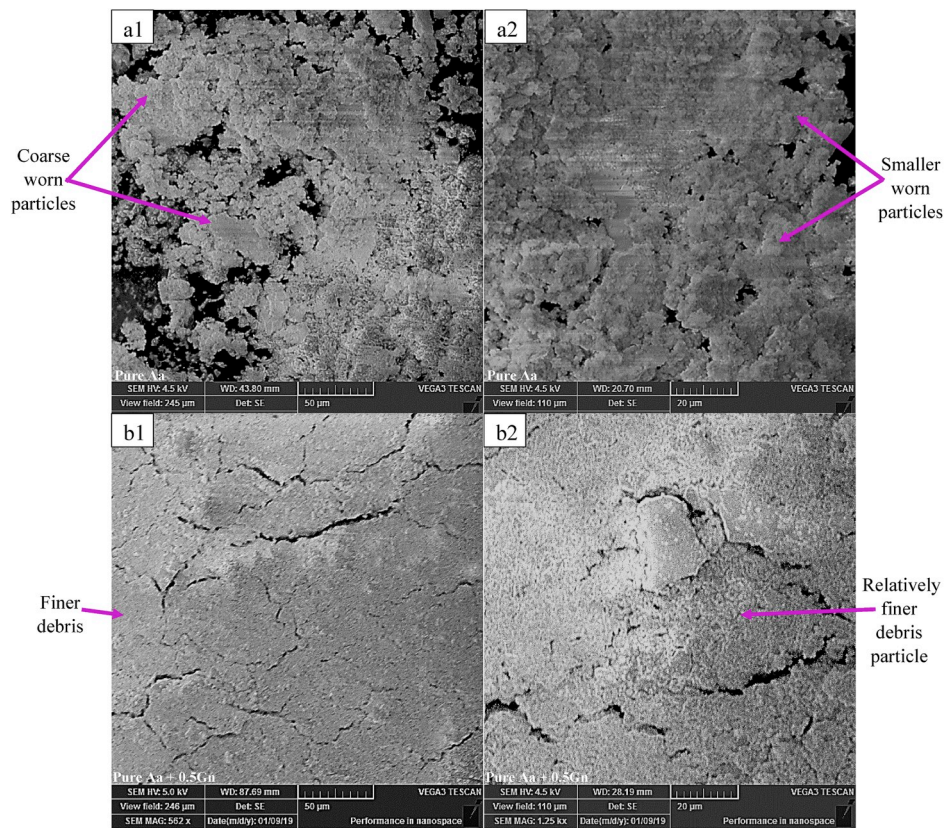


Fig. 16. SEM images showing wear debris (a) Pure Al_2O_3 with overall coarse debris (b) Al_2O_3 -0.5 wt%Gn with generally finer debris.

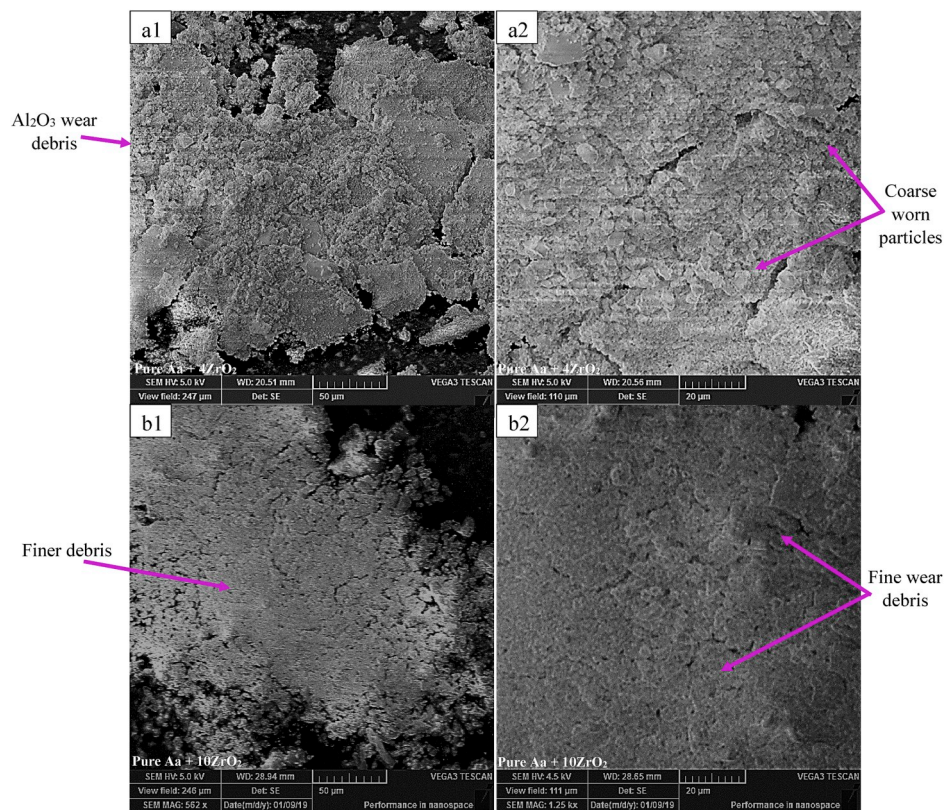


Fig. 17. SEM micrographs of wear debris revealing nature of debris particles (a) Al_2O_3 -4 wt% ZrO_2 with an overall large and coarse worn-out particles (b) Relatively finer worn particles of Al_2O_3 -10 wt% ZrO_2 sample.

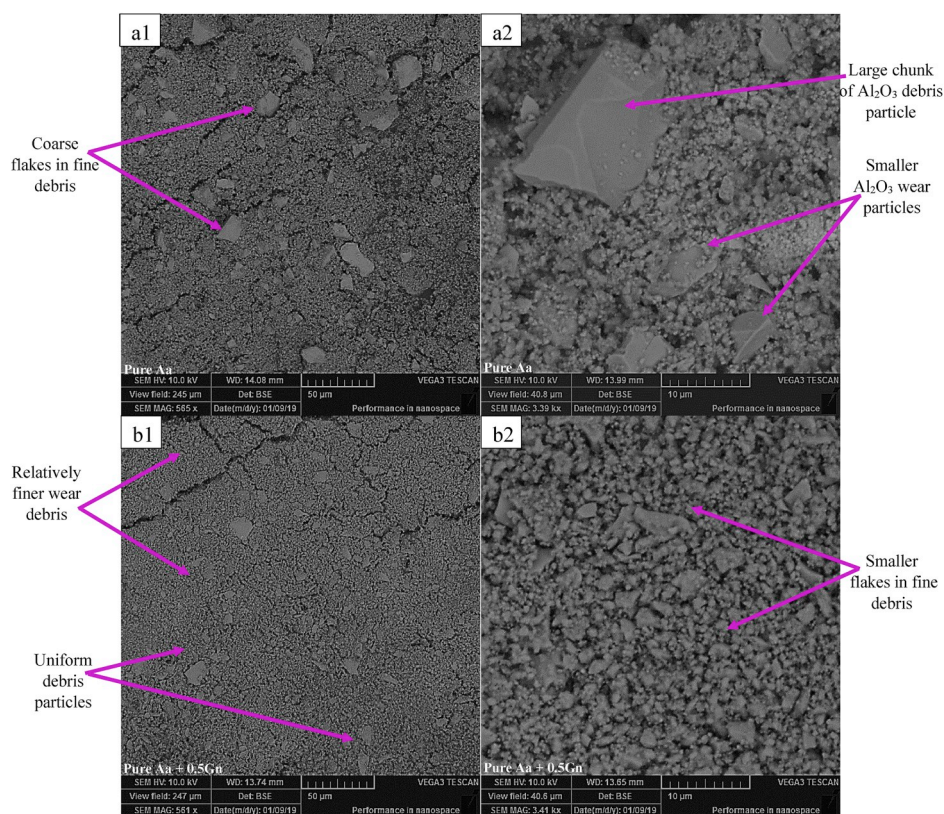


Fig. 18. SEM images of wear debris showing pulled-out particles from wear track (a) Pure Al₂O₃ with coarse pulled out particles (b) Al₂O₃ with 0.5 wt%Gn addition depicting a relatively finer and uniform pulled-out particles.

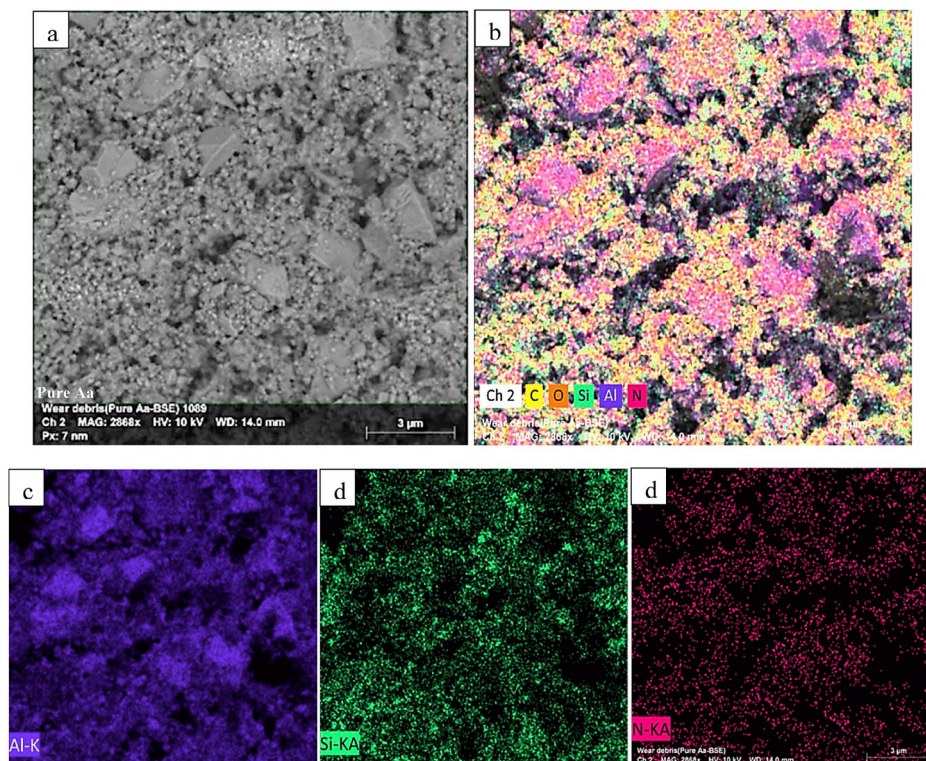


Fig. 19. EDS Mapping on wear debris of Pure Al₂O₃ sample showing deposits of Si₃N₄ counterball on worn particles of Al₂O₃ matrix.

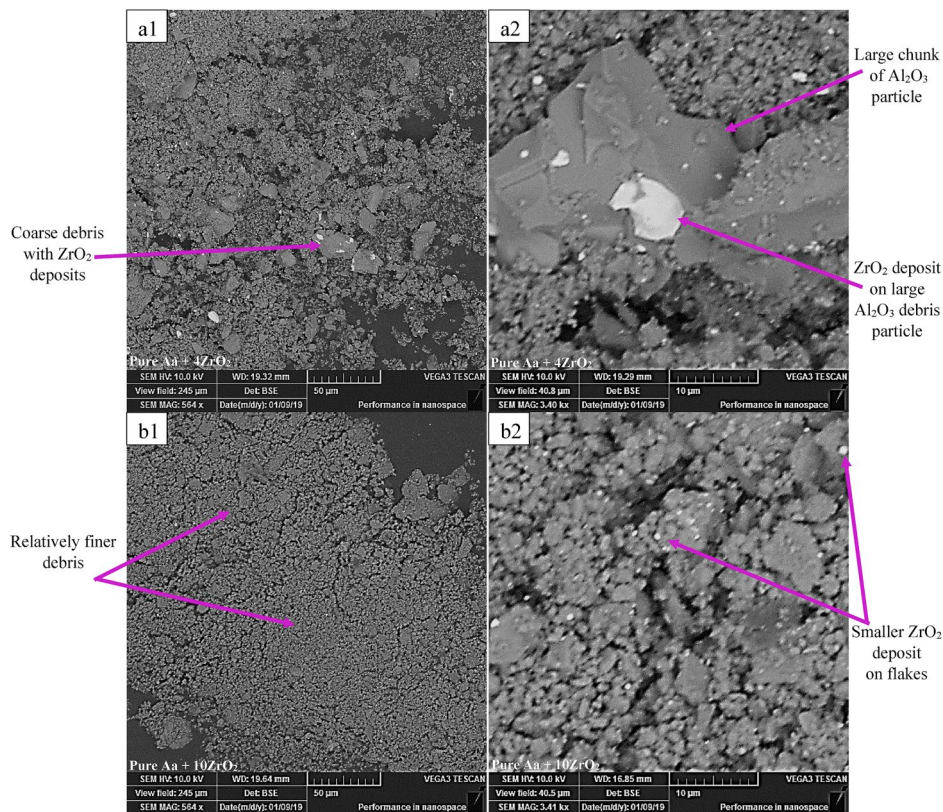


Fig. 20. SEM micrographs showing deposition of ZrO₂ particles on wear debris (a) Al₂O₃-4wt%ZrO₂ with small and large ZrO₂ deposits on peeled-off matrix particles (b) Al₂O₃-10 wt%ZrO₂ with fine deposits of ZrO₂ particles on wear debris.

the effect of these nano-materials on the mechanical properties of the processed nanocomposite were determined and discussed. The summary of the main findings from this study include:

1. The microstructure of the processed pure Al₂O₃ is characterized with coarse grains due to grain growth during sintering. The coarse-grained microstructure is responsible for the relatively higher COF and wear behaviour of the parent Al₂O₃ sample.
2. Addition of 0.5 wt%Gn to Al₂O₃ significantly refined the Al₂O₃ matrix and produced higher wear resistance than the pure Al₂O₃. Even though the COF increased during the dry sliding wear, the improved wear resistance is directly attributed to the fine-grained microstructure and the presence of intergranular graphene particles.
3. The addition of 4 wt%ZrO₂ to Al₂O₃ yielded a coarser microstructure with a higher COF and poor wear resistance. The presence of sparsely distributed and less dense ZrO₂ precipitates within the Al₂O₃ matrix after sintering directly accounted for the large grains due to grain growth and the consequent depleted wear response of the AZ4 sample.
4. Meanwhile, the addition of 10 wt%ZrO₂ to pure Al₂O₃ also exhibited led to an enormous decrease in wear rate and COF due to the extensively refined Al₂O₃ matrix structure. The uniform dispersion of very fine and dense ZrO₂ precipitates within the matrix highly accounted for the fine-grained microstructure and the overall increased wear resistance of the AZ10 sample.

Declaration of competing interest

There is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wear.2019.203067>.

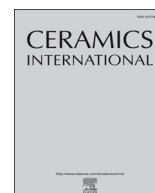
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Paper II: Characterization of the Structure and Properties of Processed Alumina-Graphene and Alumina-Zirconia Composites

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Characterization of the structure and properties of processed alumina-graphene and alumina-zirconia composites

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ABSTRACT

The onset of hybrid alumina-based composites, which combines two or more nano-particles within the alumina matrix has already shown promising improvements in the matrix material. However, variations in mechanical properties including the optimum compositions that give improved properties faced with the development of alumina-based composites require further studies to understand the underlying mechanisms and synergistic effects of the nano-particle additions on the alumina matrix. In the current study, the structure and properties of Al_2O_3 -graphene (0.5 wt%) and Al_2O_3 - ZrO_2 (4 wt% and 10 wt%) composites fabricated via hot-pressing was studied as a baseline for multiple combinations. Even though the addition of 10 wt% ZrO_2 resulted in a 23% reduction in the grain size of the alumina matrix, the 4 wt% ZrO_2 addition resulted in a 14% increase in grain size as compared to the parent alumina matrix. X-ray diffraction analysis revealed that there was approximately 85% monoclinic (*m*- ZrO_2) vs. 15% tetragonal (*t*- ZrO_2) crystal structures in the A4ZrO_2 sample whilst the $\text{A}_{10}\text{ZrO}_2$ had approximately 93% *m*- ZrO_2 vs. 7% *t*- ZrO_2 . The high-volume fraction of the monoclinic crystal structures in the $\text{A}_{10}\text{ZrO}_2$ accounts for the induced microcracks in the sample since the transition from the ductile-tetragonal to brittle-monoclinic is associated with the exertion of compressive stresses on the alumina matrix by the associated elastic volume expansion of *m*- ZrO_2 . Also, the addition of 0.5 wt%graphene resulted in about 37% reduction in the grain size of the alumina matrix, and approximately 10% increase in hardness as a result of the distribution of graphene along the grain boundaries of the parent alumina matrix, which restricts grain coalescence and growth during processing. Furthermore, an increase up to 115% and 164% were observed in the fracture toughness (K_{IC}) with the inclusion of 0.5 wt%graphene and 10 wt% ZrO_2 respectively, which was primarily ascribed to the fine-grained microstructures and toughening mechanisms of the intergranular graphene and ZrO_2 particles.

1. Introduction

Despite the appealing nature of advanced ceramics such as alumina, zirconia, silicon carbide, silicon nitride and boron carbide, which makes them adaptable for several applications in the defence, automotive, aerospace and biomedical industries, these materials have limited structural applications due to their low fracture toughness [1–4]. Several attractive qualities of these technical ceramics including low-density, high-temperature strength, thermal and electrical insulation and chemical stability coupled with ease of availability offer them as potential candidates for lightweight structural and high-temperature applications [5–7]. The brittle nature of ceramics such as alumina has specifically limited its potential to be used as material parts in

aerospace engine exhaust systems, gas turbines and space shielding systems [8,9]. However, the current widespread applications of monolithic alumina as spark plug insulators in vehicles, cutting tools, abrasives, protective coatings, wear resistant and biological implants render it a very essential material choice and therefore create the need to improve this structure for high-performance practical applications [5,10–13]. In recent years, the attempt to make alumina and other ceramics superior for demanding structural applications, where a low density but high toughness material is constantly needed, has driven many material scientists and engineers to design technical ceramics as composites or nano-composites. By transforming them into a ceramic-based composite material, the objective is to improve the low mechanical properties such as strength, hardness and fracture toughness

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without compromising the lightweight feature of the monolithic ceramic structure. Uniform dispersion of low density second-phase particles such as carbon-based materials, zirconia and silicon carbide within the alumina matrix, have been adapted as a means to counter the limitations of the monolithic ceramic structure [14–16]. Despite reports of success in designing and processing these materials, there have been other findings that show that these nano-scale additions deteriorates the inherent mechanical properties of alumina and makes it undesirable for high-performance applications [17,18].

Carbon-based particles such as graphene and carbon-nanotubes have been recently adapted to improve the low fracture toughness and other mechanical properties of monolithic alumina. The 2D geometry of graphene makes it an ideal candidate for incorporation within alumina and other brittle monolithic ceramics [19–21]. A low-density structure coupled with many other elevated mechanical properties such as high stiffness (reported modulus ranges from 0.5–1 TPa), large surface-to-volume ratios, higher electrical and thermal conductivity makes graphene a very effective reinforcement structure for high-performance practical applications [22,23]. Accounts from literature have shown that the appreciable amount of grain refinement introduced within the resulting matrix by graphene after sintering, is responsible for the overall improved mechanical properties in a graphene/ceramic composite [24]. Typically, graphene acts as an interfacial particle between the matrix grains and restricts the grain growth of the matrix during the high temperature sintering process. This is possible when there has been a significant uniform distribution of the graphene phase within the matrix structure. The refinement of grains of a matrix is known to generate an improved mechanical response following the general Hall-Petch equation, which inversely relates the grain size to the mechanical property such as strength [25–27]. Chen et al. prepared alumina/graphene nanosheets (0.2 wt% GNS) via hot pressing and reported fracture toughness value of $6.6 \text{ MPa m}^{1/2}$ corresponding to about 43.5% increase relative to the monolithic alumina. The improvement in the mechanical properties was mainly attributed to the refined grained structure with the addition of 0.2 wt% GNS, which resulted from the inhibition of alumina grain growth during sintering [28]. Lin et al. also reported a lower density and smaller grain size of alumina-graphene composite prepared using spark plasma sintering with amounts of graphene ranging from 0.88 to 8.5vol% [29]. Therefore, the adaptation of graphene into several ceramic matrices have become ideal to produce a highly advanced ceramic composites for higher performance applications.

However, graphene/alumina composites have not received much admiration as intended due to the many shortcomings associated with processing of graphene and effective incorporation into the matrix phase. High Van der Waals forces between graphene particles have constantly become a challenge in fabricating alumina-graphene composites. These forces lead to higher level of carbon agglomeration which limits the uniform dispersion of graphene within the matrix [30,31]. The result of this is the depletion in mechanical properties such as fracture toughness, hardness and tribological response of the fabricated composites due to several post-processing defects such as micropores and micro-cracks, formed within the consolidated composite microstructure [17]. In addition, the extraordinary properties of graphene have not been fully harnessed within alumina matrix due to challenges in selecting an ideal amount of graphene. Some reported works have shown that a higher concentrations of graphene ($\sim > 1.0\text{vol}\%$) supports agglomeration and consequently lowers the mechanical properties [32,33]. Currently, studies aim to improve these shortcomings by using different processing routes and also combining the graphene with second-phase nano-additives such as carbon nanotubes to complement its properties within the composites.

Also, the addition of zirconia (ZrO_2) within alumina matrix has been one of the common ways of toughening ceramic alumina for structural applications. The relative higher fracture toughness, strength, low thermal and ionic conductivity, and biocompatibility of zirconia

ceramic give it broad applications and make it attractive as a reinforcement particle in alumina [34]. In addition to restraining the abnormal grain growth of alumina during sintering, the inclusion of the zirconia particles also provides the improved strength and toughness of alumina in the form of phase transformation [35–37]. The metastable tetragonal to monoclinic phase transformation (*t-m*) of added zirconia particles is accompanied with substantial volume expansion (about 3–5%), which causes constraint of the matrix grains and provide toughening effect to the composites [34,38–40]. The degree of increase in the fracture toughness property of alumina/zirconia composites is however dependent on the distribution of the zirconia particles, grain size of the particulate zirconia and the concentration of the zirconia added [41,42]. Homogeneous dispersion of an optimum amount ($> 8\text{vol}\%$) of zirconia phases within alumina have been reported by several studies to yield significant increase in the fracture toughness and other mechanical properties of the fabricated composites [43–47]. A sufficient amount of zirconia incorporated within the alumina provide substantial inhibition of the matrix grain movements during sintering and decreases the matrix grain size, as reported by several works [43]. Rao et al. used co-precipitation route to prepare $\text{ZrO}_2\text{-Al}_2\text{O}_3$ composites and estimated the fracture toughness (K_{IC}) value using the Vickers micro-indentation method, and recorded an increase from $4.45 \text{ MPa m}^{1/2}$ to about $7.6 \text{ MPa m}^{1/2}$ when 10 wt% ZrO_2 was added to the alumina matrix. The improvement in the toughness was attributed to the fine distribution of the ZrO_2 phase and smaller grain size of the matrix [44]. Ganesh et al. also reported an approximate increase in fracture toughness up to $7.38 \text{ MPa m}^{1/2}$ in zirconia toughened alumina (ZTA) composites prepared by gel casting method with different zirconia compositions (30 wt% and 60 wt% ZrO_2) [45]. Naglieri et al. also studied the mechanical properties of alumina-zirconia composites (with ZrO_2 amounts varying from 5 to 20vol%), which were prepared using a combination of wet chemical method and pressureless sintering at 1500°C for 60 min. The composite with 10vol% ZrO_2 had the highest fracture toughness value with finer grains as compared to the 5vol% ZrO_2 which recorded the lowest toughness due to the coarsened microstructure [46]. Meena et al. also studied the effect of ZrO_2 and MgO on the physical and mechanical behaviour of spark plasma sintered MgO-ZTA composites with added ZrO_2 amounts ranging from 5 to 15vol%. The highest fracture toughness value of about $6.7 \text{ MPa m}^{1/2}$ was recorded with 15vol% ZrO_2 addition but an optimum mechanical property was achieved with the 10vol% ZrO_2 and 1vol% MgO content [47].

Even though the ideal composition of added ZrO_2 (8vol% and above) within the parent alumina matrix yields improved toughness and strength, other mechanical properties accompanied such as hardness and wear resistant properties are not necessarily improved relative to that of the monolithic alumina [46,48–51]. In the work of Naglieri et al., it was shown that the Vickers hardness decreased gradually with the addition of ZrO_2 particles having compositions from 10 to 20vol%, despite the significant improvement in matrix grain refinement and fracture toughness. The addition of 5vol% ZrO_2 rather had the highest hardness value regardless of the larger alumina grain size recorded [46]. Also, Ifthikar et al. recently prepared $\text{Al}_2\text{O}_3\text{-ZrO}_2$ nanocomposites and reported a fairly small decrease in the hardness of $\text{Al}_2\text{O}_3\text{-8vol}\%$ ZrO_2 even though the fracture toughness was largely enhanced. He suggested that microstructural defects and the $\text{ZrO}_2/\text{Al}_2\text{O}_3$ interfacial micro-cracking might be the possible cause of the decline in the hardness property [48]. Clearly, the effect of these second-phase particles on the microstructure and their direct influence on the mechanical properties are all but conclusive, despite the fact that extensive studies have been carried out on $\text{Al}_2\text{O}_3\text{-ZrO}_2$ matrix composites.

These current challenges and variations in mechanical properties faced with the development of alumina-based composites have presented material researchers with the need to further study and improve these composites. The onset of hybrid alumina-based composites, which combines two or more second-phase particles within the alumina

matrix has already shown promising improvement in the matrix material. However, the combined effect of these additions to yield superior properties are still being researched. In the current study, separate additions of graphene and zirconia within alumina matrix have been studied as a basis for the combined effect of these hybrid composites on the structure and properties of the processed materials. Understanding the effect of the individual material additions on the microstructure and properties of processed alumina-graphene and alumina-zirconia composites is critical in studying their combined synergistic effects when multiple particles are added to the parent alumina matrix.

2. Experimental procedure

2.1. Composite fabrication

Powders of alumina (mean diameter < 50 nm) and unstabilized zirconia (< 80 nm average particle size) were acquired from Sigma Aldrich, UK. Alumina slurry was formed by dispersing powders in distilled water whilst continuously sonicated. Zirconia (4 wt% and 10 wt %) suspensions were also prepared with distilled water and added to the alumina suspensions, which were thoroughly mixed and constantly sonicated to ensure a uniform dispersion. Fine graphite flakes procured from Asbury Graphite Mills Inc, UK, were modified chemically to obtain graphite oxide GO by adapting the Hummers' method discussed elsewhere [52]. Graphene was then produced from the graphite oxide using a thermal exfoliation method as accounted in previous work [53]. Specified concentration of the prepared graphene (0.5 wt%) was dispersed in distilled water and continuously stirred using the ultra-sonic probe for about 30 min. The constant agitation of the graphene/water suspension was to ensure uniform dispersion of the graphene and restrict carbon agglomeration of the graphene particles. In addition, a small amount of surfactant (sodium dodecyl sulphate, SDS) was carefully introduced into the graphene/distilled water suspension. The added SDS was intended to be adsorbed on the graphene surface and lower the Van der Waals's force of attraction. The characterization of the processed graphene has also been discussed in previous work [53]. The separately prepared alumina slurry was then added to the graphene suspension whilst stirred continuously for about an hour to achieve homogeneity.

Detailed consolidation and final sintering process of the samples are described in previous work [54]. The sintered composites were approximately 50 mm × 45 mm × 2 mm in dimension. Small rectangular composites were sectioned into smaller sizes using a diamond wire saw for microstructural analysis and mechanical tests.

2.2. Microstructural characterization of fabricated composites

A High-Resolution Field Emission SEM (Quanta 3D FE-SEM, Thermofisher) was used to analyse the evolved microstructures of the consolidated composites. The surface of each sample was ground (in the order: 400, 600, 800 and 1200 grits) using a silicon carbide (SiC) paper and finally polished with diamond suspension up to 0.05 µm. The polished surfaces were then thermally etched at 1400 °C (200 °C below sintering temperature) for about 15 min to reveal the grain structures. Etched samples were coated with a thin platinum layer to render them conductive in the SEM chamber and to prevent excessive charging. The distinct microstructures were thoroughly studied using the FE-SEM. Grain sizes of the thermally etched samples were also estimated using the line intercept method as outlined by the ASTM E112-13 and with the help of image J processing software (version 1.52n).

2.3. X-ray diffraction and ZrO₂ phase analysis

The crystalline phases of alumina-zirconia and alumina-graphene sintered samples were determined using X-ray diffraction (Rigaku Miniflex 600) with Cu-Kα radiation of $\lambda = 1.54056 \text{ \AA}$ and 2θ step size

of 0.02°. The generated XRD patterns for each sample were obtained in the 2θ range of 5–110° using a scanning rate of 1.4 °/min. The XRD data was thoroughly analysed using the JADE 6.0 software.

The monoclinic (*m*-ZrO₂) and tetragonal (*t*-ZrO₂) contents were estimated for both Al₂O₃-4 wt%ZrO₂ and Al₂O₃-10 wt%ZrO₂ samples using the intensities of the reflections from the X-ray diffraction patterns and relations by Garvie and Toraya [55,56] below:

$$X_m = \frac{[I_m(\bar{1}11) + I_m(111)]}{[I_m(\bar{1}11) + I_m(111) + I_t(111)]} \quad (1)$$

$$V_m = \frac{1.311X_m}{1 + 0.311X_m} \quad (2)$$

where X_m is the integrated intensity ratio, $I_m(\bar{1}11)$ and $I_m(111)$ are the relative intensities of monoclinic phase intensities at planes ($\bar{1}11$) and (111) respectively, $I_t(111)$ represents the tetragonal peak intensity at plane (111) in the XRD patterns, V_m is the volume fraction of the monoclinic ZrO₂ phase.

The corresponding volume fraction of tetragonal ZrO₂ was approximately deduced from the relation:

$$V_t = 1 - V_m \quad (3)$$

2.4. Vickers Hardness and fracture toughness measurements

Vickers hardness of the polished rectangular samples were measured by means of a diamond indenter installed on a Vickers microhardness tester (METLAB, Canada). The diamond indenter was used to apply a load of 9.807 N (1 kg) on the flat sample surface at a dwell time of 15s, in accordance with the ASTM C1327-15. The diagonal lengths of the diamond-shaped indent made on the sample surface after removal of the indenter was measured by means of an optical microscope attached to the microhardness equipment. The Vickers hardness (Hv) in GPa was estimated according to Eq. (4) below.

$$Hv = 0.0018544 \left(\frac{P}{d^2} \right) \quad (4)$$

where P is the applied load in N and d is the average diagonal length in mm [57]. Ten separate indentations were made using similar load and dwell time, at appreciable distance apart on the sample surface to avoid cracks connecting and ensure accuracy. Also, the indents were carefully made at fresh regions without visible pores or cracks to prevent poor indent formation.

Fracture toughness of the composites were determined from the Vickers-produced cracks after indentation using the Direct Crack Measurement (DCM) technique. Even though this technique presents some limitations as reported in literature [58–60], it was adapted for the current work due to the size limitation of the sintered samples. The length of cracks emanating from the edges of the indents made were carefully measured with the help of the optical microscope and Image J software. Using the Lawn et al. Eq. (5) below, the fracture toughness of the composites were estimated [61].

$$K_{IC} = 0.028(Ha^{0.5}) \left(\frac{E}{H} \right)^{0.5} \left(\frac{c}{a} \right)^{-1.5} \quad (5)$$

where a is half of the length of Vickers indent diagonal, H is the hardness, c is the crack length measured from the center of the diamond indent to the tip of the emanating crack, E is the Young's modulus calculated from literature values of alumina, zirconia and graphene. The final modulus value was estimated from the rule of mixture using these values and their known concentrations within the matrix.

2.5. Analysis of fractured surfaces

To critically analyse the toughening mechanisms of the second-phase particles and the nature of fracture of the composites, the

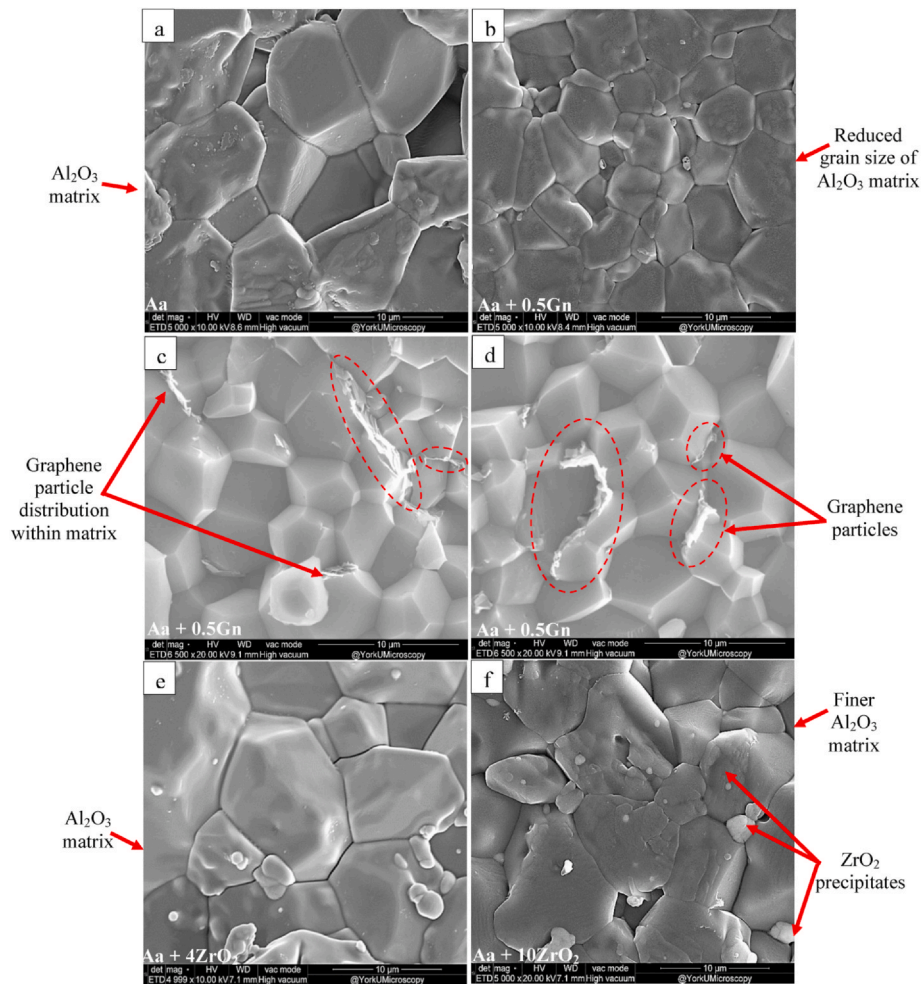


Fig. 1. FE-SEM micrographs of thermally etched composites under similar magnifications showing various grain size structures (a) Pure Al_2O_3 showing large grains (b) Al_2O_3 with 0.5 wt% graphene with relatively reduced grain size (c)–(d) SEM of fractured surface showing the uniform distribution of graphene particles within Al_2O_3 matrix (e) Al_2O_3 with 4 wt% ZrO_2 showing a coarser microstructure (f) Al_2O_3 with 10 wt% ZrO_2 showing a relatively reduced matrix grain structure and distribution of ZrO_2 particles within matrix.

fractured surfaces were studied under a high-resolution field-emission scanning electron microscope (FE-SEM, Quanta-3D). Samples fractured at higher loads (490 N) were mounted on an SEM angular mounts to expose the cross-section of the fractured surfaces within the SEM. These surfaces were also coated with the thin layer of platinum to enhance conductivity and prevent charging in the SEM chamber.

3. Results

3.1. Microstructural evolution of fabricated composites

Microstructural investigations of the fabricated composites under the same processing conditions (60 MPa consolidation and sintering at 1600 °C) were thoroughly carried out using the FE-SEM. The microstructural features characterized under similar magnifications revealed the effect of 0.5 wt% graphene, 4 wt% ZrO_2 and 10 wt% ZrO_2 inclusions on the Al_2O_3 matrix. The micrographs from Figs. 1 and 2 show the grain structure of the thermally etched monolithic Al_2O_3 , Al_2O_3 -0.5 wt% graphene (henceforth referred to as $\text{A}_{0.5}\text{GN}$ sample), Al_2O_3 -4 wt% ZrO_2 (referred to as A_4ZrO_2 sample) and Al_2O_3 -10 wt% ZrO_2 (now referred to as $\text{A}_{10}\text{ZrO}_2$ sample). Thermal etching at a temperature of about 200 °C below the sintering temperature reveals the grains and grain boundaries of the composites. As shown in Fig. 1, a significantly reduced grain size of the monolithic Al_2O_3 matrix is revealed with the addition of 0.5 wt% graphene. A relatively smaller grain size is also

illustrated in the etched $\text{A}_{10}\text{ZrO}_2$ sample doped with 10 wt% ZrO_2 (Fig. 1(d)). In addition, a relatively high amount of very fine ZrO_2 particles are seen on both grain boundaries and within the matrix grains of the $\text{A}_{10}\text{ZrO}_2$ sample, as shown in Fig. 1(d). Meanwhile, the A_4ZrO_2 sample which had added 4 wt% ZrO_2 concentration showed larger grain structure as compared to the monolithic Al_2O_3 . Table 1 and Fig. 2 show the grain size distribution of the fabricated composites with their corresponding mean grain sizes. Quantitative estimation of the grain sizes using the image analysis software revealed ~37% and 23% reduction in the sizes of the $\text{A}_{0.5}\text{GN}$ and $\text{A}_{10}\text{ZrO}_2$ respectively, as compared to the parent Al_2O_3 matrix. An approximately 14% increase in the grain size was registered for the A_4ZrO_2 sample relative to the monolithic Al_2O_3 .

3.2. Microstructural defects after sintering

The sintered composites also depicted some micro-defects that are illustrated in Fig. 3. Some micro-cracks are seen in the coarse-grained microstructure of the parent Al_2O_3 (Fig. 3(a)). Meanwhile, limited number of surface pores which may be as a result of incomplete fusion of the matrix grains are present in the $\text{A}_{0.5}\text{GN}$ sample (Fig. 3(b)). Within this structure, there is evidence of the matrix grains breaking down to cause refinement of the microstructure. No detectable micro-defects are revealed in the as-sintered structure of A_4ZrO_2 sample as illustrated in Fig. 3(c). However, in the $\text{A}_{10}\text{ZrO}_2$ sample, there exist very large pores within the matrix together with few micro-cracks along its grain

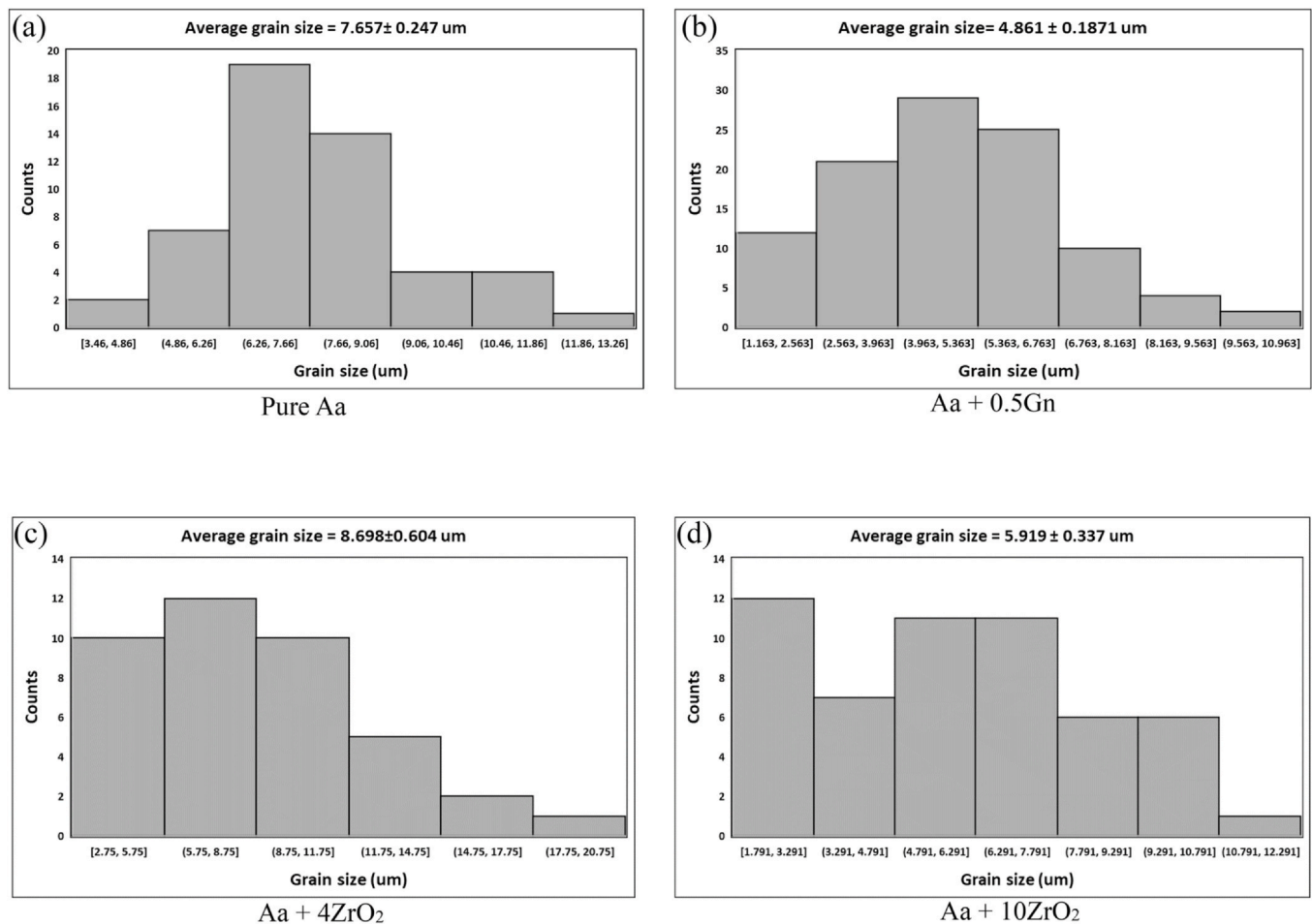


Fig. 2. Grain size distribution of fabricated composites (a) Pure Al_2O_3 (b) $\text{Al}_2\text{O}_3 + 0.5 \text{ wt}\% \text{ Graphene}$ (c) $\text{Al}_2\text{O}_3 + 4 \text{ wt}\% \text{ ZrO}_2$ (d) $\text{Al}_2\text{O}_3 + 10 \text{ wt}\% \text{ ZrO}_2$.

Table 1
Summary of fabricated composites.

Sample	Description	Grain Size (μm)
Pure Alumina	Pure A	7.657 ± 0.247
Aa + 0.5 wt%Gn	$\text{A}_{0.5}\text{GN}$	4.861 ± 0.187
Aa + 4 wt%ZrO ₂	A_4ZrO_2	8.698 ± 0.604
Aa + 10 wt%ZrO ₂	$\text{A}_{10}\text{ZrO}_2$	5.919 ± 0.337

boundaries, as seen in Fig. 3(d). The large pores exist between the Al_2O_3 matrix grains which were not completely fused during the sintering stage.

3.3. Phase analysis of composites

Fig. 4 shows the XRD spectra of the fabricated composites with the various peaks and crystalline phase formations. The peaks depicting the monoclinic ($m\text{-ZrO}_2$) and tetragonal ($t\text{-ZrO}_2$) phases are also indicated in the XRD pattern of the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ samples. Generally, the addition of 0.5 wt% graphene did not reveal any significant additional peaks within the spectra of the $\text{A}_{0.5}\text{GN}$ sample. This suggests that there were no appreciable chemical reactions between the Al_2O_3 matrix and the graphene particles during sintering to form a new phase. In addition, the absence of additional peaks in the $\text{A}_{0.5}\text{GN}$ sample might be due to the low concentration of the added graphene within the Al_2O_3 matrix, as suggested by other studies [62,63]. However, there is a decrease in the peak intensities of the $\text{A}_{0.5}\text{GN}$ sample as compared to that of the parent Al_2O_3 . The XRD spectra of the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ samples revealed a general peak increase of the $\text{Al}_2\text{O}_3\text{-4 wt}\% \text{ ZrO}_2$ relative to the $\text{Al}_2\text{O}_3\text{-}$

10 wt%ZrO₂. In both the A_4ZrO_2 and $\text{A}_{10}\text{ZrO}_2$ samples, there are additional peaks appearing with different intensities within their XRD patterns. These peaks demonstrate the ZrO_2 phases (t and m) after the high temperature sintering and ageing of the consolidated composites. In addition, there is a higher increase in the monoclinic peaks of the $\text{A}_{10}\text{ZrO}_2$ ($2\theta = \sim 28.2$ and $2\theta = \sim 31.5$) as compared to the monoclinic peaks in the A_4ZrO_2 sample at the same 2θ diffraction angles. Quantification of the monoclinic ($m\text{-ZrO}_2$) content in percentage (%) using the Garvie and Toraya equations in (1) and (2) showed about 82% and 91% monoclinic content ($m\text{-ZrO}_2$) for the A_4ZrO_2 and $\text{A}_{10}\text{ZrO}_2$ samples respectively. The corresponding volume fractions of the monoclinic (V_m) and tetragonal (V_t) were also estimated for each sample and presented in Table 2.

3.4. Hardness

Table 3 presents the mechanical properties of the composites under the specified load-bearing conditions. Fig. 5(a) shows an indented surface of a sample with cracks extending from the indents. The variation of the Vickers hardness with the addition of the second-phase materials is also shown in Fig. 5(b). Generally, the addition of 0.5 wt% graphene ($\text{A}_{0.5}\text{GN}$ sample) led to the highest Vickers hardness value, with the $\text{A}_{10}\text{ZrO}_2$ sample registering a lower hardness as compared to the A_4ZrO_2 and the parent Al_2O_3 sample. About 9.6% increase in the hardness of the $\text{A}_{0.5}\text{GN}$ sample is attributed to the homogeneously dispersed graphene within the Al_2O_3 matrix with refined microstructure. The 23.3% decrease in the Vickers hardness of the $\text{A}_{10}\text{ZrO}_2$ sample agrees with other literature results which showed similar trend [46]. This decline in hardness might be ascribed to the residual

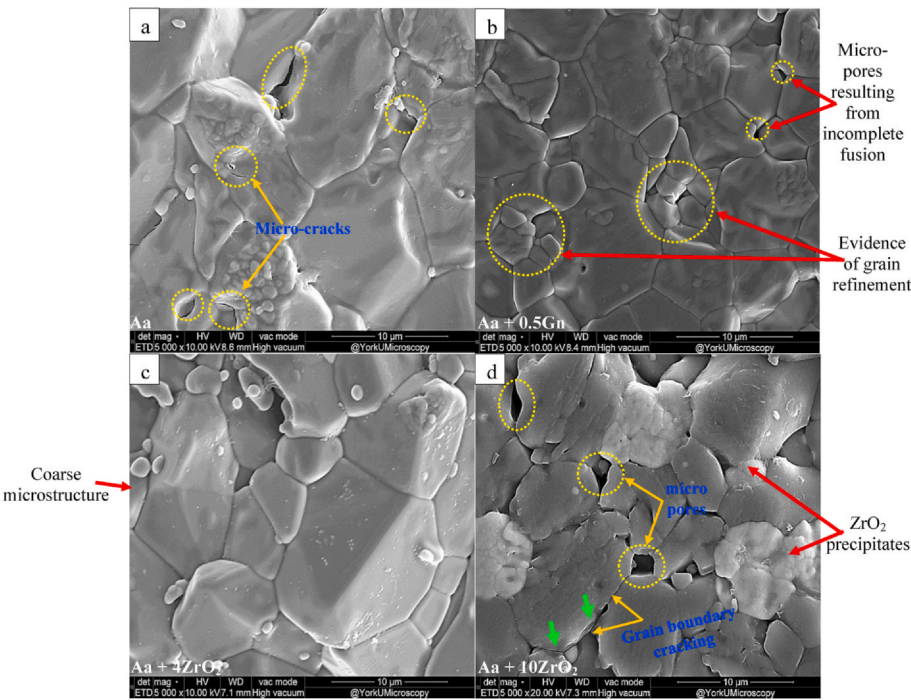


Fig. 3. FE-SEM micrographs of composites illustrating apparent microstructural defects (a) Pure Al_2O_3 showing large grains with micro-cracks (b) Al_2O_3 with 0.5 wt% graphene depicting micro-pores (c) Al_2O_3 with 4 wt% ZrO_2 showing a coarse micro-structure (d) Al_2O_3 with 10 wt% ZrO_2 showing micro-pores and grain boundary cracking.

porosities as seen in Fig. 3(d), relatively lower hardness of the added ZrO_2 phase as compared to the Al_2O_3 matrix and some microcracks within its microstructure.

3.5. Fracture toughness (K_{IC}) and mode of fracture

The direct crack measurement (DCM) method was used to calculate the indentation fracture toughness (K_{IC}) of the indented sample surface using the Lawn et al. Eq. (5). The addition of 0.5 wt% graphene and

Table 2			
Estimated ZrO_2 phase content from XRD data.			
Sample	ZrO_2 content (wt %)	Monoclinic content (%)	Tetragonal content (%)
Pure Al_2O_3	0	0	0
Al_4ZrO_2	4	85.42	14.58
$\text{Al}_{10}\text{ZrO}_2$	10	92.83	7.17

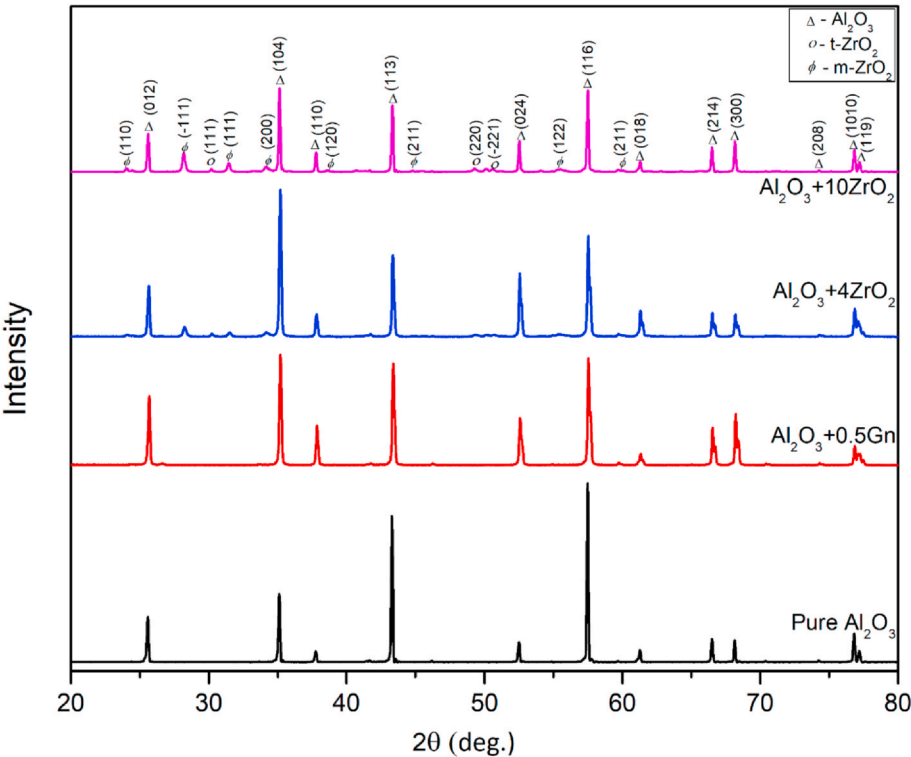


Fig. 4. X-Ray Diffraction patterns of as-sintered Al_2O_3 matrix composites showing different phases of the added ZrO_2 particles.

Table 3
Mechanical data.

Sample	Vickers Hardness, HV (GPa)	Fracture Toughness, K_{IC} (MPa.m ^{1/2})
Pure Al ₂ O ₃	18.868 ± 3.58	2.994 ± 0.412
A _{0.5} GN	20.679 ± 2.04	6.431 ± 1.190
A ₄ ZrO ₂	17.628 ± 2.43	2.660 ± 0.455
A ₁₀ ZrO ₂	14.468 ± 5.52	7.905 ± 1.497

10 wt%ZrO₂ generated higher toughness values relative to the parent Al₂O₃ as shown in Table 2 and the graph in Fig. 5(c). The A₁₀ZrO₂ sample showed approximately 164% increase in the toughness and the addition of 0.5 wt% graphene (A_{0.5}GN sample) revealed an increase up to 114% as compared to the parent Al₂O₃. However, a decrease in the fracture toughness up to 11% is revealed by the A₄ZrO₂ sample which also had the least fracture toughness value.

Various fracture modes and cracking were analysed on the fractured surface of each sample using a High-resolution FE-SEM to detect the failure and toughening mechanisms. Either intergranular fracture, transgranular fracture or both are demonstrated by the different composites. Fig. 6 shows the SEM fractography of the parent Al₂O₃ sample depicting both transgranular and intergranular fracture modes. At lower magnification, it is clearly observed that large grains of the matrix are removed, as shown in Fig. 6(a). The intergranular cracking along the grain boundaries is also demonstrated in Fig. 6(b) along with large transgranular fracture. Typically, a brittle fracture is dominant in the parent Al₂O₃ sample which is illustrated by the sharp cleavages, indicating no plasticity prior to fracture. Fig. 6(c) and (d) also reveal the nature the fractured surface having cleavages and striations which were generated during fracture.

The fracture surface analysis of the A_{0.5}GN sample also illustrates both transgranular and intergranular fracture as the predominant fracture modes within the composite. The refined microstructure with

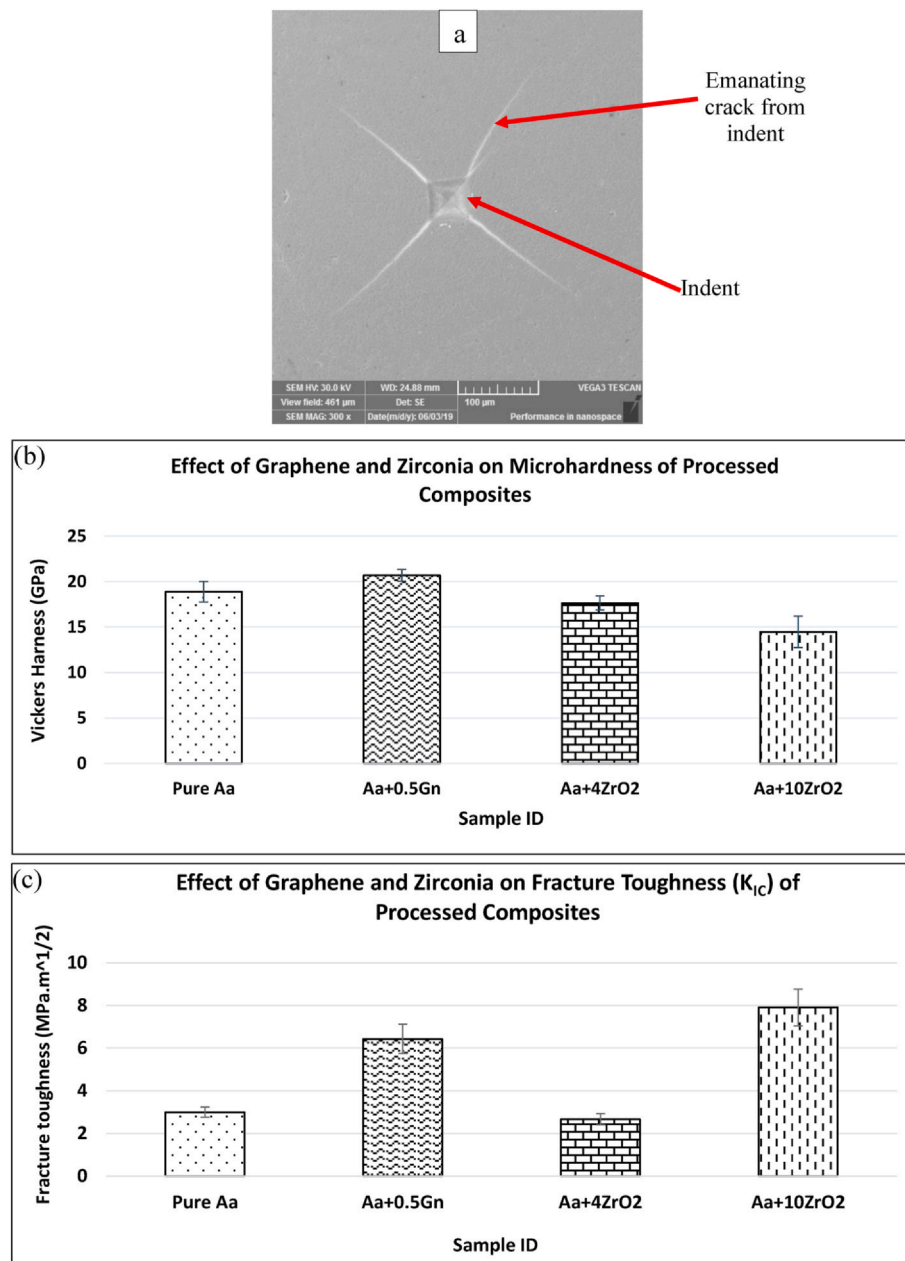


Fig. 5. (a) Optical micrographs showing indent on sample's surface with micro-cracks (b) Effect of graphene and ZrO₂ on the Vickers micro-hardness of fabricated composites (c) Effect of graphene and ZrO₂ on the fracture toughness (K_{IC}) of fabricated composites.

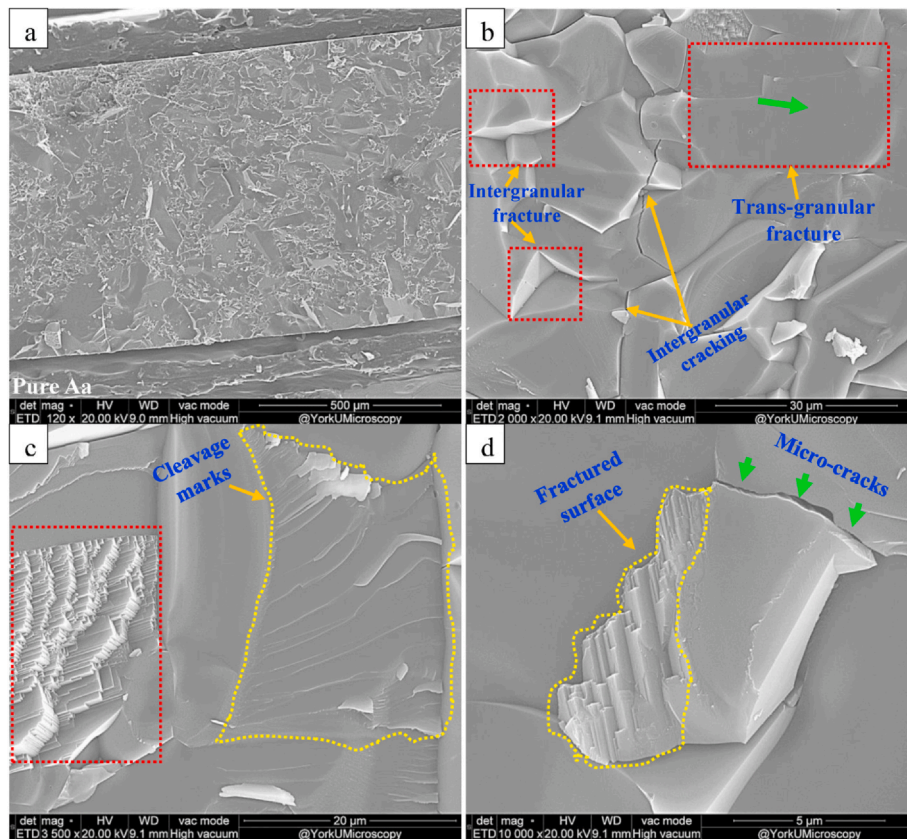


Fig. 6. FE-SEM images of fractured surface of as-sintered parent Al_2O_3 sample showing both intergranular and transgranular mode of fracture.

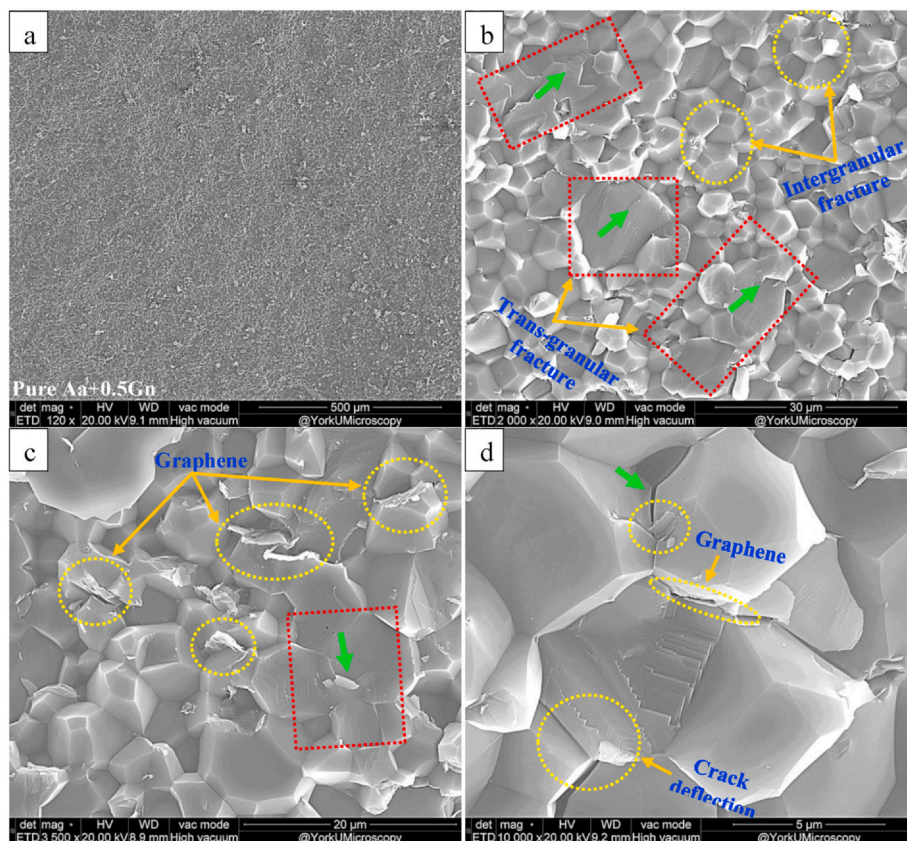


Fig. 7. FE-SEM micrographs of fractured surface of as-sintered Al_2O_3 -0.5 wt%graphene sample demonstrating both intergranular and transgranular fracture behaviour with embedded graphene particles at Al_2O_3 matrix grain boundaries.

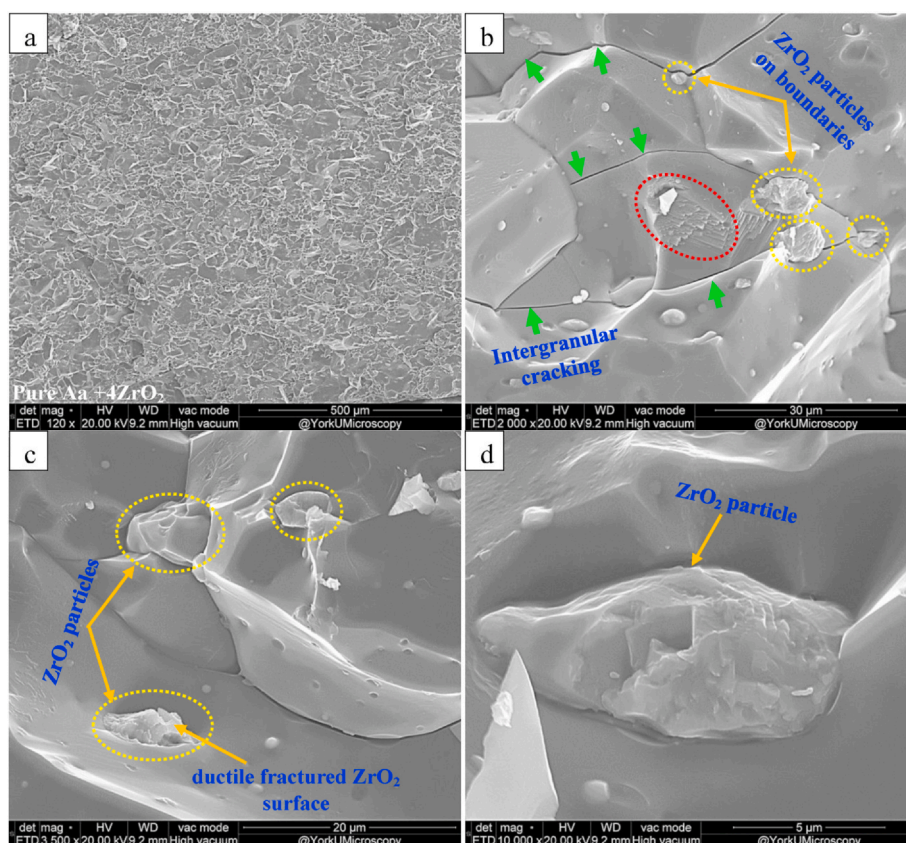


Fig. 8. FE-SEM micrographs of fractured surface of Al_2O_3 -4 wt% ZrO_2 sample depicting intergranular fracture and grain-boundary cracking, with ductile fracture of the ZrO_2 precipitates.

the addition of the 0.5 wt% graphene is also demonstrated on the fractured surfaces as evident in Fig. 7(a)–(d). The most predominant mode of fracture is intergranular with other several grain sites experiencing a transgranular fracture behaviour, as shown in Fig. 7(b). In Fig. 7(c), the evidence of pulled-out graphene occupying interstitial site of the matrix is clearly revealed. At these sites, the matrix grains are relatively smaller as compared to other regions without the graphene. In addition, the transgranular fracture is more eminent in the regions with more interstitial graphene due to the tougher and stronger grain boundary produced in the presence of the graphene. It is also observed that the intergranular fracture mode is very prevalent at areas without the grain-boundary graphene particles, indicating a weaker strength of the boundary and easy crack propagation along the grain boundary to cause fracture. Grain boundary crack arrest by the embedded graphene is also demonstrated in Fig. 7(d). Fracture across the grain is brittle and it is indicated by the sharp nature of the grain facets seen through Fig. 7.

In the A_4ZrO_2 sample, a typical brittle fracture is observed with a predominant intergranular fracture accompanied with very few transgranular fractures. The SEM fractography in Fig. 8(a) also indicates that larger grains of the Al_2O_3 matrix removed. Also, in Fig. 8(b), intergranular cracks are very evident along the grain boundaries, with interstitial ZrO_2 particles located on these boundaries. The ZrO_2 particles appear to undergo a ductile fracture as indicated by the knobby-shaped fractured surface, against the brittle fracture exhibited by the matrix fractured surface. Fig. 8(c) and (d) demonstrate the ductile fractured surface of both the intergranular and intragranular ZrO_2 particles. However, it is also observed that some of the ZrO_2 particles do not have a ductile fracture appearance but a brittle one, or appears to have been pulled out during fracture (Fig. 8(c)). In addition, there are few and very tiny intergranular pores with round and slit shape observed in the A_4ZrO_2 fractured surface (Fig. 8(b) and (c)).

Fig. 9 shows the fractured surface of the $\text{A}_{10}\text{ZrO}_2$ sample exhibiting a relatively refined grain structure as compared to the A_4ZrO_2 and parent Al_2O_3 sample (Fig. 9(a)). The fractured surface also indicates very fine ZrO_2 particles located on both the grain and grain boundaries of the matrix. The general fracture behaviour observed is intergranular, with some very few regions showing a transgranular fracture. An evidence of intergranular cracking is also shown in Fig. 9(b). Fig. 9(c) shows the dispersion of the ZrO_2 particles, large porosities and intergranular pores. The ductile fractured surface of the ZrO_2 particles and intergranular pores on the matrix grain surface is also seen in Fig. 9(d).

The ductile nature of the fractured surfaces of the intergranular and intragranular ZrO_2 particles is further demonstrated by the SEM fractographs in Fig. 10(a) and (b). Also, the matrix grain refinement and the distribution of very fine ZrO_2 particles within the fractured surface is clearly seen in Fig. 10(b). Very large pores are also indicated in the $\text{A}_{10}\text{ZrO}_2$ sample with some micro-cracks along the grain boundaries (Fig. 10(b)).

4. Discussion

4.1. Influence of graphene and ZrO_2 on microstructure after processing

The evolution of the microstructures of the fabricated Al_2O_3 -based composites is directly dependent on the processing conditions such as temperature, pressure and concentration of the added graphene (0.5 wt %) and ZrO_2 (4 wt% and 10 wt%). Fine-grained microstructure of the $\text{A}_{0.5}\text{GN}$ showing a significantly reduced matrix grain size can be attributed to the restrictive diffusion action of graphene during the sintering process. High temperature sintering of the Al_2O_3 matrix at longer duration is favourable for grain growth and larger grain size [64,65]. The location of the added graphene particles (preferably between Al_2O_3 matrix grains), as seen in the fractured surfaces (Fig. 7) limits diffusion

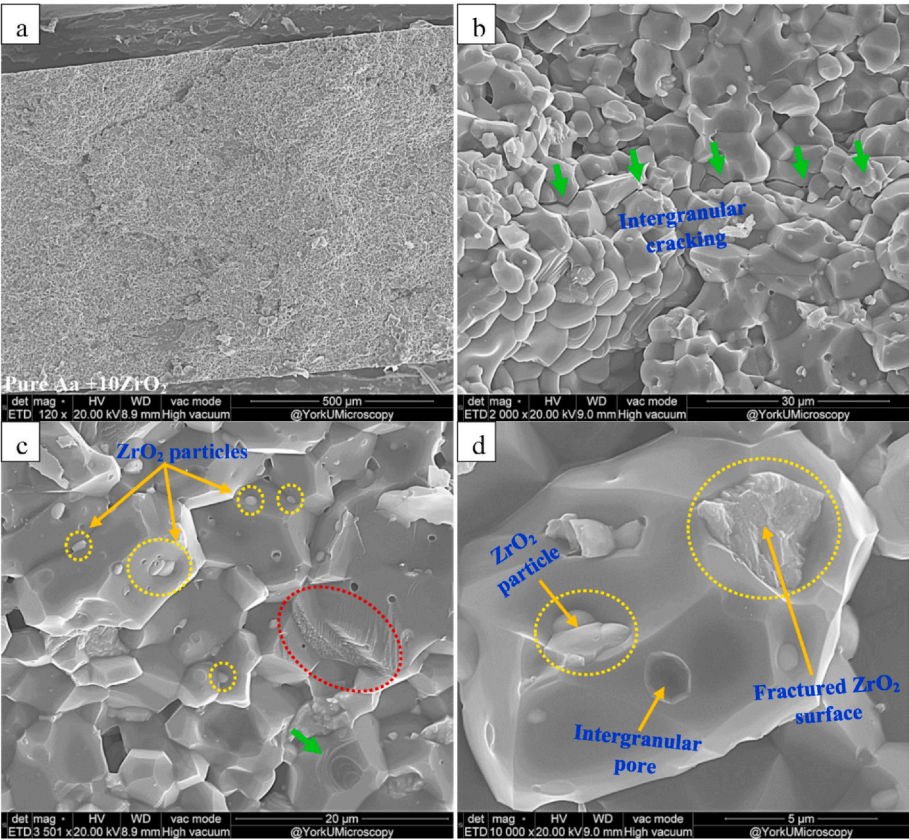


Fig. 9. FE-SEM micrographs of fractured surface of Al₂O₃-10 wt%ZrO₂ sample composite illustrating both intergranular and transgranular fracture, with some intergranular cracking and pores.

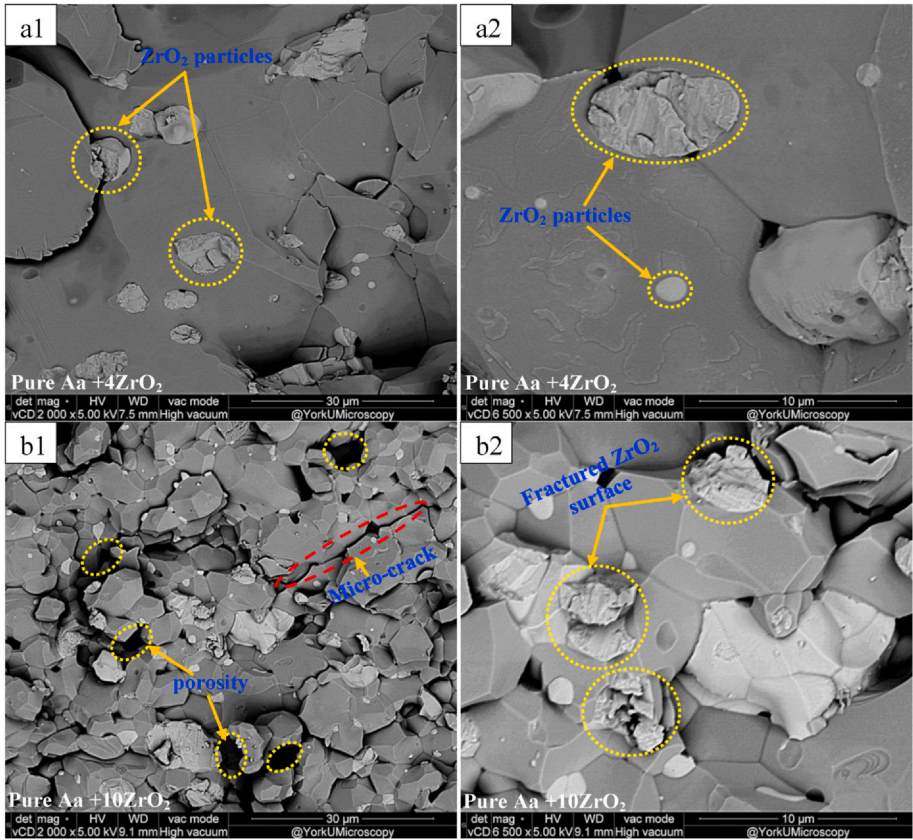


Fig. 10. Phase contrast FE-SEM of fractured surface of Al₂O₃-ZrO₂ composites detailing the nature the fracture behaviour of both Al₂O₃ matrix and ZrO₂ phases (a) Al₂O₃-4 wt%ZrO₂ showing the large intergranular fracture and ductile fracture of ZrO₂ (b) Al₂O₃-10 wt%ZrO₂ showing intergranular fracture with microcracks and some porosities on fractured surface.

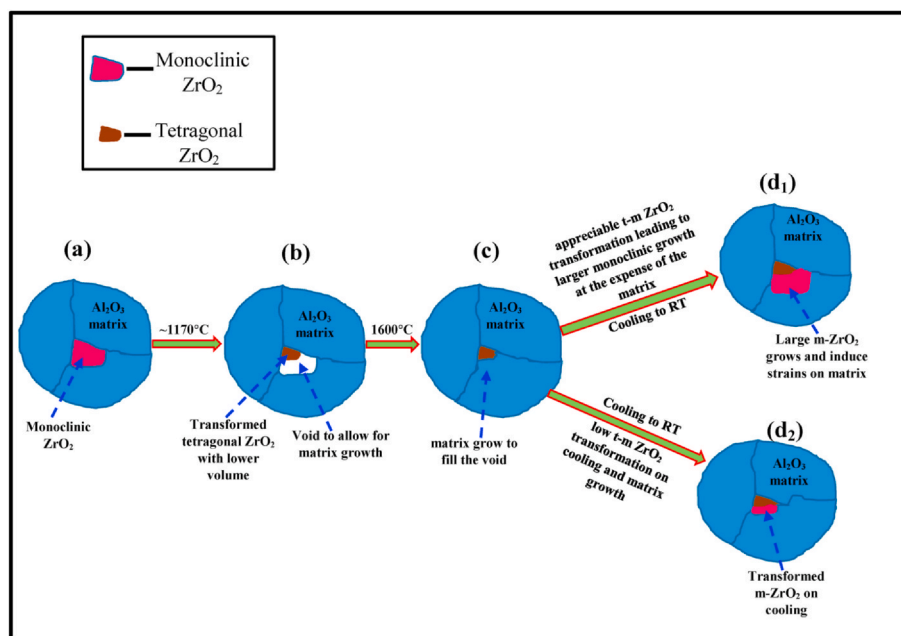


Fig. 11. Schematics of the effect of *t-m* ZrO_2 transformation on matrix grain growth during sintering and cooling.

action of the growing Al_2O_3 matrix grains during sintering. Lin et al. suggested that the reduced grain size of processed Al_2O_3 -graphene composites is due to the fact that the graphene acts a diffusion barrier and prevents the transfer of aluminium and oxygen ions, and therefore decrease their solubility during sintering at a high temperature of 1600°C [29]. The evidence of the refinement action of graphene is also illustrated in Fig. 3(b) (regions with yellow dotted circles). These sites are believed to have the presence of the intergranular graphene particles restricting further matrix grain growth.

The addition and distribution 4 wt% ZrO_2 and 10 wt% ZrO_2 particles to the Al_2O_3 matrix also had a significant effect on the microstructure of the final fabricated composites. Whilst the 10 wt% ZrO_2 addition reduced the grain size of the parent Al_2O_3 , the 4 wt% ZrO_2 inclusion resulted in larger grain size of the matrix. The added ZrO_2 amounts are insoluble in the Al_2O_3 matrix (solubility limit ~ 0), and therefore results in the formation of ZrO_2 particles preferably at the grain boundaries and junctions of the matrix [66]. The overall increase or decrease in the matrix grains of the A_4ZrO_2 and $\text{A}_{10}\text{ZrO}_2$ samples are connected to the phase transition mechanisms of the ZrO_2 within these samples. During sintering, a reversible diffusionless shear-type martensitic phase transformation occurs where the monoclinic zirconia (*m-ZrO*₂) crystal structure changes to tetragonal (*t-ZrO*₂) crystal structure with its associated changes in volume [67,68]. The schematic in Fig. 11 illustrates the sequence of transformation of the ZrO_2 phases and its effect on the grain growth of the matrix. Initially, a stable *m-ZrO*₂ structure exists at room temperature within the dispersed composite prior to the phase transition temperature (Fig. 11(a)). As temperature increases during sintering, the initial *m-t* ZrO_2 transition (occurring at about $\sim 1170^\circ\text{C}$) results in a relatively decreased volume of the transformed *t-ZrO*₂ phase and leaves larger room to allow for matrix grain growth, as shown in Fig. 11(b). The parent matrix can coalesce at this point to form larger grains as high-temperature diffusion continues up to the maximum sintering temperature of 1600°C , in the presence of the transformed *t-ZrO*₂, as illustrated in Fig. 11(c). In another instance, there is no growth of the Al_2O_3 matrix due to diffusion saturation and these voids become porosities within the final structure. However, during cooling, there is the occurrence of a tetragonal to monoclinic phase transformation (*t-m* ZrO_2) which is attributed to the cooperative change in both short and long-range interactions [67,68]. The degree of transformation, as well as the size and volume fraction of the transformed monoclinic phase (*m-*

ZrO_2) at the matrix grain boundaries has direct effect on the final grain structure of the matrix. Fig. 11d₁ and d₂ illustrate the possible routes during the *t-m* transformation and its effect on the matrix grain size. In one instance as shown in Fig. 11(d₁), there is a high volume of monoclinic transformation during cooling and this expansion causes high stress on the matrix boundaries to cause refinement of the Al_2O_3 grains as the *m-ZrO*₂ expands. This identifies with the $\text{A}_{10}\text{ZrO}_2$ sample which had most of the *t-ZrO*₂ transforming to *m-ZrO*₂ (93% monoclinic vs. 7% tetragonal), with higher induced stresses on matrix grains to reduce the grain size of Al_2O_3 matrix. Rao et al. suggested that the limitation to the Al_2O_3 matrix grain growth during sintering was due to the increased grain boundary drag force as a result of the added ZrO_2 particles (10 wt %) on the matrix grain boundaries [44]. Meanwhile, another scenario shown in Fig. 11d₂ suggests that there was not enough transformation of the monoclinic phase upon cooling and the matrix grains continue to grow and increase in size. Therefore, more tetragonal phase is retained in the structure and there is relatively lower inhibition to matrix grain growth. This might account for the larger grain size in the A_4ZrO_2 sample which had high-volume of *t-ZrO*₂ (85% monoclinic vs. 15% tetragonal) after cooling.

In addition, the presence of the microcracks within the structure of the $\text{A}_{10}\text{ZrO}_2$ is due to the volume expansion of the ZrO_2 during the *t-m* phase transformation from high temperature sintering to room temperature cooling. The high-volume fraction of the monoclinic crystal structure in the $\text{A}_{10}\text{ZrO}_2$ accounts for the high volume of cracks in the sample since the transition from the ductile tetragonal to brittle monoclinic is associated with initiation and propagation of cracks [39,40,67,68]. Therefore, the compressive stresses exerted by the *m-ZrO*₂ particles on the matrix due to their elastic volume expansion induced micro-strains that were not completely dissipated by the matrix structure. As part of attaining a lower energy state, this induced micro-strains are translated into crack formation by the Al_2O_3 matrix system as the *m-ZrO*₂ expansion continues during cooling.

4.2. Effect of microstructural features on mechanical properties

The mechanical response of the fabricated composites is directly dependent on the overall microstructural elements generated after the high temperature sintering. The coarse-grained microstructure of the parent Al_2O_3 led to lower fracture toughness value as compared to the

$\text{Al}_{0.5}\text{GN}$ and $\text{Al}_{10}\text{ZrO}_2$ sample. The obtained indentation fracture toughness value of the parent Al_2O_3 sample, which was about $\sim 3 \text{ MPa m}^{1/2}$ has been derived by most studies [48,69]. Moreover, the fractography analysis of the surfaces after fracture reveals the sharp removal of coarser grain elements mostly by intergranular fracture (Fig. 6) which is common in monolithic ceramics such as Al_2O_3 .

The addition of 0.5 wt% graphene to the Al_2O_3 matrix led to an increment in the microhardness due to the presence of the graphene particles at interstitial sites within the matrix grain. The enormous decrease in the grain size resulted in higher number of grain boundaries to hinder the movement of dislocations and accounted for the improved hardness value. This directly obeys the Hall-Petch relationship which states that a finer microstructure gives an increase in mechanical response of the material [70]. As part of the toughening and load-bearing capabilities of graphene, there is an effective transfer of load between the matrix and the tough interfacial graphene particles due to a stronger matrix-graphene bonding. This also reflects the increase in the fracture toughness value of $\sim 6.43 \text{ MPa m}^{1/2}$ obtained for the $\text{Al}_{0.5}\text{GN}$ sample which correlates with results from other studies [28,71–73]. The fractured surface analysis in Fig. 7 shows a predominance of both intergranular and transgranular fracture within the $\text{Al}_{0.5}\text{GN}$ sample. The toughening mechanism provided by the embedded graphene is also observed in the fractured surface. Regions with the transgranular fracture show that there exists a stronger interfacial bonding between the matrix and graphene to restrict the propagation of cracks along the grain boundary. Therefore, the crack tends to move across the matrix grains to cause fracture along the grain with large removal of grain structures as illustrated in Fig. 7(b) and (c).

The degradation of the fracture toughness value with the addition of 4 wt% ZrO_2 could be essentially attributed to the coarse-grained microstructure due to the drastic matrix grain growth during sintering and the concentration of the added ZrO_2 that were insufficient for effective toughening and load-carrying activities. This is evident in the large grain-structure removal with propagation of cracks along the grain boundaries of the fractured surface. The lowered fracture toughness value recorded for the A_4ZrO_2 sample, which had small amount of ZrO_2 addition was about $\sim 2.66 \text{ MPa m}^{1/2}$. Similar toughness value has also been reported in other works [46]. The limited presence of ZrO_2 particles on the grain boundaries restricts the toughening effect of these intragranular structures. Also, the decline in toughness in this structure might be due to the restricted phase transformations (*t-m*) in the presence of the applied stress. Therefore, cracks can propagate within the sample without sufficient intergranular ZrO_2 particles serving as a barrier or restriction which led to the decreased fracture toughness. The microhardness, however, was almost comparable to that of the parent Al_2O_3 because of the lower concentration of the added ZrO_2 particles and the absence of detectable defects such as micro-cracks and porosities as shown in Figs. 1(c) and 3(c).

Although the addition of 10 wt% ZrO_2 produced a fine-grained microstructure, the hardness was significantly declined but had an increase in the fracture toughness value. The decrease in microhardness can be primarily ascribed to certain microstructural parameters after sintering such as porosity, higher concentration of a relatively softer ZrO_2 particles and micro-cracks [48,70]. Thus, upon indentation, the regions with high concentration of ZrO_2 will tend to yield a lower hardness value as compared to indenting on the relatively harder Al_2O_3 matrix. Since there is a high concentration of these fine ZrO_2 particles uniformly distributed within the Al_2O_3 matrix, there is inevitably a higher chance of indenting on these phases and generating an overall lower micro-hardness value. A similar trend in the hardness value of Al_2O_3 - ZrO_2 composites with a higher amount of ZrO_2 ($> 8 \text{ vol\%}$) have been reported in literature [46,48]. Several inherent pores and micro-cracks after sintering, as illustrated in Figs. 3(d) and 10(b) also directly affect the hardness value of the $\text{A}_{10}\text{ZrO}_2$ sample. Meanwhile, the fracture toughness value was relatively increased as compared to the A_4ZrO_2 and parent Al_2O_3 . A sufficient and homogenous distribution of

very fine and tougher ZrO_2 particles within the matrix might account for this improvement. The fractured surface analysis of the $\text{A}_{10}\text{ZrO}_2$ sample in Figs. 9 and 10(b) also reveal the ductile fracture of the ZrO_2 particles coupled with various micro-crackings. Even though these micro-cracks are evidence of volume expansion of the intergranular ZrO_2 particles, their presence also signify appreciable amount of toughening within the matrix structure. Stress-induced micro-cracks are nucleated and propagated as a result of the subsequent phase transformation during fracture. This is dependent on the amount of metastable tetragonal phase within the matrix structure at the point of load application. The inhibition of the propagation of the micro-cracks due to the constant compressive stresses of the matrix as load is applied might also account for the increased toughness in $\text{A}_{10}\text{ZrO}_2$ sample. Also, the expanded ZrO_2 grains tend to close on these cracks and provide toughening in the parent matrix. An estimated volume fraction of *t*- ZrO_2 ($\sim 7\%$) in the sintered $\text{A}_{10}\text{ZrO}_2$ sample suggests retained metastable tetragonal converted to monoclinic (*m*- ZrO_2) and caused expansion of ZrO_2 grains and consequent micro-cracking in the presence of the external applied stress during the indentation.

5. Conclusion

The mechanical properties of fabricated alumina-based composites reinforced with graphene (0.5 wt%) and ZrO_2 (4 wt% and 10 wt%) using hot-pressing method is directly influenced by the microstructure. Toughening mechanisms presented by the processed samples is due to the evolved microstructural features such as grain size, distribution of intergranular and intragranular second-phase particles and presence of some micro-defects after sintering. Major findings from the current studies are outlined as follow:

1. The parent Al_2O_3 microstructure suggests an appreciable grain growth during sintering. The hardness response of the hot-pressed pure Al_2O_3 sample was relatively higher than that of the $\text{A}_{10}\text{ZrO}_2$. The presence of micro-cracks within the structure accounts for the fracture toughness (K_{IC}) value estimated for the parent Al_2O_3 sample.
2. In the $\text{Al}_{0.5}\text{GN}$ sample which had 0.5 wt%Gn to Al_2O_3 , a fine-grained structure with reduced grain size produced higher hardness and fracture toughness values. This was mainly due to the homogeneous distribution of the graphene phase making the load-transfer effective within the Al_2O_3 matrix.
3. The microhardness and fracture toughness behaviour of A_4ZrO_2 sample with added 4 wt% ZrO_2 was also related to the structure and distribution of limited amount of ZrO_2 particles. The relative increase in hardness property as compared to the $\text{A}_{10}\text{ZrO}_2$ sample is due to the higher hardness of the matrix Al_2O_3 and lower concentration of the ZrO_2 particles with relatively lower hardness. However, a decline in the toughness value suggests that an insufficient load-bearing activity of the added ZrO_2 due to the limited *t-m* ZrO_2 transformation.
4. Adding 10 wt% ZrO_2 to the parent Al_2O_3 also exhibited an improved fracture toughness but a significant decline in the hardness value. A relatively finer microstructure coupled with a uniform dispersion of the ZrO_2 particles directly account for the increase in fracture toughness. In addition, presence of micro-cracks as a result of *t-m* ZrO_2 phase transformation also contributed to the enhanced toughness. On the other hand, the microhardness decreased due to the lower hardness of the ZrO_2 particles and other detected microstructural defects such as residual micro-pores and micro-cracks within the sample.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ceramint.2020.08.142>.

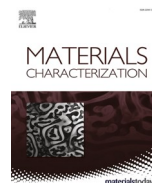
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Paper III: Synergistic effect of Graphene and Carbon Nanotubes on Wear Behavior of Alumina-Zirconia nanocomposites

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Synergistic effect of graphene and carbon nanotubes on wear behaviour of alumina-zirconia nanocomposites

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ABSTRACT

In this study, Al₂O₃-based nanocomposites reinforced with multiple nano-materials, namely zirconia (ZrO₂), graphene (GN) and carbon nanotubes (CNTs) were processed to investigate the synergistic effect of the multi-materials on the microstructural evolution, mechanical properties and tribological behaviour, including the mechanism of wear. The monolithic Al₂O₃ and Al₂O₃-based nanocomposites reinforced with 10wt%ZrO₂, 0.5wt%GN and 2wt%CNTs were prepared using a colloidal mixing and sintered at a temperature of 1600°C. Benchmarked against the monolithic Al₂O₃, a single addition of 10wt%ZrO₂ gave about 25% decrease in matrix grain size, whilst a remarkable reduction in both the matrix and ZrO₂ grains, up to 80% and 46% respectively, was achieved with the multiple combination of ZrO₂, GN and CNTs. This was due to the effective parallel pinning action of the matrix grains by the homogeneously dispersed multi-materials to the monolithic Al₂O₃. Vickers hardness also increased to 48% with combined additions of GN and CNTs, as opposed to the 25% decrease with a single addition of ZrO₂ relative to the monolithic Al₂O₃ material, which was attributed to the refined grain structures and effective load transfer capabilities of the combined multi-phase materials. In addition, the fabricated nanocomposite incorporated with only 10wt%ZrO₂ resulted in 88% decrease in wear rate, whilst the multiple additions of GN and CNTs exhibited better wear resistance, with up to 93% wear rate reduction as compared to the monolithic Al₂O₃. The improved wear resistance of the nanocomposites with the multiple additions of GN and CNTs was due to the micro-crack bridging and restriction to intergranular fracture that leads to pull-out of the matrix grains under sliding wear. Also, the combined crack pinning by the finely dispersed ZrO₂ particles, and bridging action of the GN and CNTs suggest a synergistic response of these multi-materials to the wear performance of the fabricated multi-material nanocomposites.

1. Introduction

Alumina-based structural ceramics are widely used in diverse engineering application fields such as the biomedical, aerospace and materials research industries. The availability of raw materials coupled with other attractive mechanical properties such as high refractoriness, high hardness, good chemical stability, good thermal and electrical insulation make this advanced ceramic ideal for these applications. The major setback of ceramic alumina however is its brittle nature, which tends to limit several high-performance applications [1–4]. Efforts made to overcome this flaw and develop advanced alumina with superior physical and mechanical properties over the years have involved the addition

of second-phase materials to the alumina matrix. Most commonly known ones include graphene, carbon nanotubes and zirconia, silicon carbide, titanium carbide [5–7]. Several researchers have reported that these second-phase materials have provided improved toughness, and other mechanical properties. Individually, these additives act as interfacial particles within the alumina matrix and provide appreciable toughness to the matrix [4,8]. In addition, there is a significant amount of grain refinement of the overall microstructure by these additives when homogeneously dispersed within the matrix phase which results in the improved mechanical properties in accordance with the Hall-Petch theory [9–11].

The addition of carbon-based materials such as graphene and carbon

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nanotubes have been used recently to reinforce alumina matrix [5,8]. Exceptional properties of two-dimensional graphene including high stiffness (~ 1 TPa) and strength (up to 130GPa), good flexibility, low density, higher electrical and thermal conductivity and higher surface area (~ 2600 m²/g) make it a potential nanofiller for producing tough, wear resistant and electrically conductive alumina composites for industrial applications [8,12–15]. Carbon nanotubes, which are one-dimensional (1-D) rolled graphene sheets, also exhibit combined physical and mechanical properties such as high aspect ratio (length/diameter aspect ratios of about 1250–3750 is typical for MWCNT), tensile strength (20–100GPa), high thermal (>3000 W/mK) and electrical ($>10^5$ S/m) conductivity, and high Young's modulus (up to 1000GPa), which present significant toughening in ceramic structures [16–20]. In the last decades, the addition of these nano-scale additives in alumina-based composites has become an interesting field due to their effect on the matrix grain structure and the enhanced mechanical properties generated. For example, reports have shown that the addition of low content of carbon nanotubes (<2 wt%) results in fine-grained structure with improved mechanical properties [21,22]. It is also perceived that the addition of certain amounts of graphene (less than 1.0 wt%) refines the matrix grain structure and improves the wear resistance and mechanical properties [11]. In both carbon-based systems, a carbon-rich tribofilm formed from the wear-induced action increases the wear response by acting as a lubricant to protect the contacting surfaces. This is also accustomed to the exceptional lubricating properties of graphite which merits these carbon-based composites with high wear resistance [23]. Yazdani et al. added 0.5 wt% of graphene to alumina matrix and achieved about 75% increase in the wear rate with a 23% decrease in the friction coefficient. This was due to the formation of a smooth tribofilm on the worn surface which decreased the friction between contact bodies when the low content graphene was added [24]. Winarto et al. also used a cold spray process on Al–Si surface to fabricate alumina-CNT nanocomposites and recorded an improvement in both hardness and wear properties with the addition of 2 wt% CNTs. Uniform distribution of the CNT particles with increased load-bearing capacity contributed to the enhanced mechanical properties [25]. Gutierrez-Gonzalez et al. also reported about half the wear rate and $\sim 10\%$ decline in the coefficient of friction of alumina-graphene composite, as compared to the parent alumina under similar reciprocating wear testing conditions when 0.22 wt% added to the matrix. This was ascribed to the presence of a self-lubricating layer of the embedded graphene platelets that provided sufficient lubrication in the alumina-graphene composite [26].

Contrary to the improvements in mechanical and wear properties by the additions of these nanofillers to a ceramic matrix, other studies have also shown that the individual additions result in the depletion of the properties. The decline in both the physical and mechanical properties are mainly due to the problems with homogeneous dispersion of the individual nano-scale additives and their interfacial bonding with the matrix [27,28]. For instance, the Van der Waals forces and large specific surface area of graphene nanoplatelets (GNPs) lead to inhomogeneity in the dispersion by promoting agglomeration and limiting matrix-graphene interface bonding [29]. Agglomeration of carbon nanotubes and graphene in the reinforced nanostructures also limits their effect on matrix grain refinement, weakens bond formation and hamper sintering activities to produce denser structured composites [29,30]. In addition, graphene re-stacking which is caused by the strong sheet-to-sheet Van Der Waals interactions tend to limit the inter-sheet contact area and results in small gaps between sheets. This phenomenon reduces the active surface properties of graphene and consequently lead to pore formation in the composite [31,32]. Bernal et al. reported about 40% decrease in the fracture toughness of Al₂O₃-CNT composite with 0.1 wt % synthesized via Spark Plasma Sintering (SPS). Agglomeration of the CNTs, increased grain size and weak interfacial bonding accounted for the decline in the fracture toughness [33]. Wang et al also claimed a

comparable fracture toughness value of alumina/CNT composite with the brittle monolithic alumina, when reinforced with 10 vol% CNTs [34]. In the work of Ruthowski et al., adding graphene content of more than 2 wt% increases the material wear rates, which was ascribed to the graphene removal process and filling of voids by the wearing off of fine silicon nitride particles on the track after the friction test [35]. Therefore, it is clear that the addition of single-phase carbon-based additives (having various amounts) to the alumina matrix still presents challenges that need further studies.

Alumina-zirconia composites have also been commercially produced as an advanced structural ceramic material by the uniform dispersion of ZrO₂ particles within the alumina matrix. Mechanical properties such as fracture toughness and flexural strength of alumina have been reported to show improvement with optimized addition of fine ZrO₂ particles. The relatively superior toughness of alumina-zirconia have been attributed to the tetragonal to monoclinic (t-m) phase transformation of ZrO₂ and refined alumina structure by the ZrO₂ particles existing between triple-point grain junctions of the alumina matrix [36–38]. In the work of Trabelsi et al., ZrO₂ content up to 10 vol% registered the highest fracture toughness value in the zirconia toughened alumina composite. This was due to the distribution of the metastable ZrO₂ particles in the alumina matrix leading to the toughening by a stress-induced phase transformation [39]. Kerkwijk et al. also produced a dense, fine-grained alumina-zirconia ceramic composites using a colloidal process and having 89 vol% Al₂O₃ and 11vol%ZrO₂. An increment of more than 3 orders in the wear resistance and a low coefficient of friction were recorded and attributed to the homogenous dispersion of the ZrO₂ phase in Al₂O₃ and the overall higher toughness as compared to the monolithic Al₂O₃ [40]. Despite these reports on the enhancement of mechanical properties of alumina-zirconia systems, there have been substantial efforts in recent years to improve their hardness and tribological behaviour, which are often found to be less than or comparable to the monolithic alumina [41,42]. The homogeneous distribution of ZrO₂ particles (which has a relative lower hardness), as well as the presence of micro-pores and micro-cracks have been known to account for the depletion in wear resistance and hardness properties of alumina-zirconia composites [39,43–45].

Currently, extensive studies to optimize the overall mechanical properties of alumina and other ceramic-based composites through microstructural design have led to the onset of hybrid nanocomposites. These nanocomposites are formed by carefully dispersing two or more reinforcement phases into the matrix structure to achieve relatively superior mechanical properties. The motive is to effectively combine two or more nanometer-sized second-phase particles such as graphene and CNTs within the matrix structure, with the aim to explore the complementary properties of one reinforcement with the addition of the other, and achieve a higher performance by enhancing dispersion and providing a synergistic effect of the hybrid nanofillers [46]. For example, it is perceived that the high agglomeration of CNTs within the matrix can be countered with the wrapping action of uniformly dispersed graphene nano-particles [47]. Moreover, the re-stacking challenges of 2D graphene sheets that leads to porosity and reduces interfacial activities within the matrix can be reduced with the presence of 1D CNTs. In a typical graphene-carbon nanotube hybrid reinforcement system, it is also believed that the CNTs are able to occupy the graphene inter-sheet gaps caused by the re-stacking effect, and enhance the surface activity of the graphene and interfacial bonding of the matrix when they are uniformly dispersed [48,49]. This suggests that there may be a synergistic role of both carbon nanotubes and graphene in monolithic structures. This has motivated more studies into hybrid multi-material reinforcements of monolithic ceramics such as alumina.

Hybrid multi-material nanocomposites therefore have the potential to provide an enormous enhancement in mechanical response relative to a single-phase reinforced nanocomposite. However, there is still the

Table 1
Summary of fabricated hybrid multi-material nanocomposites.

Composition	Sample (A_{x-y-z})	Relative density (%)
Pure Alumina (Aa)	A ₀₋₀₋₀	99.08
Aa+10wt%ZrO ₂	A ₁₀₋₀₋₀	95.43
Aa+10wt%ZrO ₂ + 0.5wt%Gn	A _{10-0.5-0}	98.48
Aa+10wt%ZrO ₂ + 2wt%CNT	A ₁₀₋₀₋₂	97.42
Aa+10wt%ZrO ₂ + 0.5wt%Gn + 2wt%CNT	A _{10-0.5-2}	97.82

NB: For notation A_{x-y-z} , x represents wt% of ZrO₂, y represents wt% of Graphene and z represents wt% of CNTs.

need to understand the synergistic effect of multi-material additions on the microstructure, mechanical and tribological properties of ceramic-based nanocomposites, in order to tailor them for high-performance structural applications. Hence, in this work, an attempt has been made to fabricate Al₂O₃ based-hybrid nanocomposites reinforced with multiple combinations of ZrO₂, GN and CNT using colloidal mixing followed by hot-pressing. The synergistic effect of the homogeneously dispersed multi-material reinforcements on the microstructural evolution, as well as their influence on wear behaviour and mechanisms on alumina matrix nanocomposites will be discussed in detail.

2. Experimental Procedure

2.1. Nanocomposite Fabrication

Commercially made nanopowders of α -Al₂O₃ having average diameter $\sim$ 50 nm and ZrO₂ having average particle size $<$ 80 nm were procured from Sigma Aldrich, UK. Carbon nanotubes (Multi-walled) with length 15 μ m and diameter about 50 nm were also obtained from MK Imprex, Canada. To enhance interfacial bonding and remove impurities, the CNTs were functionalized by treating in acidic solution. Detailed characterization of the treated CNTs are discussed elsewhere [45]. The CNTs were suspended and continuously dispersed in distilled water as detailed in the previous studies [45]. Meanwhile, processed graphene with concentration of 0.5 wt% was homogeneously dispersed in a separate bath using an ultrasonic, as described in previous works [50,51]. Characterization of the processed graphene particles is previously discussed in earlier studies [52]. 10 wt% of ZrO₂ and Al₂O₃ were uniformly mixed via a colloidal process to form a slurry and added to both the 2wt%CNT and 0.5wt%Gn. These mixtures were continuously stirred followed by drying at a temperature of 120°C. Milling and final consolidation of dried powders with compositions described in Table 1 was carried out in a graphite die at a pressure of 60 MPa followed by hot-pressing for 60 min under Ar atmosphere, as discussed in other works [50,53,54]. Fabricated nanocomposites had rectangular dimensions of about 50 mm $\times$ 40 mm $\times$ 2 mm.

2.2. Density Measurement and Microstructural Analysis

Table 1 illustrates the summary of densified hot-pressed multi-material nanocomposites which were grouped with respect to their reinforcement compositions. Thus, for samples designated with A_{x-y-z} , the x, y and z represent the concentration (wt%) of ZrO₂, Graphene and Carbon Nanotube constituents respectively. Bulk densities of the prepared nanocomposites were determined using the Archimedes method, with distilled water as the medium of immersion. Relative density values were then estimated by dividing the measured density by the theoretical density. Rule of mixture was used to calculate the theoretical densities using literature density values of 3.97gcm⁻³, 5.87gcm⁻³, 2.21gcm⁻³ and 1.85gcm⁻³ for monolithic Al₂O₃, ZrO₂, Graphene(GN) and Carbon Nanotubes (CNTs) respectively [47,55].

Microstructural analysis was also carried out on the samples to

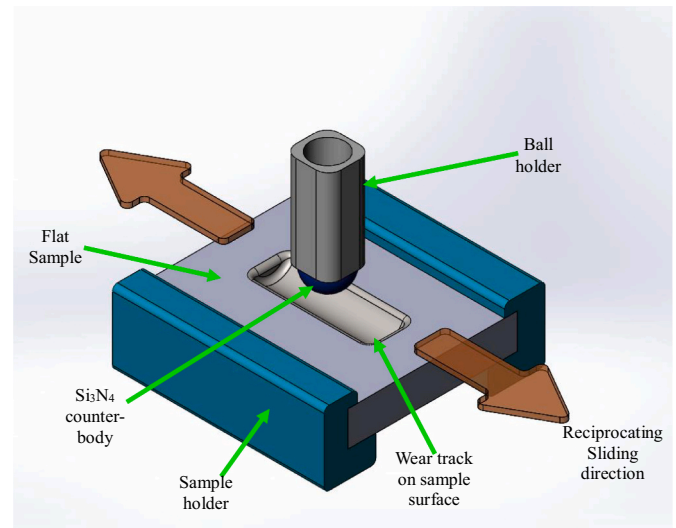


Fig. 1. Illustration of ball-on-flat reciprocating sliding wear test.

determine the morphological and microstructural features of the sintered nanocomposites. Samples for the microstructural characterization were first ground with SiC paper (in the order: 400; 600; 800 and 1200 grit size) and then polished up to 0.05 μ m to obtain a mirror finish with a diamond suspension. A field emission scanning electron microscope (FE-SEM, Quanta 3D) operating at a voltage of 20 kV used to assess the microstructure. The distribution of the added ZrO₂ samples were also determined using a backscattered electron imaging mode (BSE) in a thermionic emission SEM (TESCAN VEGA 3) coupled with an EDS detector. The grain size distribution of the processed multi-material nanocomposites was quantitatively estimated using the FE-SEM micrographs, in conjunction with image J software, according to the ASTM E112–13.

2.3. Surface Properties and Tribological Measurements

Three-dimensional (3D) surface roughness of each polished samples was measured prior to wear test using a non-contact optical profilometer (Bruker Contour GT Optical profilometer). A $\times$ 5 magnification lens was used for each sample with a scan size of 0.721 mm $\times$ 0.961 mm determined by the optical system. Surface roughness (S_a) of each nanocomposite was estimated in accordance with the ISO 25178 standard. An average of ten separate measurements was used as the surface roughness value for each sample.

Fig. 1 illustrates a schematic of the ball-on-flat reciprocating wear of a spherical counter-surface and flat specimen. The linear reciprocating wear test was carried out using the Universal Mechanical Tester (UMT) Tribolab (Bruker Tribometer, Canada) and in accordance with the ASTM G133-15 [56]. A hard silicon nitride (Si₃N₄) ball with diameter of 9.525 mm was used as the countersurface against the flat Al₂O₃ nanocomposites. This ceramic-on-ceramic tribo-system was selected due to their proposed applications in orthopedics for hip and knee replacements [57]. Rectangular samples with dimensions 15 $\times$ 10 $\times$ 2 mm were sectioned from the bulk fabricated nanocomposites using the diamond wire-saw. Both the counter-body and samples were thoroughly cleaned with ethanol and dried at room temperature. The ball was then secured in the Tribolab system equipped with a 100 N load cell. The flat samples were secured in a metal holder and fixed on an oscillating plate which is meant to slide against the stationary counter-ball. The ball was gently pushed against the flat polished samples with a constant applied normal load of 25 N. The samples slide against the ball in a linear

Table 2

Mechanical and wear properties of multi-material nanocomposites.

Sample	Vickers micro-hardness (Hvn)	Wear volume (mm ³)	Wear rate(mm ³ /nm)
A ₀₋₀₋₀	1875±38	0.3740	1.4961×10 ⁻⁴
A ₁₀₋₀₋₀	1409±77	0.0320	1.2792×10 ⁻⁵
A _{10-0.5-0}	1916±84	0.0436	1.7443×10 ⁻⁵
0			
A ₁₀₋₀₋₂	2071±62	0.0302	1.2078×10 ⁻⁵
A _{10-0.5-2}	2775±117	0.0252	1.0067×10 ⁻⁵
2			

reciprocating manner and at a frequency of 5 Hz which represents a sliding velocity of 100 mm/s. A stroke length of 10 mm was predetermined for the wear test for a duration of 16.40 min. The set frequency (5 Hz) and duration (1000s) of the wear test simulate a total of 5000 cycles for a stroke length of 10 mm. The coefficient of friction (COF) and frictional forces were determined from the tribometer at every 0.01 s during the test operations. The tests were performed under dry sliding contact conditions at ambient temperature and at a relative humidity of 40–60%. Three separate tests were done for each sample and on unworn regions of the polished flat surface. The mean coefficient of friction was estimated for all the 3 tests. The texture and topography of the worn regions and the generated wear debris were critically assessed using the FE-SEM. The mode of wear of the nanocomposites during sliding action of the contacting surfaces was also analysed.

For volume loss and wear rate calculations, the worn surface was first cleaned thoroughly by blowing dry air to remove loose worn-out or tribomaterials which would otherwise interfere with wear track depth and width measurements. This was followed by a quick cleaning using solvents such as acetone, and later dried with ethanol. This was done to ensure accurate measurement of the actual wear depth and width of the worn region. The 2D profile and 3D map of the wear tracks were generated using the optical profilometer, in order to determine the wear track width and depth, as recommended by the ASTM G133 after a typical reciprocating-on-flat sliding test [56]. These were used to estimate the volume loss and wear rate of the nanocomposites according to the equation below:

$$W_{rate} = \frac{V_f}{F \times D} \quad (1)$$

where V_f is the wear volume calculated from the product of stroke length (mm), and average cross-sectional area of the wear profile (wear width × depth, mm²) [56], F is the applied load (N) and D is the total sliding distance (m).

Finally, the wear scar generated on the Si₃N₄ counter-ball after constant interaction with the flat samples were also inspected after the experiment. The ball was thoroughly cleaned after each test using acetone followed by drying with ethanol. The scratched surface was then visualized using the optical microscope to detect possible wear scratches on counter-ball surface.

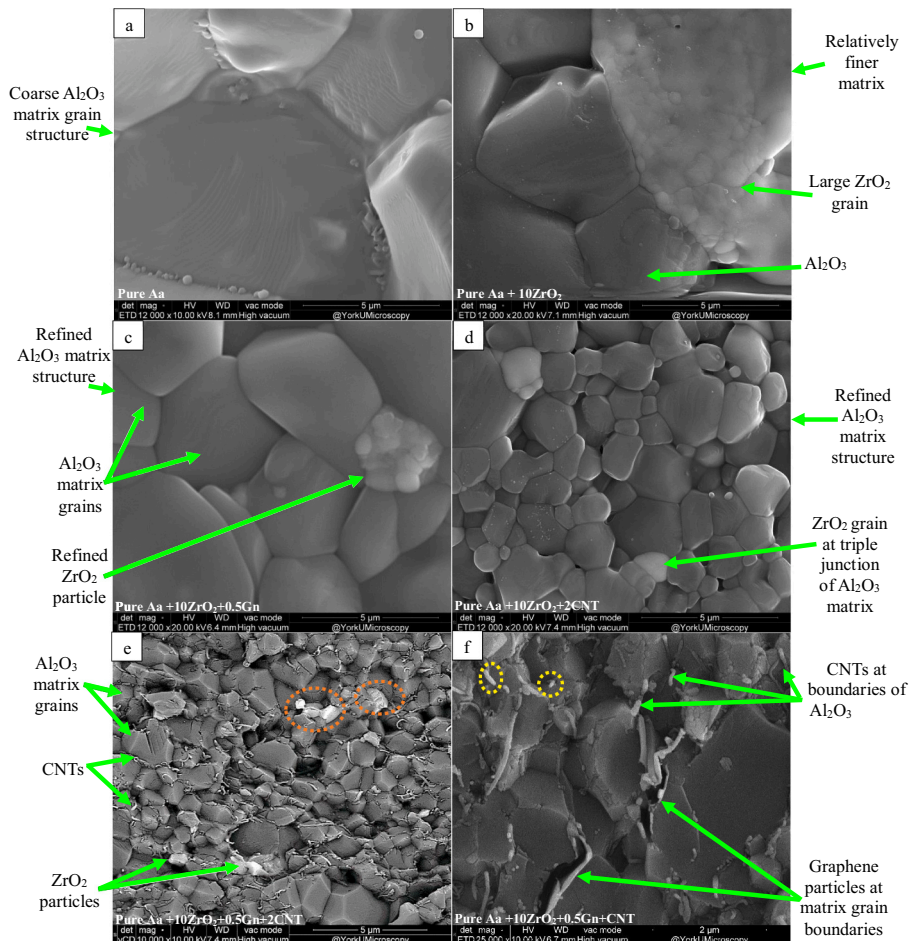


Fig. 2. FE-SEM micrographs of sintered nanocomposites before wear test (a) Pure Al₂O₃ (b) Al₂O₃-10ZrO₂ (c) Al₂O₃-10ZrO₂-0.5Gn (d) Al₂O₃-10ZrO₂-2CNT (e) Al₂O₃-10ZrO₂-0.5Gn-2CNT with distribution of CNTs and ZrO₂ particles (f) Al₂O₃-10ZrO₂-0.5Gn-2CNT with distribution of GN and CNTs.

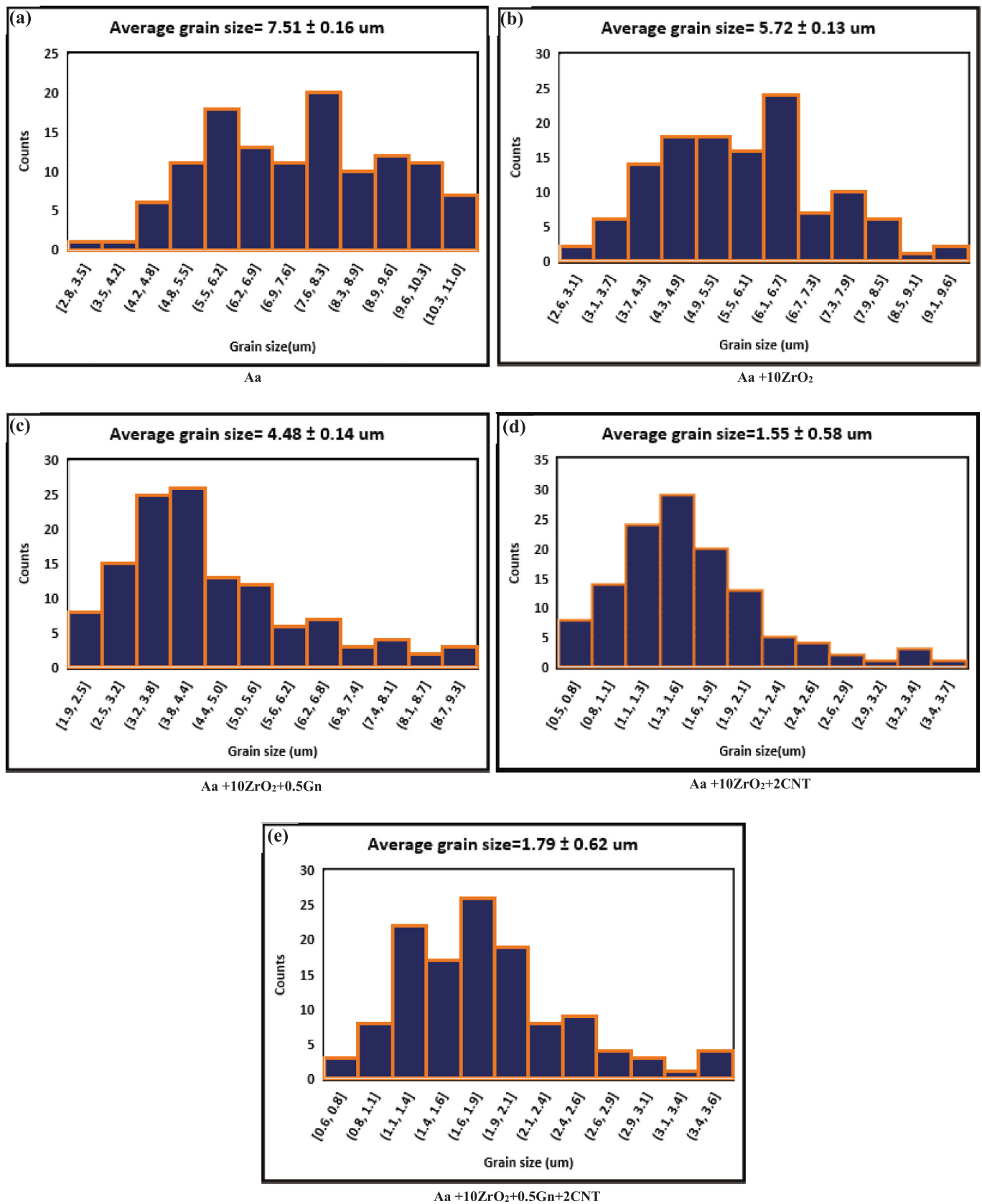


Fig. 3. (a)-(e) Sample SEM and histogram showing grain size distribution of nanocomposites (f) variation of the Al_2O_3 matrix and ZrO_2 grain size as a function of the multi-material additions.

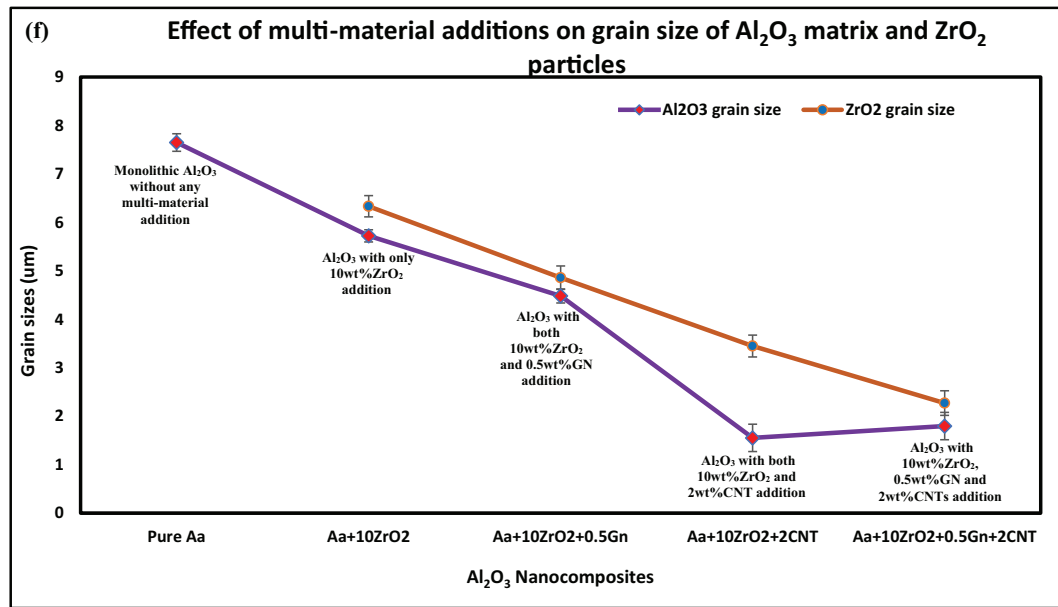


Fig. 3. (continued).

2.4. Vickers Hardness Measurement

The microhardness of the nanocomposites at room temperature were also determined using a Vickers microhardness tester (METLAB, Canada) prior to the wear tests. An indenter with a pointed diamond pyramid and a square base was used to impact the sample surface. The sample was secured firmly in the hardness tester to prevent rocking and shifting during the measurements. The indenter was gently pressed on the flat sample surface at a selected load of 1 kgf (9.807 N) and a dwell time of 15 s, as outlined in the ASTM C1327–15. The mean diagonal lengths of the resulting indentation were measured with the aid of an optical microscope coupled to the hardness tester. The Vickers hardness number (HVn) was computed for each nanocomposite using Eq. (1) given below [58]:

$$HVn = \left(0.102 \times 1.8544 \right) \left(\frac{P}{d^2} \right) \quad (2)$$

where P is the load applied in N and d is the mean length of the two diagonals after indentation, in mm . The final harness number was estimated from the average of ten separate indentations on the sample surface. Each indentation was made from a significant distance apart in order to ensure accuracy. Table 2 illustrates the hardness results of the fabricated nanocomposites with different compositions.

3. Results

3.1. Microstructural Evolution of Fabricated Multi-material Nanocomposites

Basic characteristics and chemical composition of the prepared multi-material nanocomposites are summarized in Table 1. From the Table, it shows that all the hot-pressed nanocomposites had densities above 95% of the theoretical value, but lower than that of the reference Al₂O₃ sample, which had a near dense-structure (~99%). The incorporation of reinforcement particles such as ZrO₂, GN and CNTs tend to slightly decrease the density after the high temperature sintering. Sample A₁₀₋₀₋₀ with only 10wt%ZrO₂ addition was about

4% lower in density when compared with the theoretical density of the monolithic Al₂O₃. However, samples A_{10-0.5-0}, A₁₀₋₀₋₂ and A_{10-0.5-2} with multiple additions of ZrO₂-GN, ZrO₂-CNTs and ZrO₂-GN-CNTs had comparable density values (~98%) after sintering, registering approximately 1% decrease in density relative to the fabricated monolithic Al₂O₃.

Fig. 2 shows a high-magnification FE-SEM of the nanocomposites which illustrates the effect of the multi-material additions on the grain morphology, grain sizes and microstructural features of the nanocomposites. The microstructure and grain size of the reference Al₂O₃ and Al₂O₃-10wt%ZrO₂ have been previously studied in other works [50,51,53]. The grain size distribution with the corresponding average grain sizes of the fabricated multi-material nanocomposites, estimated from the quantitative analysis of the FE-SEM micrographs is clearly shown in Fig. 3. Generally, the reference Al₂O₃ which had no added second-phase material (sample A₀₋₀₋₀) depicted a coarse-matrix grain structure after hot-pressing (Fig. 2(a)). However, it can also be observed from Figs. 2(b-e) and 3 that the addition of the second-phase materials resulted in a reduced grain-sized microstructure as compared to the reference Al₂O₃ structure. Sample A₁₀₋₀₋₀ which had only 10wt%ZrO₂ addition exhibited about 25% reduction in the Al₂O₃ matrix grain size relative to the reference monolithic Al₂O₃ sample. The added ZrO₂ particles were insoluble within the matrix and were seen as coarse grain structures at the matrix boundaries within this sample (Fig. 2(b)). In Fig. 2(c), it is seen that the multiple additions of both 10wt%ZrO₂ and 0.5 wt% GN (Sample A_{10-0.5-0}) resulted in about 41% decrease in the grain size of the Al₂O₃ matrix and 23% reduction in the ZrO₂ grain size. Typically, the added GN particles also appear insoluble and reside on the grain boundaries of the matrix [46,47]. Most ZrO₂ particles were also located between the matrix grain boundaries and within its grains. A drastic reduction of the Al₂O₃ matrix grains is also depicted with the incorporation of both 10wt%ZrO₂ and 2wt%CNTs in the A₁₀₋₀₋₂ sample, as seen in Figs. 2(d). There was approximately 80% reduction in the Al₂O₃ matrix grain size, coupled with about 46% decrease in the size of the added ZrO₂ grains (Figs. 3(d) and (f)). Meanwhile, a refined structure of sample A_{10-0.5-2}, which had the multi-material additions of 10wt %ZrO₂, 0.5wt%GN and 2wt%CNTs is also demonstrated in Fig. 2(e). The

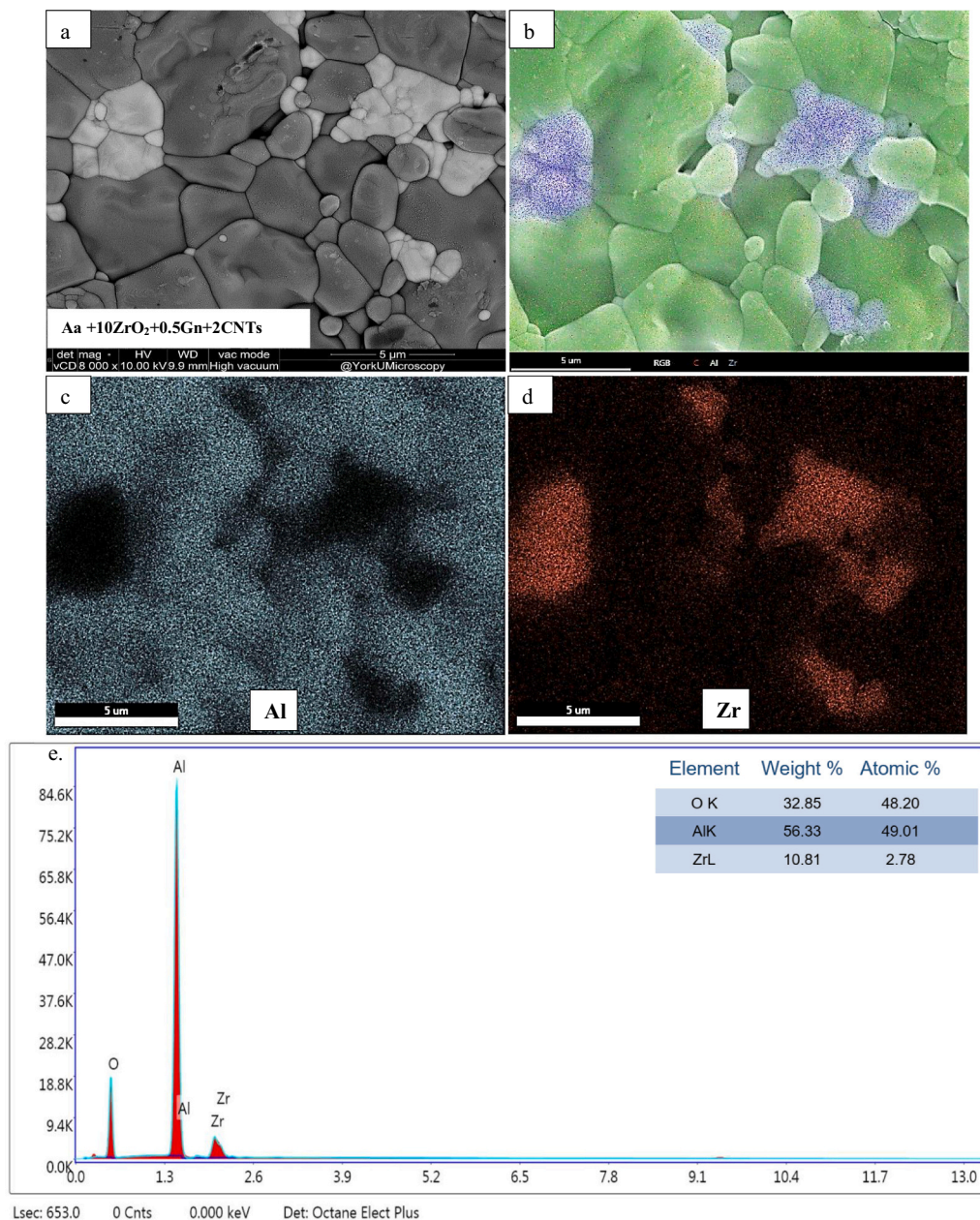


Fig. 4. EDS elemental mapping of Al_2O_3 -10wt% ZrO_2 -0.5Gn-2CNTs sample identifying the presence of ZrO_2 particles (a) FE-SEM micrograph of sample (b) overall mapped data (c) EDS mapping of element Al (d) EDS mapping showing Zr elements and ZrO_2 distribution within the Al_2O_3 matrix (e) EDS spectrum of element distribution with quantitative results of elements.

Al_2O_3 matrix grain size in this sample was reduced by about 77%, with a corresponding 64% decline in the insoluble ZrO_2 grain size, as illustrated in Figs. 3(e) and 3(f). This suggests that the addition of 2wt% CNTs is more effective in the extensive refinement of the Al_2O_3 matrix grains than the 0.5wt% GN. On the other hand, adding both 2wt% CNT and 0.5wt% GN results in significant refinement of both Al_2O_3 matrix and ZrO_2 grains than the 0.5wt% GN addition. The distribution of the GN and CNT particles within the Al_2O_3 matrix are also seen in Fig. 2(e-f).

The EDS mapping in Fig. 4 identifies the ZrO_2 particles in a typical multi-material nanocomposite such as the $\text{Al}_{10-0.5-2}$ sample. A good contrast between the matrix (grey background) and the ZrO_2 particle dispersions (white particles) is also indicated in Fig. 4. Fig. 5(a-d) illustrates the variations of the size and spatial distributions of the ZrO_2

particles with the addition of GN and CNTs. It is generally observed that some regions had uniform distribution of fine ZrO_2 particles whilst other regions revealed agglomeration the added ZrO_2 particles forming large chunks within the Al_2O_3 matrix. The BSE micrographs also reveal dark regions in the nanocomposites which indicates the presence of micropores in the structure after sintering. These pore sizes and distributions were also reduced with the addition of both 0.5wt% GN and 2wt% CNTs.

3.2. Hardness Property

Table 2 summarizes the micro-hardness property of the hot-pressed nanocomposites. The variation of the Vickers micro-hardness number (HVn) as a function of the added second-phase particles is clearly shown.

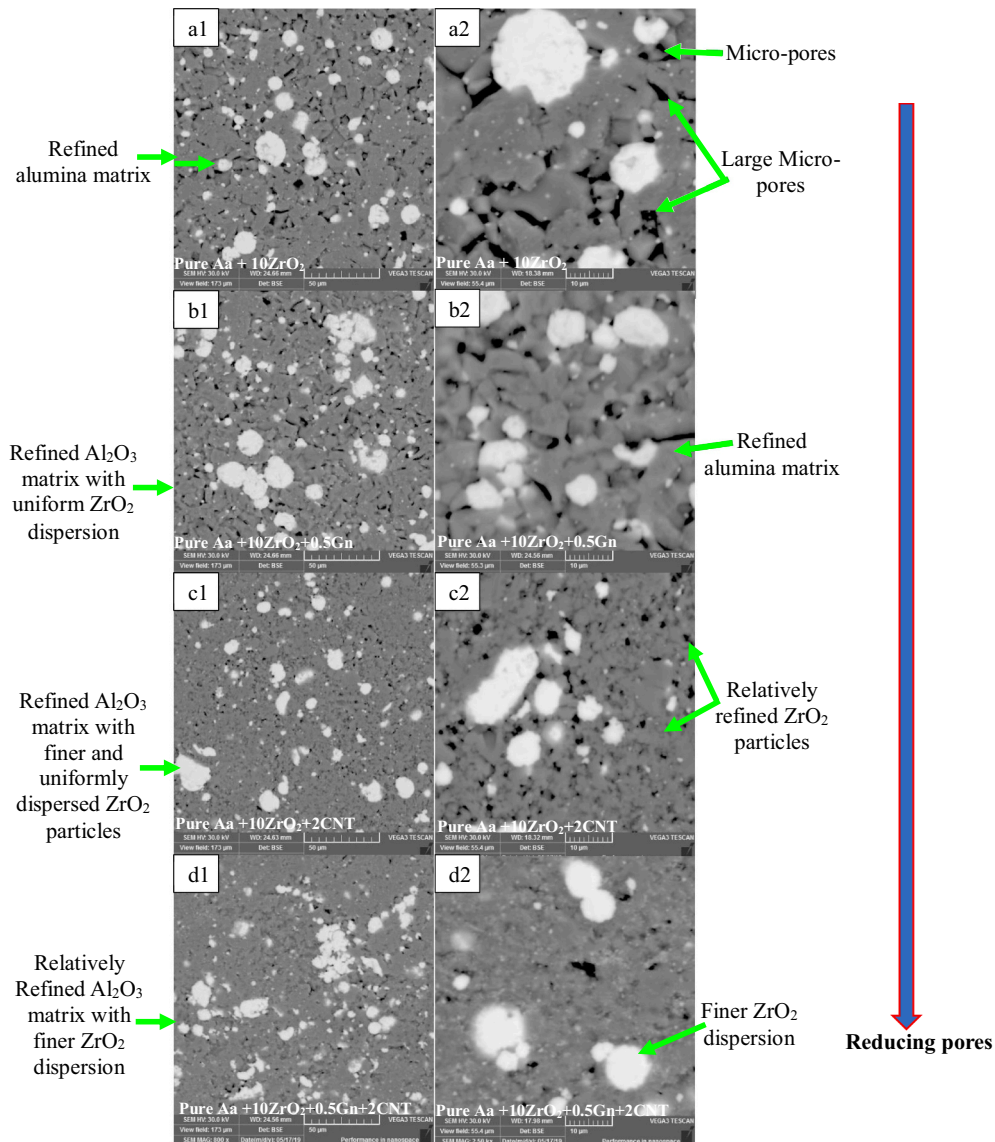


Fig. 5. BSE-SEM micrographs of as-sintered samples showing distribution of ZrO_2 precipitates and micropores (a) Al_2O_3 -10 ZrO_2 (b) Al_2O_3 -10 ZrO_2 -0.5Gn (c) Al_2O_3 -10 ZrO_2 -2Cn (d) Al_2O_3 -10 ZrO_2 -0.5Gn-2Cn.

It was observed that the addition of 10wt% ZrO_2 alone to monolithic Al_2O_3 decreased the hardness number of the A_{10-0-0} sample from 1875 to 1409, representing approximately 25% decline in the hardness of the A_{10-0-0} sample, despite the reported 25% reduction of the Al_2O_3 matrix grain size. Even though the addition of 0.5wt%GN yielded about 41% reduction in the matrix grain size and 23% decrease in the ZrO_2 grains, it resulted in only 2% increase in the hardness. In addition, the 2wt%CNTs addition which gave an extensive grain refinement of the matrix with 80% decrease in matrix grain size and 46% decrease in ZrO_2 grains, revealed only 11% increase in the hardness of the A_{10-0-2} sample. Nevertheless, the incorporation of both 0.5wt%GN and 2wt%CNTs to the matrix which resulted in 77% decrease in Al_2O_3 matrix grains and 64% reduction in the ZrO_2 grains gave an appreciable 48% increase in the hardness of the $\text{A}_{10-0.5-2}$ sample. This means that a combination of 0.5wt%GN and 2wt%CNTs refine the grain structures of both the matrix and ZrO_2 , and result in a significant increase in the hardness property of

the monolithic Al_2O_3 .

3.3. Wear Results

Fig. 6 demonstrates the effect of the additives on the surface roughness of each nanocomposites. Surface roughness (S_a) per the scan area ranges from 77.6–22.4 nm. The tribological performance of the hot-pressed nanocomposites under dry reciprocating sliding wear conditions is also illustrated in Table 2 and Figs. 7–13. Fig. 7 also summarizes the variation of the coefficient of friction (COF) and wear properties of the fabricated nanocomposites as a function of the reinforcing phases used, under constant loading of 25 N. It is observed in Fig. 7(a) that the least COF value (~76% reduction relative to the monolithic Al_2O_3) is depicted by the A_{10-0-0} sample which had only 10wt % ZrO_2 addition. The addition of the carbon-based materials increased the COF values for samples $\text{A}_{10-0.5-0}$, A_{10-0-2} and $\text{A}_{10-0.5-2}$, up to about

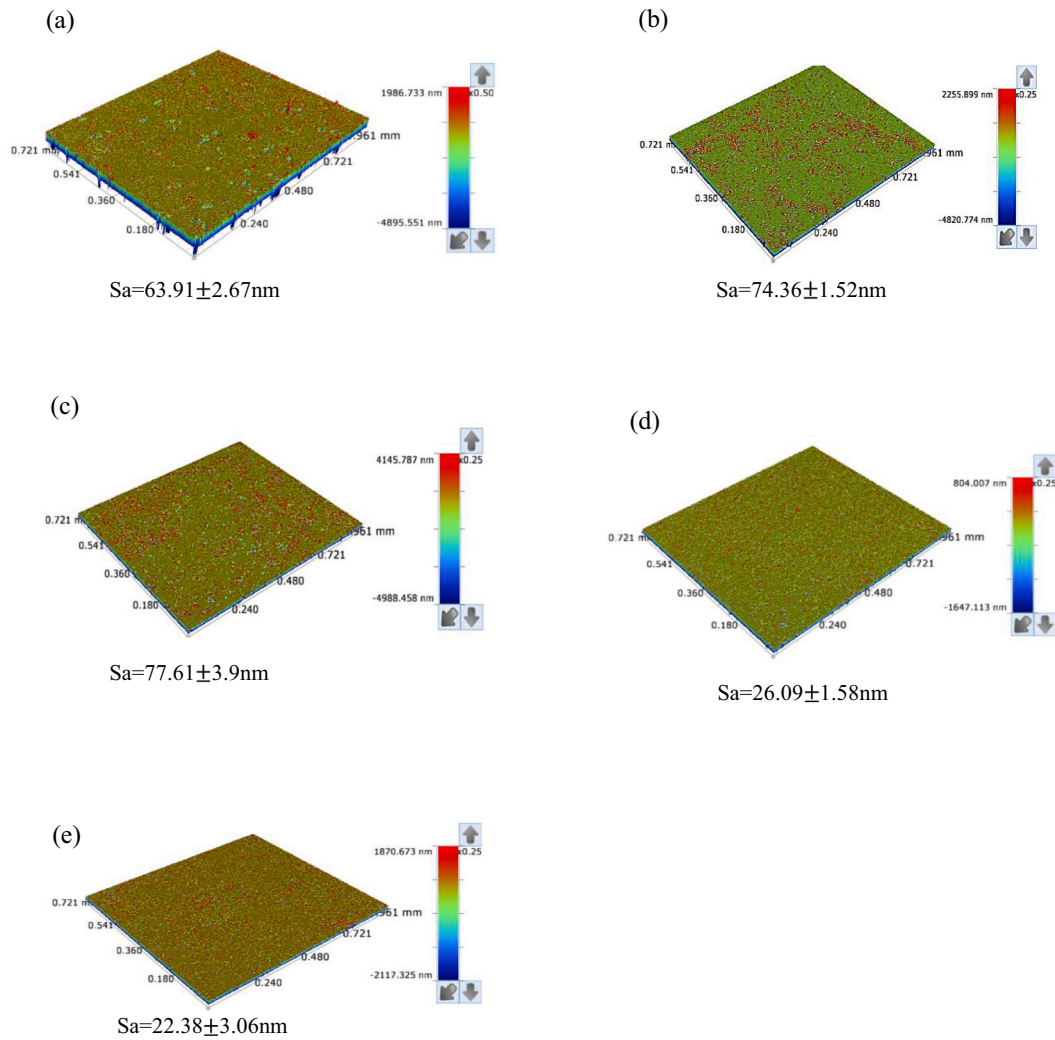


Fig. 6. 3D surface texture measurement of samples using the optical profilometer (a) Pure Al_2O_3 (b) Al_2O_3 -10ZrO₂ (c) Al_2O_3 -10ZrO₂-0.5Gn (d) Al_2O_3 -10ZrO₂-0.5Gn-2Cn

17% relative to the monolithic Al_2O_3 . The volume loss and corresponding wear rates of each nanocomposite after the constant dry sliding wear is also shown in Table 2. Fig. 7(b) illustrates the wear rate of the Al_2O_3 matrix with the different reinforcement particles. It is seen from Table 2 that the wear rate of the monolithic Al_2O_3 , recorded as $1.4961 \times 10^{-4} \text{ mm}^3/\text{Nm}$, is significantly reduced to $1.279 \times 10^{-5} \text{ mm}^3/\text{Nm}$ with the incorporation of only 10wt%ZrO₂, which represents about 91% decrease in sample A_{10-0-0} . Also, the addition of 0.5wt%GN in sample $\text{A}_{10-0.5-0}$ exhibited a better wear resistance than the reference monolithic Al_2O_3 , with approximately 88% decrease in the wear rate. Sample A_{10-0-2} , having 2wt%CNTs addition also displayed an improved wear performance, with about 92% reduction in the wear rates relative to the monolithic Al_2O_3 but comparable to the A_{10-0-0} sample having only 10wt%ZrO₂. The multi-material additions of ZrO₂, GN and CNTs into the Al_2O_3 matrix also resulted in a relative high wear resistance of the $\text{A}_{10-0.5-2}$ sample, with about 93% decline in the wear rate. It is noteworthy that the addition of 10wt%ZrO₂ alone to the Al_2O_3 matrix showed a comparable wear resistance improvement relative to the combination of ZrO₂, GN and CNTs (88% vs 93%). This suggests that a combined effect of the multi-material addition is only slightly demonstrated on wear performance of the nanocomposites.

Fig. 8 shows the SEM image and 3D surface profile of the wear track of the reference monolithic Al_2O_3 sample under constant loading, showing the depth and width of the worn surface. The 3D profile also indicates the rough texture of the wear track and high-volume loss which corresponds with the values in Table 2. The 3D profiles of the nanocomposites after the wear test are also illustrated in Fig. 9, which shows the nature of their wear tracks. These profiles are consistent with the volume loss and the corresponding wear rates under the reciprocating dry sliding.

3.4. Microstructure After Wear

The effect of the multi-material additions of ZrO₂, GN and CNTs on the morphology and the microstructural features of the wear track is also analysed using the FE-SEM micrographs shown in Figs. 10–12. Both mild and severe abrasive wear, which is typical in oxide ceramics were observed from the texture of the worn surface of the nanocomposites. High contact pressure coupled with the relative sliding of the counterbody and the flat surface led to grain fracture and chippings within the worn surface. Areas of delamination and grooves as a consequence of the grain removal and fracture was also evident in the various worn

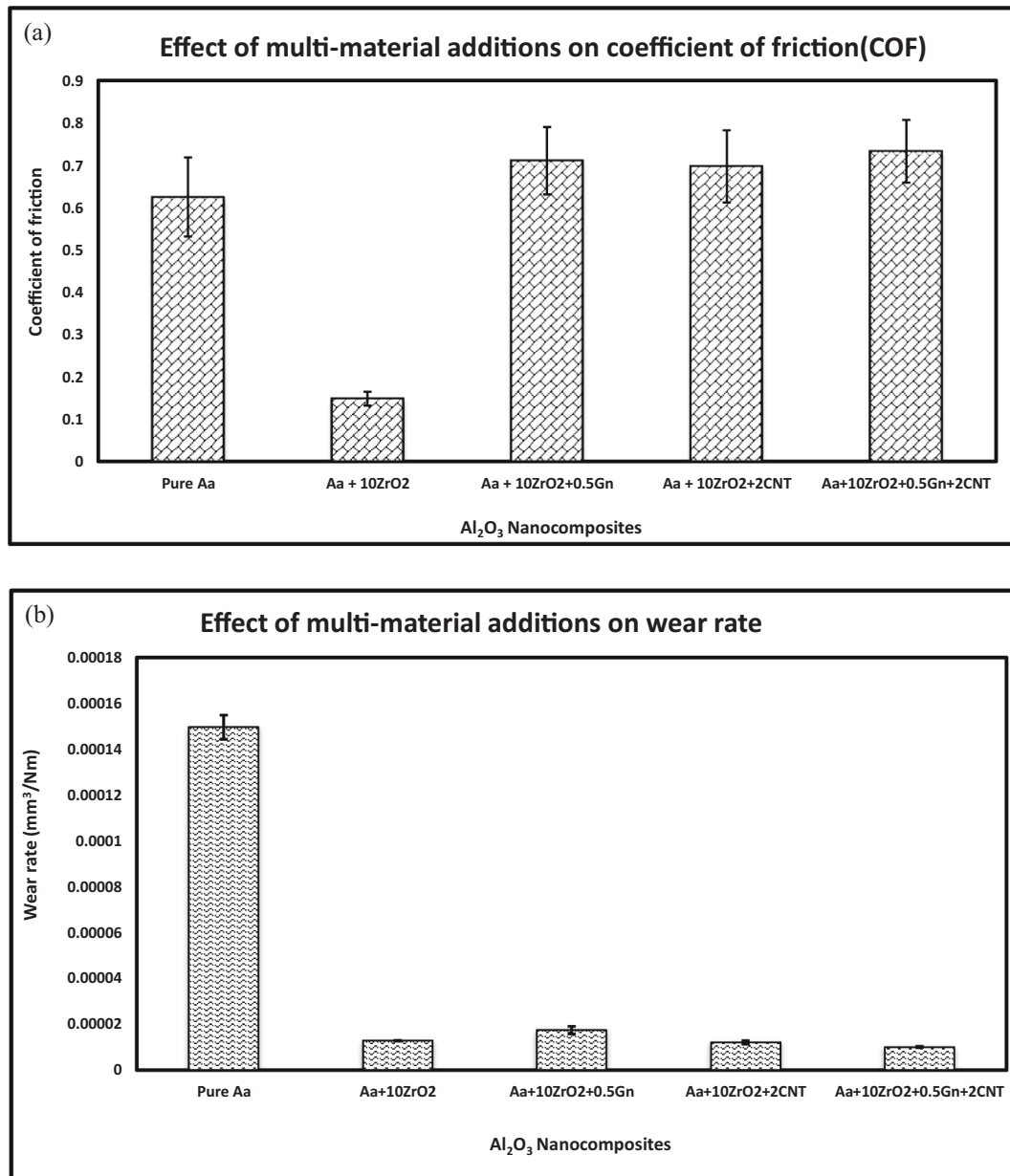


Fig. 7. Effect of the multi-material additions on (a) coefficient of friction (b) wear rate of nanocomposites.

regions. Micro-cracking of the matrix grains was the dominant sub-mechanism demonstrated in the worn regions of the nanocomposites. Fig. 10(a) illustrates the wear track of the pure Al₂O₃ sample, which had rougher profile with large areas of delaminations, which are very consistent with the 3D profile seen in Fig. 8. The wider and deeper grooves are evident of the large grain pull-out during the constant sliding of the hard Si₃N₄ counter-surface at load of 25 N. In addition, there were smaller fragments of the pulled-out grains which tend to fill the worn-out cavities and agglomerates within the wear track surface. The SEM micrograph showing the worn region of sample A₁₀₋₀₋₀, which had only 10wt%ZrO₂ depicts both smooth and rough regions with shallow depths, as seen in Fig. 10(b). In Fig. 10(c), there were multiple shallow grooves and smooth regions within the wear track of the A_{10-0.5-0} sample. In contrast, few large but shallow grooves were revealed by the wear track of the A₁₀₋₀₋₂ sample, which also had a lot of smooth sliding regions (Fig. 10(d)). For the A_{10-0.5-2} sample with the synergistic

addition of all the reinforcement materials, the wear track showed relatively few regions of pull-out grooves but large smooth areas after wear, in the direction of the counter-surface sliding (Fig. 10(e)). The nature of the matrix grain pull-outs, grooves and distribution of the ZrO₂ particles within the worn regions are more evident with the contrast imaging SEM micrographs as shown in Fig. 11. The smooth and rough regions are also seen more clearly in these micrographs. In addition, micro-cracks within the wear tracks are also seen mostly in the smooth areas of the wear track. Both coarse and very fine ZrO₂ particles were seen in the worn areas of these multi-material nanocomposites.

Various wear resistance mechanisms by the added second-phase materials to the matrix is demonstrated by Fig. 12. Micro-cracks generated during the continuous sliding were inhibited by the reinforcement particles as seen in the micrographs. Crack bridging and deflection is also observed in nanocomposites reinforced with either graphene or CNTs or both. Fig. 12(a) illustrates the pinning action of

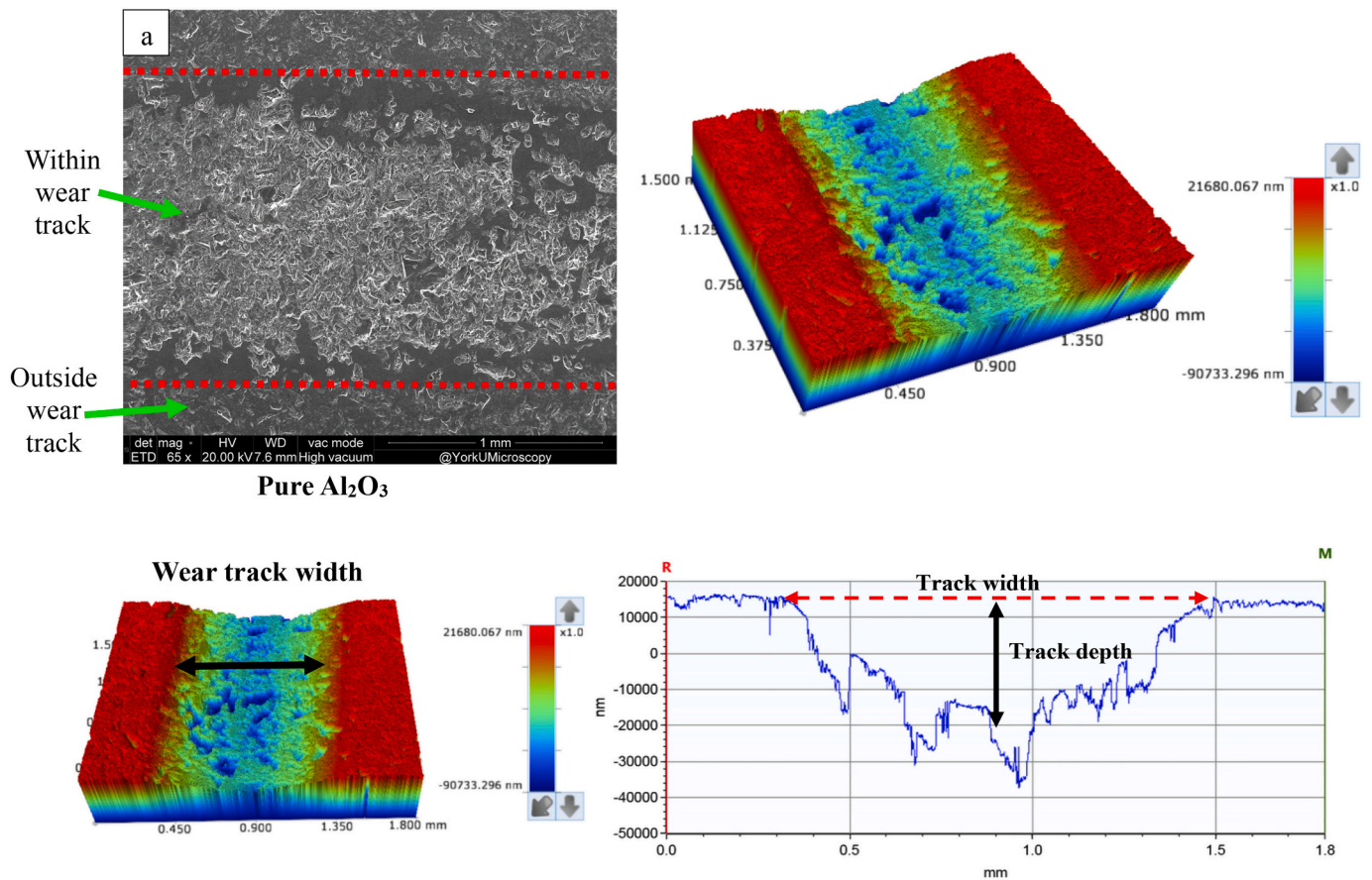


Fig. 8. 3D optical profilometry of monolithic Al₂O₃ after wear with wear track profile.

ZrO₂ particles within an observed micro-crack. Other areas of crack pinning and bridging are also seen within the worn surface of the A_{10-0.5-0} sample (Fig. 12(b)). Crack bridging which is more prevalent in nanocomposites with embedded carbon-nanotubes is demonstrated by Fig. 12(c). This mechanism is also observed in the worn region of the A_{10-0.5-2} sample having all 3 multi-materials embedded (Fig. 12(d)).

Fig. 13 shows optical micrographs of the Si₃N₄ counter-ball with mild wear scars after 5000 cycles of reciprocating sliding on the flat nanocomposite samples. In contrast to the fabricated nanocomposites, the countersurface did not undergo significant wear after relative dry sliding with the flat samples. However, the circumference of the contact region shows appearances of wear scratches which is due to the continuous abrasive sliding on the nanocomposite surface.

3.5. Wear Debris Analysis

The nature of wear of the hot-pressed nanocomposites can also be analysed with the appearance of the wear debris during the reciprocating sliding wear test. Fig. 14 depicts the dispersion of the wear debris collected after the reciprocating sliding test for each sample. As shown in Fig. 12(a), the wear behaviour of the reference Al₂O₃ sample is coupled with large chippings of matrix grains and small fragments from the continuous sliding. The large grain pull-outs generate regions with larger delaminations and grooves as illustrated in Figs. 10(a) and 11(a). Wear particles of the A₁₀₋₀₋₀ sample reveals mostly micron-sized chippings from the shallow grooves and scratches, as shown in Fig. 14

(b). In Fig. 14(c), both large and small chunks of the matrix grain particles were seen in the debris of the A_{10-0.5-0} sample. The wear particles generated in sample A₁₀₋₀₋₂ also had few micro-chippings from the fine grain pull-out during the sliding test, as shown in Fig. 14(d). However, very fine grain particles with average sizes were observed in the wear debris of the A_{10-0.5-2} sample having the combined addition of ZrO₂, GN and CNT (Fig. 14(e)).

4. Discussions

4.1. Synergistic Effect of ZrO₂, GN and CNTs on Matrix Grain Refinement

The relative density result of the fabricated monolithic Al₂O₃ as shown in Table 1 suggests a near-dense structure which might be attributed to the good sinterability of the pristine Al₂O₃ powder, coupled with high sintering temperature [59,60]. Hot-pressed ceramics normally have denser structure (up to 98–99%) with minimum level of porosity. During sintering, the bulk diffusion induces high transportation of mass, which consequently reduces pore formation and enhance the density of monolithic Al₂O₃ [61,62]. In addition, a combination of a constant uniaxial mechanical pressure (60 MPa) and longer dwell time (60 min) at high isothermal temperature were needed to achieve high density structure of the monolithic Al₂O₃. Meanwhile, the addition of multi-materials such as ZrO₂, GN and CNTs tend to slightly impair the density after sintering, as shown in Table 1. This may be attributed to the

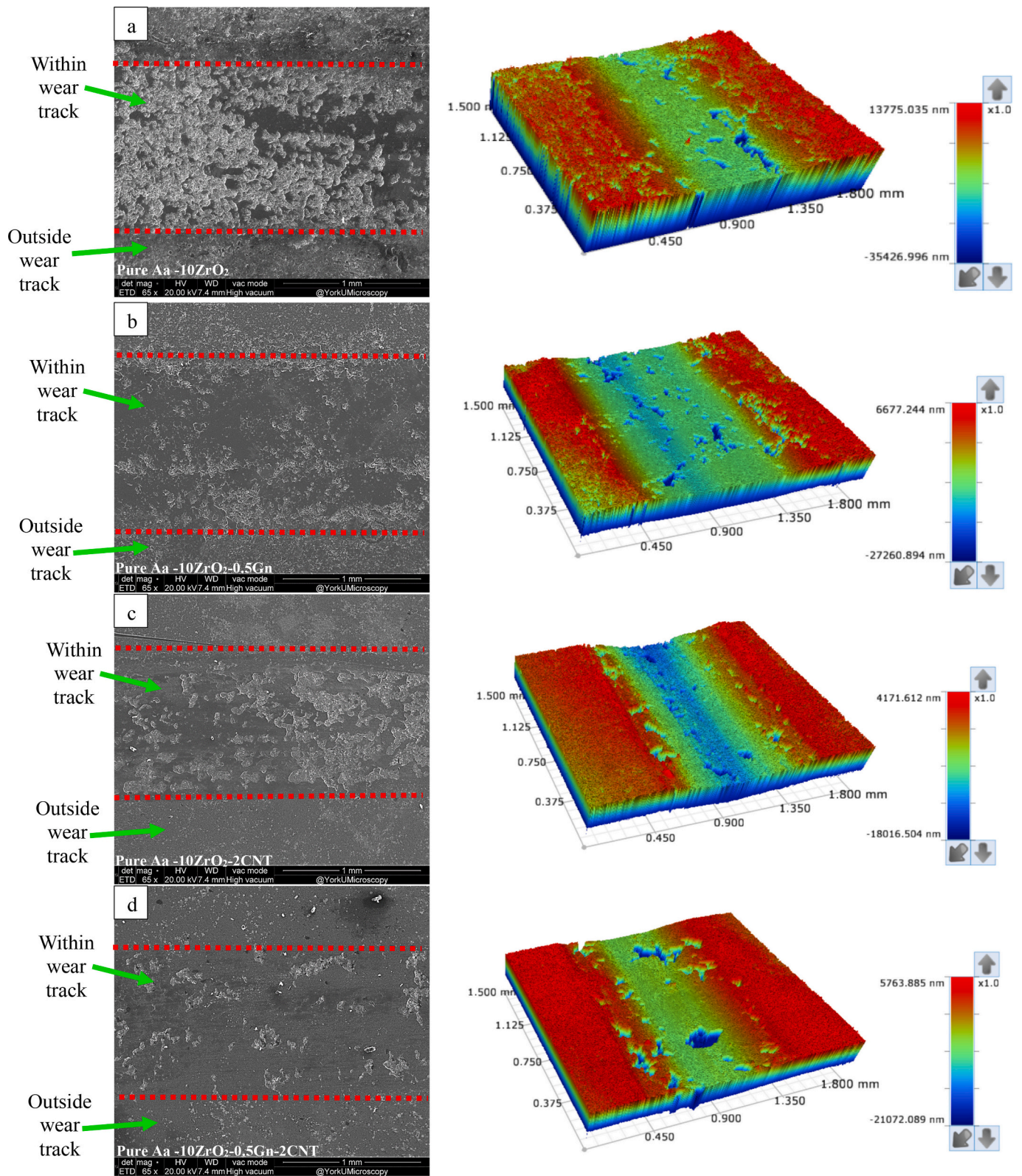


Figure 9: 3D optical profilometry after wear (a) $\text{Al}_2\text{O}_3-10\text{ZrO}_2$ (b) $\text{Al}_2\text{O}_3-10\text{ZrO}_2-0.5\text{Gn}$ (c) $\text{Al}_2\text{O}_3-10\text{ZrO}_2-2\text{CNT}$ (d) $\text{Al}_2\text{O}_3-10\text{ZrO}_2-0.5\text{Gn}-2\text{CNT}$

Fig. 9. 3D optical profilometry after wear (a) $\text{Al}_2\text{O}_3-10\text{ZrO}_2$ (b) $\text{Al}_2\text{O}_3-10\text{ZrO}_2-0.5\text{Gn}$ (c) $\text{Al}_2\text{O}_3-10\text{ZrO}_2-2\text{CNT}$ (d) $\text{Al}_2\text{O}_3-10\text{ZrO}_2-0.5\text{Gn}-2\text{CNT}$.

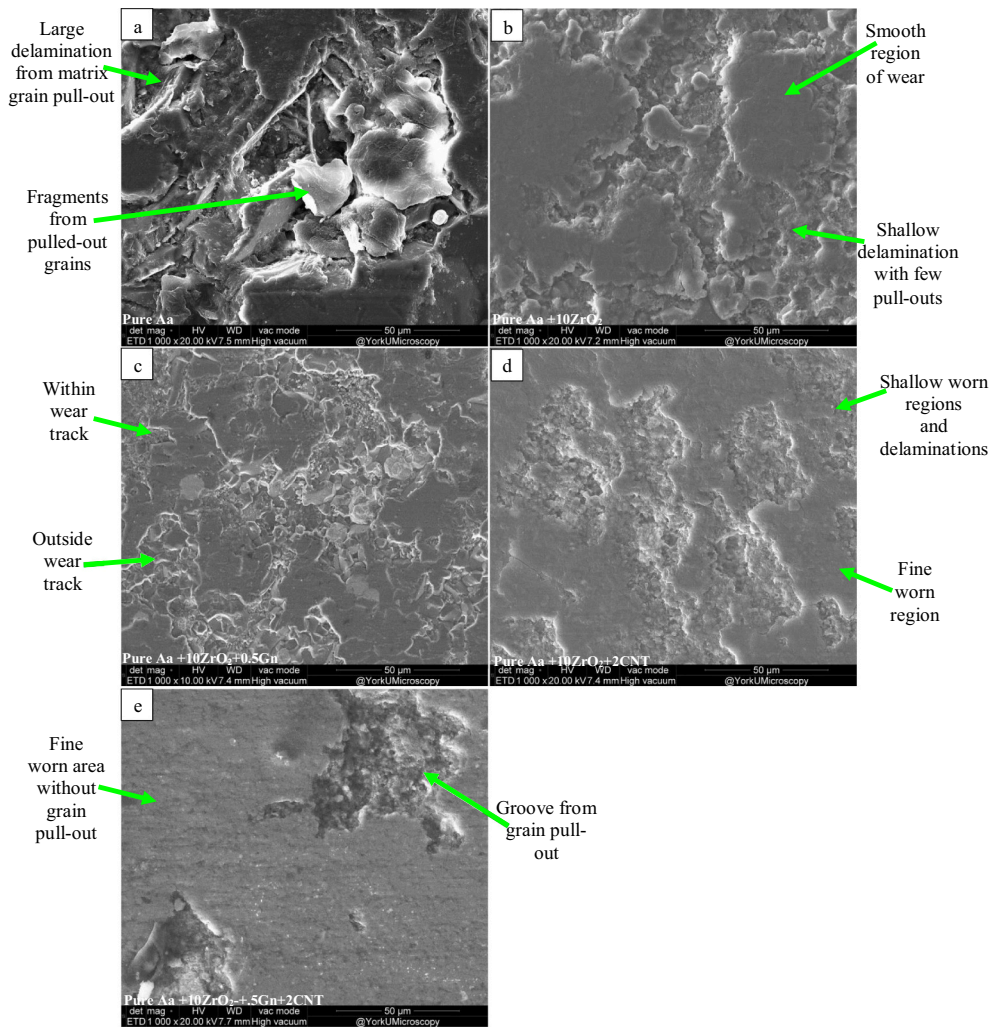


Fig. 10. Within wear tracks showing peel-offs and laminations (a) Pure Al₂O₃ (a) Al₂O₃-10ZrO₂ (b) Al₂O₃-10ZrO₂-0.5Gn (c) Al₂O₃-10ZrO₂-2CNT (d) Al₂O₃-10ZrO₂-0.5Gn-2CNT.

micro-pores indicated in the BSE micrographs (Fig. 5) [51]. The decline in density with the addition of only 10wt%ZrO₂ might be due to the limited restrictive action of the ZrO₂ particles which limits the mass diffusion of the Al₂O₃ atoms along the grain boundaries [63]. In addition, GN and CNTs have been reported to decrease the density of sintered ceramics when embedded within the matrix [64]. These particles are mostly stuck at the Al₂O₃ grain boundaries (as illustrated in Fig. 2 (d)), where they inhibit the flow of matrix materials and thereby retard the densification of the matrix [65,66]. Baksh et al. also reported that the agglomeration of CNTs at the grain boundaries causes the decrease in the density of the fabricated Al₂O₃-CNT nanocomposites in the course of sintering [59].

The significant grain refinement of the Al₂O₃ matrix with the addition of the ZrO₂, GN and CNTs, as illustrated in Figs. 2 and 3, were due to the restriction to the abnormal grain growth of the matrix material during sintering. Further, the addition of GN and CNTs lowered the grain size of the added ZrO₂ particles, which yielded an overall fine-grained structure of samples A_{10-0.5-0}, A_{10-0.2} and A_{10-0.5-2} as compared to sample A₁₀₋₀₋₀. The uniformly dispersed multi-materials are preferably located at the matrix grain boundaries, where bulk diffusion of the matrix is inhibited by the insoluble ZrO₂ and carbon-based additives

during sintering. The presence of ZrO₂ at triple junction impedes the Al₂O₃ grains by exerting a pinning action as reported in other studies [63,67,68]. This is the dominant refinement mechanism in the structure of the A₁₀₋₀₋₀ sample with only 10wt%ZrO₂ addition to the monolithic Al₂O₃. The matrix grain size decrease (up to 41%) in sample A_{10-0.5-0} with 0.5wt%GN was due to the simultaneous grain boundary pinning of both ZrO₂ and GN during sintering [69–71]. The small amount of GN used is known to support grain refinement when dispersed uniformly within the matrix [11]. Other refinement mechanisms such as matrix grain wrapping/anchoring by the added GN particles have also been identified to be predominant in Al₂O₃/GN systems [72,73]. The synergistic effect of ZrO₂ and GN are therefore demonstrated on the grain refinement Al₂O₃ matrix grains. Fig. 15(a) shows a schematic which illustrates the combined restriction to bulk diffusion process by the ZrO₂ and GN particles at the matrix boundaries, thereby limiting grain growth of the matrix. This phenomenon is similar in sample A₁₀₋₀₋₂, with 2wt% CNTs addition, which reduced the matrix grain size up to 80% after sintering. The effective refinement action of the added CNTs, in the form of grain boundary pinning as reported in literature, is due to the optimized amount of CNTs used (up to 2 wt%) [74,75]. Above this concentration (>2 wt%), this mechanism is restricted as a result of CNT-

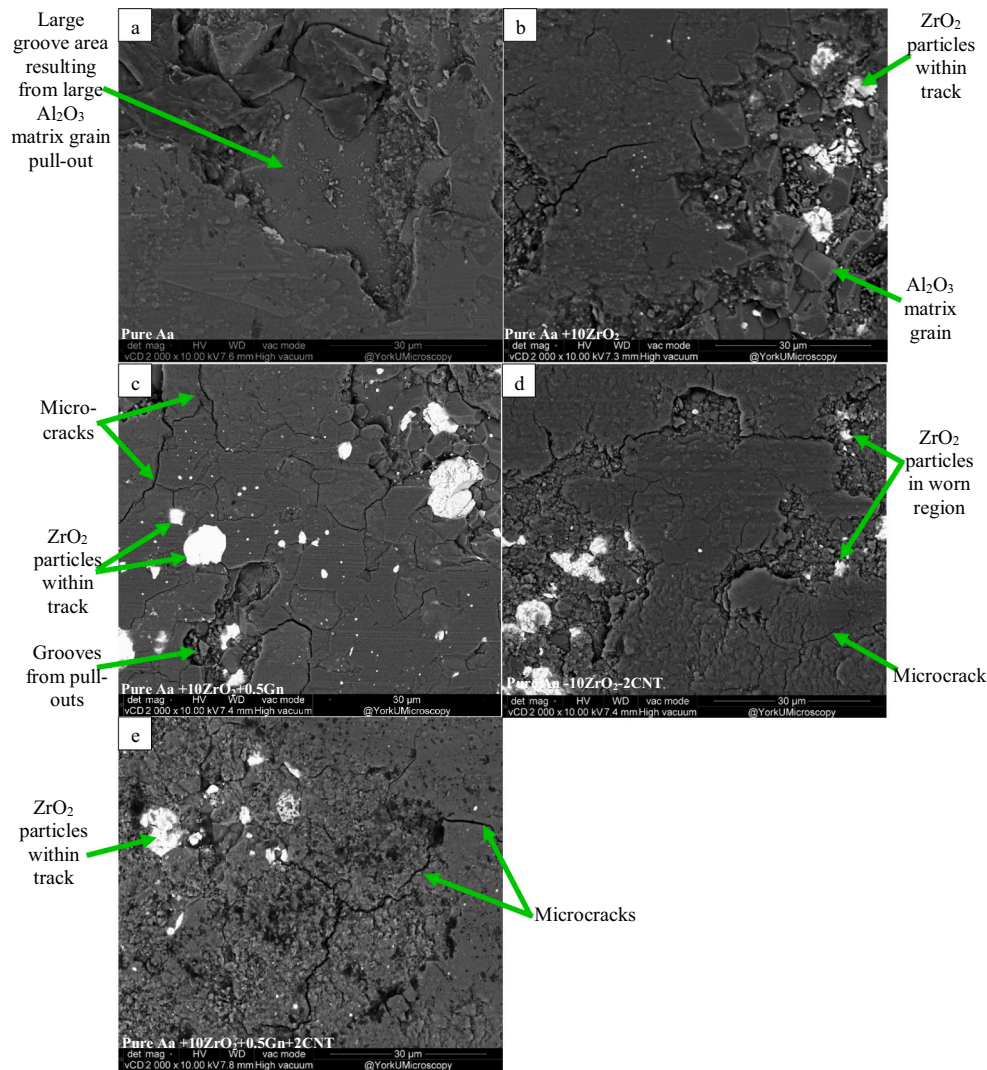


Fig. 11. Within wear track showing ZrO_2 particle distributions and micro-cracks (a) Pure Al_2O_3 (b) Al_2O_3 -10 ZrO_2 (c) Al_2O_3 -10 ZrO_2 -0.5Gn (d) Al_2O_3 -10 ZrO_2 -2CNT (e) Al_2O_3 -10 ZrO_2 -0.5Gn2CNT

agglomeration leading to matrix grain growth [21,22,74]. The synergistic role of ZrO_2 , GN and CNTs on grain refinement is further seen in the $\text{A}_{10-0.5-2}$ sample, which had all the multi-material combinations, with 77% and 64% reduction in Al_2O_3 and ZrO_2 grains respectively. Asiq et al. suggested that parallel grain refinement mechanisms by the GN and CNTs within the Al_2O_3 matrix yields a relatively lower matrix grains at high temperature. GN wrapping of matrix grains, coupled with the pinning action of the CNTs during diffusion is responsible for the grain growth limitation during high temperature sintering [76–79]. In addition, the pinning effect of GN and CNTs is also exerted on the ZrO_2 particles during diffusion, which consequently retards the its rate of diffusion within the matrix, thereby refining the ZrO_2 grains [80].

4.2. Synergistic Effect of Multi-phase Materials on Hardness and Wear Behaviour

Mechanical properties of sintered ceramics are imputed to the grain structure of the matrix, as well as the nature and distribution of the reinforcement particles. The incorporation of ZrO_2 , GN and CNTs to the monolithic Al_2O_3 hindered the grain growth of the matrix, which

directly influenced their mechanical response. As expected on the grounds of the Hall-Petch theory, the mechanical performance such as hardness is enhanced with the reduced matrix grain size [81]. However, in this work, the hardness value of the A_{10-0-0} sample with only 10wt% ZrO_2 addition was depleted by 25% when compared to the monolithic Al_2O_3 , even though its grain size decreased (up to 25%), which goes contrary to the above theory. This might be due to the fact that the insoluble ZrO_2 particles form large grains within the Al_2O_3 matrix (Fig. 2 (b)), which are relatively softer than the matrix, and tend to decrease the bulk hardness of sample A_{10-0-0} during indentation. In addition, the presence of micro-pores within this sample also contributes to the reduced hardness response, as previously reported [51,63]. On the other hand, GN and CNTs in addition to lowering the Al_2O_3 matrix and ZrO_2 grain sizes, increased the hardness value in samples $\text{A}_{10-0.5-0}$, $\text{A}_{10-0.2}$ and $\text{A}_{10-0.5-2}$. In spite of the appreciable amount of reduction in grain size of both the matrix (~41%) and ZrO_2 particles (~23%), only small amount of increment (~2% increase) was recorded with the addition of GN in the $\text{A}_{10-0.5-0}$ sample relative to monolithic Al_2O_3 . This is ascribed to the parallel refinement of the matrix and ZrO_2 grain structures, and the presence of tough ultra-fine GN particles at the grain boundaries (Figs. 2

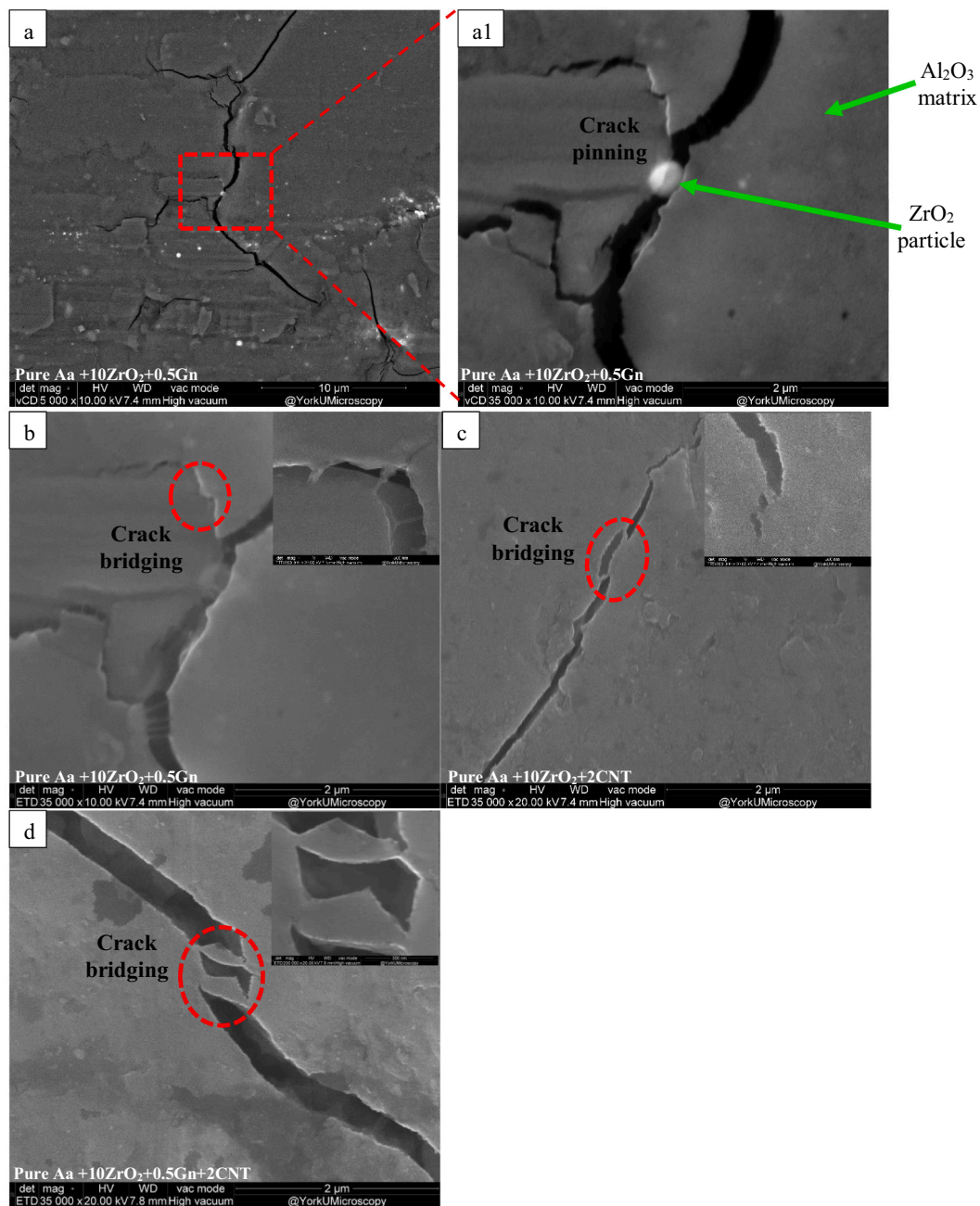


Fig. 12. Crack pinning and bridging mechanisms by ZrO_2 , graphene and carbon nanotubes during within wear track (a) Al_2O_3 -10 ZrO_2 -0.5Gn (b) Al_2O_3 -10 ZrO_2 -2CNT (c) Al_2O_3 -10 ZrO_2 -0.5Gn-2CNT

(c) and(d)). Meanwhile, the 11% increase in hardness with the addition of 2wt%CNTs was due to the extensive refinement of both the matrix and ZrO_2 grains. Also, the load-carrying activities of the CNTs existing at the matrix grain boundaries, as well as crack bridging actions, contribute to the enhanced hardness during indentation [74]. The synergistic role of GN and CNTs in the hardness property of sample $\text{A}_{10-0.5-2}$ is clearly seen in Table 2. The 48% improvement in the hardness value coupled with the refined grain structures is in direct agreement with the Hall-Petch theory. In addition to the grain refinement, excellent coordination between the tough and uniformly dispersed GN and CNTs within the matrix provided appreciable transfer of load from the matrix to these tough materials, resulting in a relatively higher hardness value.

The wear behaviour of the reference monolithic Al_2O_3 sample as well as the hot-pressed nanocomposites is highly dependent on the micro-structural features rather than their friction coefficients and relative densities. The high COF of the nanocomposites with carbon-based GN and CNTs additives have been reported in other works [82–84]. Wang et al. ascribed the increase in COF to the high dynamic friction coefficients of both GN and CNTs [84]. Belmonte et al also suggested that the increase in COF might be due to the parallel orientation of the GN particles to the sliding direction [82]. The high-volume loss and wear rate of the monolithic Al_2O_3 , which was characterized by rough regions and large grain pull-outs was due to the intergranular fracture mode during continuous sliding. It has been demonstrated that an increased

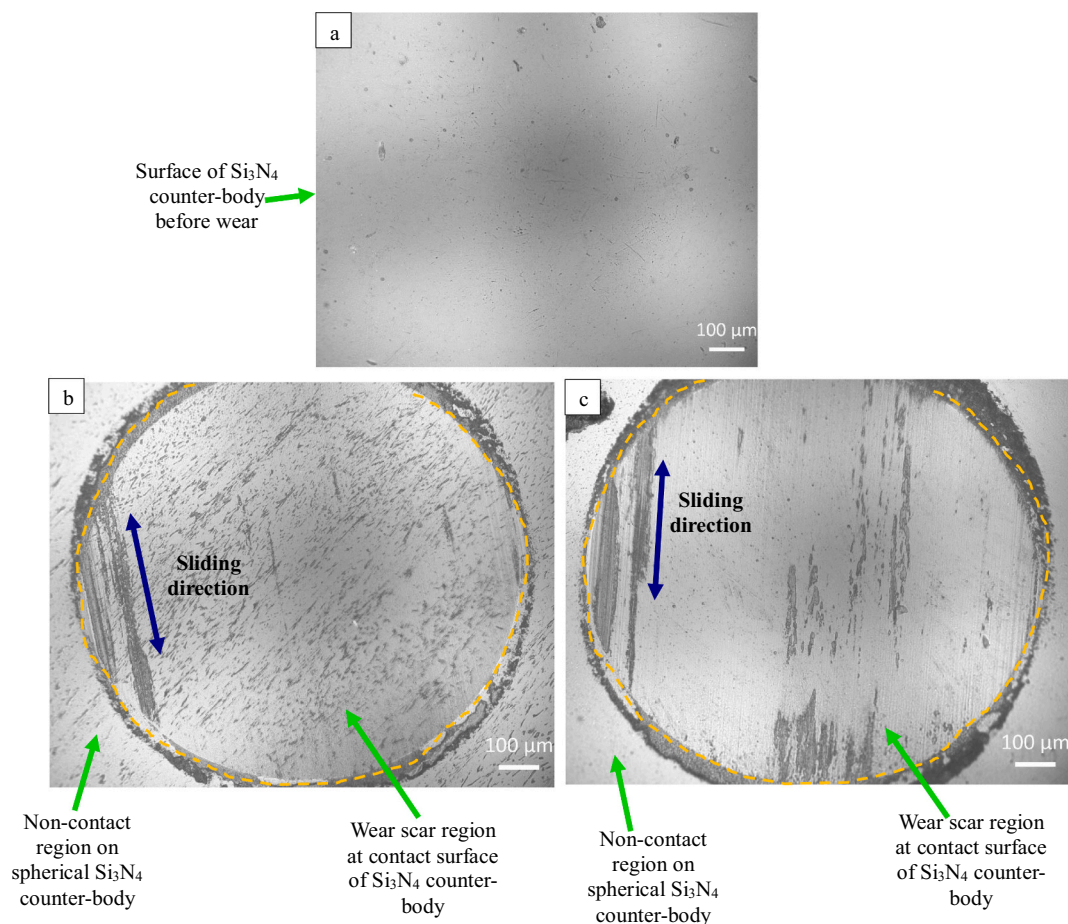


Fig. 13. (a) Optical micrograph of Si_3N_4 counter-body showing surface prior to wear testing (b)-(c) worn surface of Si_3N_4 counter-body after 5000 cycles of reciprocating sliding.

grain size increases the rate of wear of brittle oxide ceramics [85]. As the hard counter-surface with high load is pressed against the reference Al_2O_3 surface, there is mechanical damage/brittle fracture. The brittle fracture is caused by the tangential forces which induce stresses as these bodies continuously slide relative to each other. The high tangential forces at the high load causes fracture along the matrix grain boundaries due to micro-cracking, leading to the grain pull-outs and rough patches seen in the worn surface and wear debris particles (Figs. 8, 10-12), [86]. However, the role of the added ZrO_2 and carbon-based GN and CNTs in the nanocomposite influenced the wear performance and its mechanisms. For instance, the addition of 10wt% ZrO_2 alone to Al_2O_3 yielded a shallow wear track with smooth regions due to the limited amount of matrix grain removal. The homogeneous distribution of fine ZrO_2 particles at matrix grain boundaries prevents intergranular fracture by impeding the propagation of micro-cracks generated from the sliding along the boundaries, which consequently lead to complete grain pull-out. This is also illustrated in Fig. 12 and schematics in Fig. 15(b). Addition of 0.5wt%GN led to many smooth regions within the worn surfaces of sample A_{10-0-2} , with few micro-chippings of the matrix grains. This is due to the formation of the tribofilm formed on the worn surface by the added ultra-fine GN. The presence of tribofilm limits the friction interaction between the nanocomposite surface and the counter-surface during sliding [83,87]. In addition, the thin graphene resides at the matrix boundaries providing a reinforcement and impeding grain removal through the crack bridging as illustrated in Fig. 15(b). This also contributes to the relative high wear resistance of the $\text{A}_{10-0.5-0}$ sample. Therefore, here, the synergistic effect of the combined ZrO_2 and GN is

seen within the worn surface of $\text{A}_{10-0.5-0}$ sample, even though the wear rate was slightly higher than the A_{10-0-0} sample having only 10wt% ZrO_2 addition (91% vs 88%). The bridging action within the wear track of sample A_{10-0-2} having 2wt%CNTs addition was also identified to be a dominant wear resistance mechanism during sliding (Fig. 12(c)). Hence, the narrow-worn surface coupled with the smooth regions and lower grain pull-outs, as illustrated by Figs. 9(c) and 10(d) demonstrate the improved wear performance with the addition of CNTs. For sample $\text{A}_{10-0.5-2}$ with the multi-material composition of ZrO_2 , GN and CNTs, the low wear volume along with a 93% reduced wear rate can be ascribed to the excellent coordination between the homogeneously dispersed materials. Formation of tribofilm by GN, the pinning effect of ZrO_2 and bridging action of the embedded CNTs contribute to its high wear resistance. Thus, a synergy effect is demonstrated by these additives during the sliding wear. This is further shown by the schematics in Fig. 15(b) which illustrates these mechanisms within the grain structure of the matrix. For these systems, the micro-chippings seen in the wear debris could be attributed to the transgranular fracture of the matrix grains. As micro-cracks induced by the shear stress are impeded on the grain boundaries, the propagations tend to go through the matrix grains to cause fracture as the sliding at the constant load continues. Yazdani et al. suggested that the low wear rate of hot-pressed Al_2O_3 -GNPs-CNTs nanocomposites was due to the uniform distribution of the carbon additives and their complementary bridging and toughening actions under the sliding wear [47].

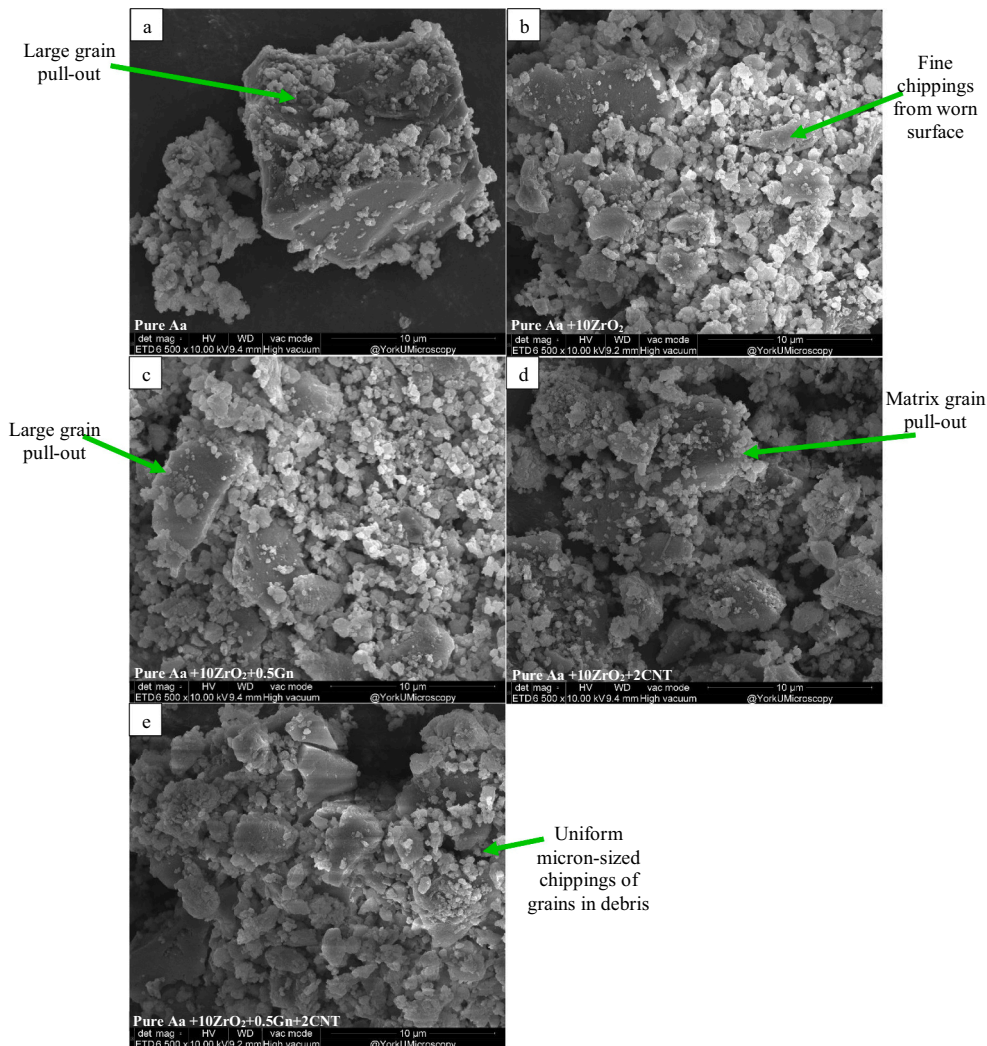


Fig. 14. Nature of wear debris after wear test (a) Pure Al_2O_3 (b) Al_2O_3 -10 ZrO_2 (c) Al_2O_3 -10 ZrO_2 -0.5Gn (d) Al_2O_3 -10 ZrO_2 -2CNT (e) Al_2O_3 -10 ZrO_2 -0.5Gn-2CNT.

5. Conclusion

In this work, second-phase ZrO_2 (10 wt%), Graphene (0.5 wt%) and CNTs (2 wt%) were introduced into monolithic Al_2O_3 matrix structure to form multi-material nanocomposites. Compared to the reference Al_2O_3 sample, the hardness and wear performance of the multi-material nanocomposites were improved up to 80% and 93% respectively, due to the refined grain structure of both the Al_2O_3 matrix and ZrO_2 grains, and substantial load-bearing activities of the homogeneously dispersed multi-materials at matrix grain boundaries. Major findings from the current work are summarized below:

1. The addition of only 10wt% ZrO_2 , resulted in a 25% reduction in grain size and high wear resistance (up to 88% increase), but hardness was depleted by 25%. The pinning action of ZrO_2 at junctions of matrix grain boundaries caused grain refinement and improved wear resistance.
2. The incorporation of 0.5wt%GN gave a 41% decrease in the Al_2O_3 matrix grain size along with a 23% reduction in ZrO_2 grains. Even though only 2% increase in the hardness value was recorded relative to the monolithic Al_2O_3 , the wear resistance was highly improved up to 91%. ZrO_2 pinning effect and bridging by the added GN restricted microcrack propagation to cause high volume loss and wear rate.
3. As 2wt%CNTs was added, the matrix grain size was reduced by 80%, along with a 46% reduction in the ZrO_2 grain size, which suggested that 2wt%CNTs was most effective for refining matrix grains. The hardness and wear resistance in turn increased up to 11% and 92% respectively, due to the fine-grained microstructure. Dominant mechanisms such as crack bridging by CNTs and grain pinning by ZrO_2 illustrate a combined effect of these added materials within the matrix, leading to the improved mechanical and wear resistance properties.
4. Addition of both 0.5wt%GN and 2wt%CNTs also demonstrated the synergistic effect in the parallel refinement of the Al_2O_3 matrix (77%) and ZrO_2 grains (64%), coupled with an exceptional 48% increase in the hardness value and a 93% reduction in the wear rate properties. Excellent coordination between the homogeneously dispersed materials yielded a higher wear resistance through the pinning and bridging effect of the embedded ZrO_2 , GN and CNTs.

Declaration of Competing Interest

None.

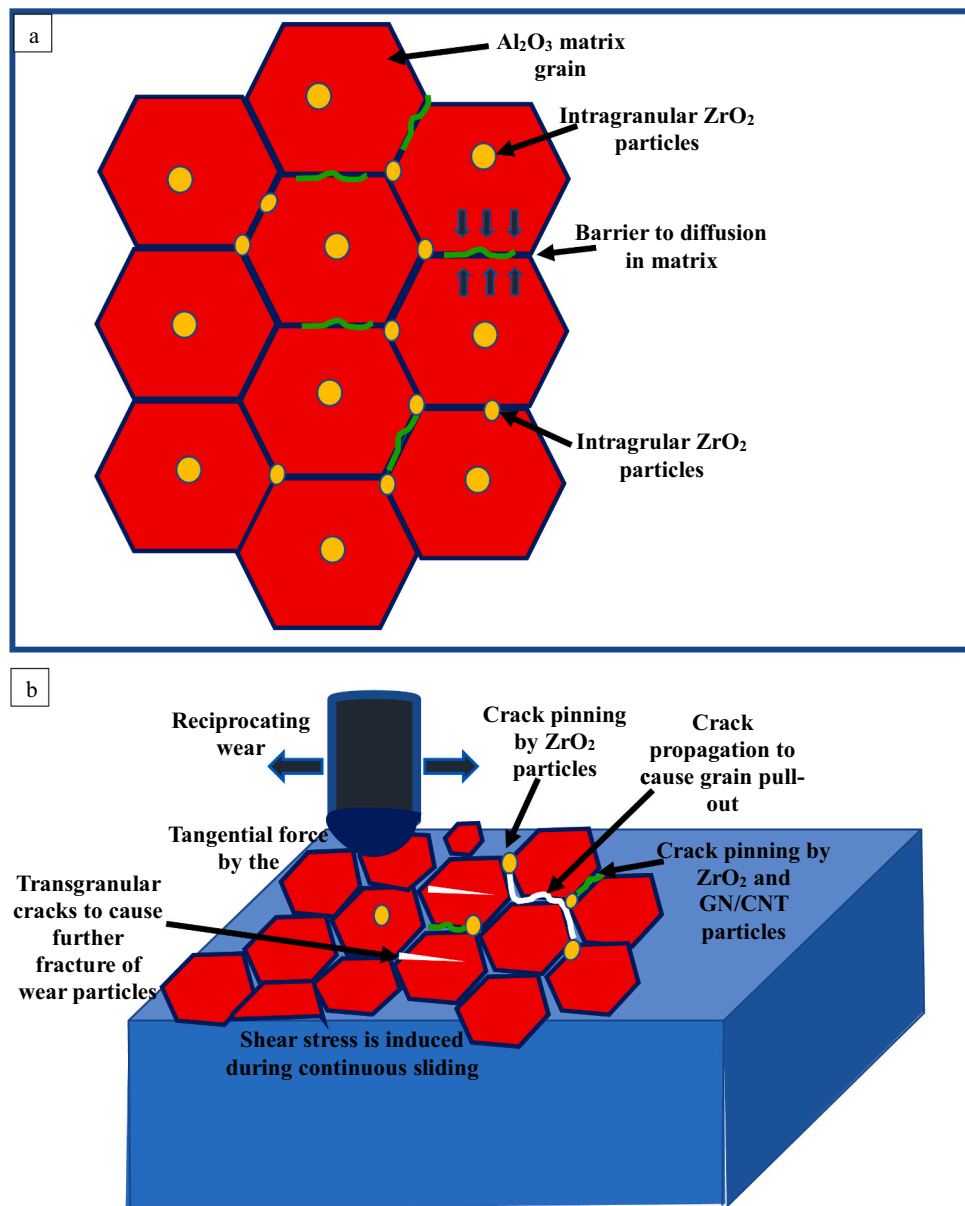


Fig. 15. (a) Schematics illustrating grain refinement mechanism by reinforcement phases (b) Schematic illustrating grain pull-out resistance during sliding contact in multi-material nanocomposites.

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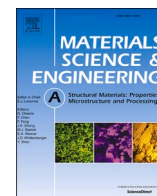
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Paper IV: Deformation and Fracture Behaviour of Alumina-Zirconia Multi-Material Nanocomposites Reinforced with Graphene and Carbon Nanotubes

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Deformation and fracture behaviour of alumina-zirconia multi-material nanocomposites reinforced with graphene and carbon nanotubes

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ABSTRACT

An effort to improve the low fracture toughness of monolithic alumina (Al_2O_3) ceramic demands microstructural manipulation with nanostructured materials such as zirconia (ZrO_2), Graphene (GN) and Carbon Nanotubes (CNTs). Despite these attempts, the fundamental understanding of the mechanical properties and deformation behaviour of multiple combinations of these second-phase additives within the advanced Al_2O_3 structure are still being explored. In this respect, Al_2O_3 -based nanocomposites reinforced with optimum amounts of ZrO_2 (10 wt%), GN (0.5 wt%) and CNTs (2 wt%) were evaluated via hot-pressing at 1600 °C, preceding colloidal mixing of the Al_2O_3 matrix and nanostructured additives. Mechanical properties such as fracture toughness (K_{IC}) and bending strength (σ_f) measured using three-point bending techniques including single edge notched beam (SENB) test, and direct crack measurement (DCM) methods were calculated from the near-dense fabricated multi-material nanocomposites and benchmarked against the monolithic Al_2O_3 material under similar experimental conditions. From the conventional SENB test, the fracture toughness values increased by up to 60% on the addition of only 10 wt% ZrO_2 to the monolithic Al_2O_3 , whilst a drastic increase by up to 159% was achieved with the incorporation of both GN and CNTs within the Al_2O_3 - ZrO_2 structure, as compared to the monolithic Al_2O_3 . The K_{IC} values obtained from SENB tests were typically lower than the DCM method, but similar trend in the toughness behaviour were realized regardless. Bending strength of the prepared monolithic Al_2O_3 was also increased by up to 46% with the combined additions of ZrO_2 , GN and CNTs. Toughening and strengthening mechanisms including pull-outs by GN and CNTs, crack arrest and crack bridging were identified as the main source of enhancement in the mechanical properties of the multi-material nanocomposites. The addition of carbon additives also influenced monoclinic and tetragonal ZrO_2 phase transformations, which also contributed to the overall mechanical behaviour of the Al_2O_3 -10 wt% ZrO_2 nanocomposites.

1. Introduction

The quest for structural materials that are tougher and have tolerance for extreme environments such as high pressures (>90 GPa), temperatures (>3000 °C), chemical and nuclear radiations has been the current demand for many advanced technologies [1,2]. Also, in recent times, the need to minimize overall carbon footprint and improve fuel efficiency of vehicles and aircraft has called for the adaptation of materials with relatively lower densities [3,4]. Therefore, lightweight structural materials with appreciable mechanical qualities such as toughness and strength, coupled with high resistance to harsh

environmental conditions are ideal for current high-performance applications in the automobile, aerospace and military sectors. For structural attributes that satisfy these engineering requirements, advanced polycrystalline ceramics such as alumina (Al_2O_3), zirconia (ZrO_2), silicon carbide (SiC), silicon nitride (Si_3N_4) and their composites present several advantages over metals and polymers [2,5,6]. In particular, alumina (Al_2O_3) ceramic with useful properties such as low density ($\sim 3.97 \text{ g/cm}^3$), low sensitivity to corrosion, high temperature strength and hardness, has promising potential for high performance structural applications including biomechanical components, gas turbine, cutting tools, drill bits, electronic structural parts and low-density armor

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components [7,8]. Despite these inspiring mechanical characteristics, the poor fracture toughness of monolithic Al_2O_3 restricts its use for these advanced engineering structures. The incorporation of toughening agents such as carbon nanotubes (CNTs), graphene (GN), zirconia (ZrO_2) and magnesia (MgO) to form ceramic-matrix composites has been widely studied but more investigation is still needed, since reports have shown inconclusive results [9–11]. Whilst some literatures present mechanical property enhancement with the single additions of these toughening materials, other studies demonstrate deteriorating fracture toughness, bend strength, hardness and wear attributes of the final ceramic matrix [12,13].

The discovery of carbonaceous nano-phase materials such as Graphene and CNTs has sparked promising interest in their use as toughening agents in advanced ceramics. Strategies proposed to adopt these materials as reinforcement phases in these matrices stem from their many attractive physical and mechanical properties including lower density ($\sim 2.55 \text{ g/cm}^3$ for GN and $\sim 1.4 \text{ g/cm}^3$ for CNTs), high stiffness ($\sim 1 \text{ TPa}$ for GN and $\sim 1.8 \text{ TPa}$ for CNTs), flexural and tensile strength, thermal and electrical properties [14–16]. Potential of these additives to impart toughness, strength and improve electrical and thermal conductivity increases the structural and multifunctional applications of ceramic matrix composites [17,18]. In recent years, the use of single additions of either graphene or CNTs within alumina matrix has shown interesting results. More specifically, the enhancement in fracture toughness and bend strength by these additives has piqued attention [6, 11,12]. In addition, literature has reported on various toughening mechanisms displayed by these individual carbon-based additives within the ceramic matrix including crack bridging, graphene/CNTs pull-out, and crack deflection [6,19]. For instance, Centeno et al. demonstrated about 50% increase in fracture toughness of alumina composite reinforced with 0.22 wt% graphene. Crack bridging action by the graphene was identified as the main phenomena for inducing toughening in the composite [20]. Further, the pull-out and crack bridging mechanisms illustrated by CNTs (0 – 3 vol%) in the alumina matrix yielded improved fracture toughness (K_{IC}) value up to 40% (from $3.32 - 4.68 \text{ MPa}^{1/2}$), as demonstrated in the work by Kim et al. [21]. In a more recent studies by Guo et al., both the fracture toughness and bending strength of CNTs/alumina having different CNTs amounts (0–2 wt%) were evaluated using 3-point bending and Single Edge Notched Beam (SENB) tests. They reported about 182% and 55% increment in the toughness and strength of the composite with 0.5 wt% CNTs concentration, as compared to the monolithic alumina. High load-bearing capacity, as well as CNT pull-outs and bridging of cracks within grains were outlined as the main toughening and strengthening mechanisms in the fabricated CNTs/alumina composites [22]. Other literature studies have however concluded a decline or comparable bulk fracture toughness values after dispersing either graphene or carbon nanotubes within the Al_2O_3 matrix [23,24]. In Aguilar's report, after 0.05–0.1 wt% of CNTs were added to pure alumina matrix to form alumina/CNTs composites via pressureless sintering, both the hardness and toughness lowered, with the K_{IC} values declining up to about 41% [24]. A similar trend was also identified in alumina-GNPs system incorporated with 1.33 vol%GNPs by Liu et al., who realized no significant increment in the hardness and K_{IC} values [25]. In both reports, poor dispersion, agglomeration of GNPs and CNT bundles, and pore formation restricted the toughening efficiency of the composites and its constituents, which degraded the mechanical properties. Hence, it is obvious that the single addition of either CNTs or GN to ceramic matrix have not yielded conclusive results.

Currently however, a growing interest has been demonstrated in the use of both carbon-based structures to toughen these advanced ceramic materials. This is inspired by the idea that the superior properties of both graphene and carbon nanotubes can be synergistically imparted on these ceramic structures to make them suitable for high-performance structural applications [26]. Other studies also suggest that the limitations of reinforcing a matrix with either GN or CNTs only, such as agglomeration

and graphene re-stacking can be minimized when both carbon-based structures are combined in the matrix [27–29]. Up till now, there have been few reports on the toughening effects of these multiple reinforcement phases within the ceramic matrix. In the studies of Rahman et al., about 250% increase in fracture toughness was achieved in consolidated alumina /1 wt%GNPs /0.5 wt%CNTs nanocomposites, which were prepared via spray drying followed by spark plasma sintering (SPS). The abrupt toughness enhancement was associated with known toughening mechanisms such as CNT pull-out, crack-bridging and deflection, CNT embedded graphene and CNT yarning [28]. In another similar work, Yazdani et al. utilized ultrasonication and hot-pressing to reinforce alumina-based nanocomposites with both 0.5 wt%GNPs and 1 wt% CNTs, and reported about 63% and 18% increase in the fracture toughness and flexural strength respectively, relative to the parent alumina. Though there was no significant reduction in the grain size, the improved mechanical properties were accustomed to the unique structural morphologies of the combined carbon-based materials, and toughening effects including GNP pull-out, CNT pinning and pull-out, and CNT crack bridging [30]. The concept of reinforcing ceramic matrices with multiple additives can therefore offer drastic improvement to their mechanical properties. However, more studies are needed to further understand the microstructural and mechanical performance of these novel ceramic-based multi-material nanocomposites.

Commercially produced zirconia (ZrO_2) has been known to offer effective toughening properties to the alumina matrix. The perks of being a lightweight ceramic material accompanying high strength and toughness, especially at elevated temperatures make it a suitable reinforcement particle in plain alumina [31,32]. Transformation toughening involving phase transformation from tetragonal ($t - \text{ZrO}_2$) to monoclinic ($m - \text{ZrO}_2$) is known to produce essential toughness and structural properties to the alumina- ZrO_2 structure [33]. Also, in the presence of applied stress, the $t - m$ ZrO_2 phase conversion is eminent accompanied with about 3–5% volume expansion, which tend to restrict surrounding crack propagation in the matrix and consequently enhance the toughness and strength of alumina [34,35]. Conversely, various reports have also demonstrated that the mechanical properties of alumina/ ZrO_2 composites such as bulk hardness, strength and wear are sometimes impaired with the addition of the ZrO_2 additive [36,37]. This has motivated studies to explore a third phase addition to alumina/ ZrO_2 including CNTs and GN to form multi-material composites [38,39]. There are, however, scarce reports on the combined toughening mechanisms of ZrO_2 and third phase particles on the toughening and mechanical behaviour of the alumina/ ZrO_2 composites.

Adding multiple toughening materials to the alumina/ceramic matrix thus presents a research direction that appears most promising in exploring the structure and performance of advanced ceramic-based nanocomposites. However, there is the need to understand the fundamental toughening mechanisms and microstructural effects of the multiple additives in such nanocomposites. The current work demonstrates the effect of multi-material additions on the mechanical properties such as fracture toughness and bending strength of hot-pressed alumina-based nanocomposites reinforced with multiple additions of zirconia (ZrO_2), Graphene (GN) and Carbon nanotubes (CNTs). Characterization of the fabricated multi-material nanocomposites to correlate their microstructural features to the mechanical performance, as well as their combined toughening and strengthening mechanisms will also be discussed.

2. Materials and methods

2.1. Fabrication of multi-material nanocomposites

Monolithic alumina (Al_2O_3) and alumina/zirconia (ZrO_2) with additions of graphene (GN) and carbon nanotubes (CNTs) powder mix were prepared using colloidal method. Details of the prepared powder mix for each nanocomposite having various compositions of 10 wt%

ZrO₂, 0.5 wt%GN, 2 wt%CNTs are previously discussed [40,41]. Bulk nanocomposite samples were then consolidated and sintered in a rectangular graphite die using a uniaxial pressure of 60 MPa and hot pressing at a temperature of 1600 °C for 1 h. The sintering was conducted in an argon (Ar) atmosphere with a heating rate of 10 °C/min. Final sintered nanocomposites with rectangular geometries and approximate dimensions of 50mmx40mmx2mm were produced and prepared for various microstructural and mechanical characterizations [42–44]. Hot-pressing of the parent Al₂O₃ sample was also done under identical experimental conditions for reference. Table 1 shows the details of the fabricated samples.

2.2. Characterization of microstructural features

The sintered multi-material nanocomposites were subjected to routine metallographic procedures involving grinding using SiC pads (up to 1200 grits) and polishing down to 0.5μm with a diamond suspension and polishing cloths. Archimedes method with distilled water as the immersion medium was used to measure the bulk density (g/cm³). The relative densities (densification) of the nanocomposites which were estimated by dividing the apparent density with the theoretical density have been previously presented [43]. The polished sections of the fabricated samples were also observed using a Field Emission Scanning Electron Microscope (FE-SEM, Quanta 3D, Thermofisher) operating at an accelerating voltage of 10 kV to reveal the morphology of the grain and structural features of the prepared nanocomposites.

2.3. X-ray diffraction (XRD) analysis and crystallite size estimation

The different phase compositions of the sintered monolithic alumina and alumina-based multi-material nanocomposites were detected using X-ray diffraction (XRD) (Rigaku Miniflex 600). The XRD system was equipped with Cu-Kα radiation of $\lambda = 1.54056 \text{ \AA}$. XRD patterns were collected in a 2θ range from 5 to 110°, at a 1.4°/min scanning rate. Post-processing of the XRD patterns was also done using MDI JADE 6.0 to identify the crystallite phases and their corresponding planes.

Even though the nanocomposites had similar ZrO₂ amounts (10 wt %), the content of the monoclinic (*m*-ZrO₂) and tetragonal (*t*-ZrO₂) were determined and compared to analyze the possible effect of GN and CNTs additions on the phase transformations of the ZrO₂. The XRD intensities were used to quantitatively estimate the *m*-ZrO₂ and *t*-ZrO₂ amounts in the alumina-zirconia multi-material nanocomposites. The respective volume fractions were approximately calculated using reflections of the various patterns coupled with equations proposed by Toraya and Garvie below [54,55]:

$$X_m = \frac{[I_m(\bar{1}\bar{1}1) + I_m(111)]}{[I_m(\bar{1}\bar{1}1) + I_m(111) + I_t(111)]} \quad (1)$$

$$V_{m-ZrO_2} = \frac{1.311X_m}{1 + 0.311X_m} \quad (2)$$

where X_m is the integrated intensity ratio of the *t*-*m* ZrO₂ phases, V_m is the monoclinic ZrO₂ phase volume fraction, $I_m(\bar{1}\bar{1}1)$ and $I_m(111)$ are the intensities of the monoclinic phase at planes $(\bar{1}\bar{1}1)$ and (111) respectively, and $I_t(111)$ denotes the tetragonal (111) reflection. The

tetragonal volume fraction (V_t) was approximately estimated from the relation:

$$V_{t-ZrO_2} = 1 - V_{m-ZrO_2} \quad (3)$$

2.3.1. Crystallite size (*D*)

The crystallite sizes of the fabricated monolithic Al₂O₃ and nanocomposite samples were estimated from the XRD patterns by measuring the full width at half-maximum (FWHM) of the various diffraction peaks within each sample. The measured FWHM values were coupled with Scherrer equation below to calculate the crystallite sizes [45],

$$D = \frac{K\lambda}{B \cos \theta} \quad (4)$$

where D is the crystallite size in nm, K is the crystallite shape factor with a known value of ~ 0.9 , λ represents the wavelength of the incident X-rays given as 0.154056 nm, B is the FWHM value of a specific diffraction peak in radians, and θ is the peak position (Bragg angle) in radians.

2.4. Evaluation of mechanical properties

2.4.1. Micro-hardness estimation

The micro-hardness was measured on a Vickers microhardness tester using a 1 kg force as previously reported [43]. For each sample, ten (10) separate indents were made on sample's surface. The hardness values in GPa was calculated for each indentation using the equation [46]:

$$Hv_{GPa} = 0.0018544 \left(\frac{P}{d^2} \right) \quad (5)$$

where P is the applied load (N) and d is the mean value of the diagonal lengths in mm. The average value is then recorded as the bulk hardness of the nanocomposite.

2.4.2. Fracture toughness (K_{IC}): Single edge notched beam (SENB) test

Single edge notched beam (SENB) test (Fig. 1a) was used to evaluate the fracture toughness (K_{IC}) values of the nanocomposites under ambient conditions using the Hybrid Rheometer (Discovery 3). A 30 mm (length) × 2 mm (width) × 2 mm (thickness) was used as the test sample, which was sectioned from the bulk fabricated nanocomposite. A notch was created in the centre part of the test specimen with the aid of a diamond saw, having a typical notch-depth ratio (a/W) of $\sim 0.45 - 0.55$ [30]. Three samples with similar geometry were tested for each nanocomposite. A span length of 25 mm and crosshead speed of 0.05 mm/min were applied to each test specimen during the test. The fracture toughness (K_{IC}) was subsequently calculated using the following equations [46,47]:

$$K_{IC} = \left(\frac{3 \times L_{max} \times S}{2 \times B \times W^{3/2}} \right) \times a^{1/2} \times Y \quad (6)$$

where L_{max} is the maximum applied load during fracture, S is the span length, B and W are the width and thickness (height) of the test specimen respectively, a is the notch depth, α is the notch ratio (a/W) and Y is a coefficient (calibration factor) estimated from the equation [46,47]:

Table 1

Chemical composition of fabricated Al₂O₃/ZrO₂ multi-material nanocomposites.

Sample ID	Matrix material	Zirconia (ZrO ₂) content (wt%)	Graphene (GN) content (wt%)	Carbon nanotubes (CNTs) content (wt%)	Measured bulk density (g/cm ³)	Crystallite sizes from Scherrer equation (nm)
Pure A	Al ₂ O ₃	0	0	0	3.95	64.55
A10Z	Al ₂ O ₃	10	0	0	3.88	57.05
A10ZG	Al ₂ O ₃	10	0.5	0	3.90	56.22
A10ZCN	Al ₂ O ₃	10	0	2	3.92	53.37
A10ZGCN	Al ₂ O ₃	10	0.5	2	3.94	53.40

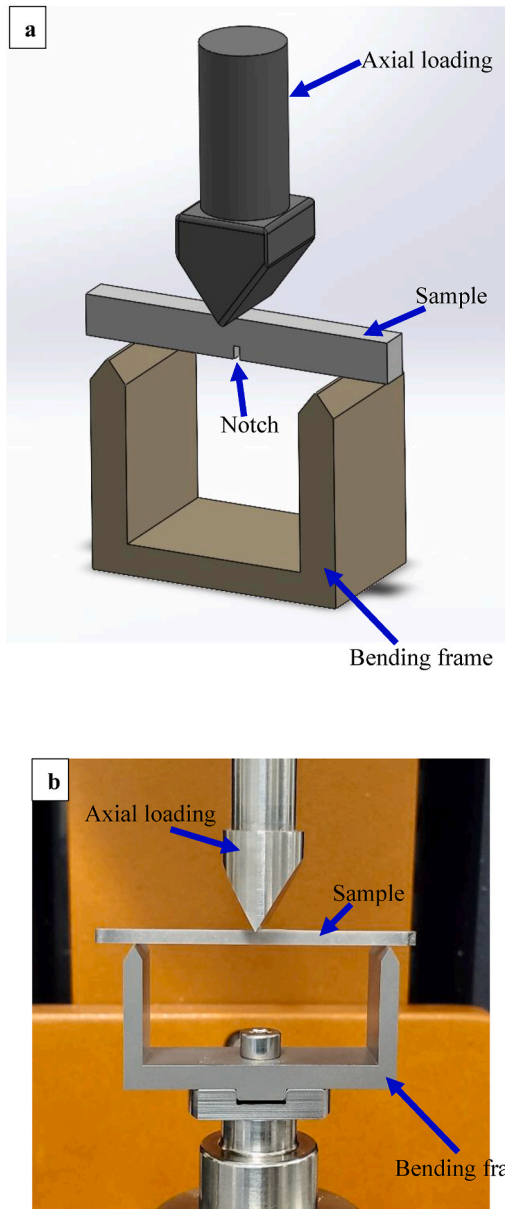


Fig. 1. Illustration of (a) Single Edge Notch Beam (SENB) (c) 3-point bending test experiment.

$$Y = \frac{1.99 - \alpha(1 - \alpha)((2.15 - 3.93\alpha + 2.7\alpha^2)}{(1 + 2\alpha)(1 - \alpha)^{3/2}} \quad (7)$$

2.4.3. Fracture toughness (K_{IC}): Direct crack measurement (DCM) technique

Another method used to estimate the fracture toughness (K_{IC}) is the direct crack measurement (DCM) using the Niihara equation. The K_{IC} values were calculated by measuring crack extensions from the indents made on samples' surface during the Vickers hardness measurements. With the aid of an attached optical microscope and Image J software, the lengths of the emerging cracks were determined for the indents made. The measured crack lengths were combined with known Niihara equation to estimate the K_{IC} values as follows:

Niihara equation [48]:

$$K_{IC} = 0.203 \left(\frac{c}{a} \right)^{-1.5} \cdot H \cdot a^{0.5} \quad (8)$$

where a is half of the length of Vickers indent diagonal (mm), H is the Vickers microhardness (GPa), and c is the length of the measured crack (mm) from the crack tip to the center of the diamond-shaped indent. The results of the estimated K_{IC} values from the SENB test and theoretical equation (DCM) were also compared and discussed in this study.

2.4.4. Bending strength using 3-point bending test

The bending strength (α_f) of the nanocomposites was determined using the 3-point bending configuration on the Hybrid rheometer (Discovery 3), as shown in Fig. 1 (b). The dimension of the test samples was 50 mm (length) $\times$ 2 mm (width) $\times$ 2 mm (thickness). A bending span of 40 mm was used, with an axial loading speed of 0.5 mm/min. Crack initiation and subsequent fracture occurred at regions closer to the applied axial load during the bending. Three different test samples were used for each fabricated nanocomposite and the bending strength evaluated from the equation below [49]:

$$\alpha_f = \frac{3 \times P_{max} \times L}{2 \times b \times h^2} \quad (9)$$

where P_{max} is the fracture load, L is the bending span, b and h denote the sample width and thickness, respectively.

2.5. Fractography studies

After mechanical testing, the fractured samples were prepared for fractographic studies to analyze and identify different modes of fracture, and various fracture mechanisms by the added reinforcement materials to the alumina matrix. Surfaces were first secured on specially made angular mounts and coated with a thin layer of platinum to prevent charging of the surfaces in the SEM chamber. The fractured surfaces were then analyzed at high vacuum using the FE-SEM (Quanta 3D, Thermofisher).

3. Results

3.1. Structural characterization of fabricated nanocomposites

The compositions of the prepared multi-material nanocomposites with their measured bulk densities in g/cm^3 are presented in Table 1. Density results from the Table shows a comparable value of the fabricated monolithic Al_2O_3 matrix (3.93 g/cm^3) to the theoretical density value of 3.98 g/cm^3 . The nanocomposites with different additions of 10 wt% ZrO_2 , 0.5 wt%GN and 2 wt%CNTs also exhibited similar density values to that of the monolithic Al_2O_3 matrix and the theoretical value. This follows the relative density trend which was previously discussed by the authors [43]. FE-SEM micrographs at high magnification shows the evolution and morphology of the grain structure of the Al_2O_3 matrix when 10 wt% ZrO_2 , 0.5 wt%GN and 2 wt%CNT (Fig. 2a–e)). The grain size and distribution have been presented in previous work [43], with the combination of GN and CNTs exhibiting an immense grain refinement of both the parent Al_2O_3 matrix and the added ZrO_2 particles. The dispersion of the carbonaceous structures such as GN and CNTs within the Al_2O_3 matrix were also illustrated from the fractographic details of the nanocomposites (Fig. 2f). Relatively large sheets of GN appeared to rest mostly on the matrix grain boundaries, whilst the CNT bundles were identified on both the grain boundaries and within the large matrix grains at different orientations.

Fig. 3 shows the XRD patterns of the sintered multi-material nanocomposites with the various crystalline peaks for monolithic Al_2O_3 , ZrO_2 and graphite phases. The distinct peak shapes identified in each peak of the XRD patterns demonstrate minimum or no detection of impurities and any carbide phase, which shows no appreciable reaction between GN, CNTs and the Al_2O_3 matrix. Typical diffraction peaks of the monolithic Al_2O_3 with specific intensities were observed, which indicates crystalline $\alpha\text{-Al}_2\text{O}_3$ having a corundum rhombohedral phase

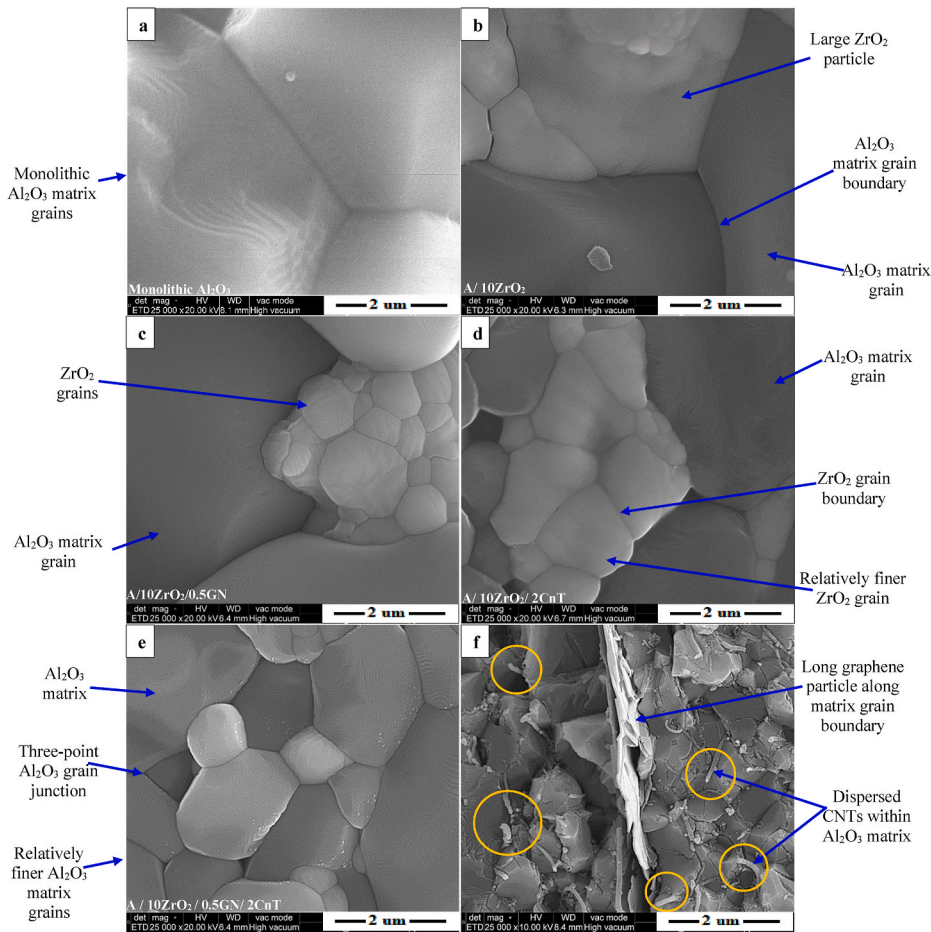


Fig. 2. FE-SEM micrographs showing the structures of hot-pressed nanocomposites (a) Monolithic Al_2O_3 (b) $\text{Al}_2\text{O}_3/10\text{ZrO}_2$ (c) $\text{Al}_2\text{O}_3/10\text{ZrO}_2/0.5 \text{ GN}$ (d) $\text{Al}_2\text{O}_3/10\text{ZrO}_2/2\text{CNTs}$ (e) $\text{Al}_2\text{O}_3/10\text{ZrO}_2/0.5\text{GN}/2\text{CNTs}$ (f) distribution of GN and CNTs structures within Al_2O_3 matrix.

(PDF#46-1212). However, these peak intensities changed with the addition of ZrO_2 , GN and CNTs. The Al_2O_3 – 10ZrO_2 nanocomposite (A10Z sample) with the addition of the 10 wt% ZrO_2 exhibited extra peaks, indicating the monoclinic (m - ZrO_2) and tetragonal (t - ZrO_2) phases observed initially at 17.5° and 30.3° respectively. Using the reflexes from the peaks in the XRD pattern, the content of the m - ZrO_2 and t - ZrO_2 were also estimated to be approximately 90% and 10% respectively (Table 2) [42]. With the addition of 0.5 wt%GN only to the Al_2O_3 – 10ZrO_2 (A10ZG sample), a new peak appearing at a diffraction angle of 26.3° was indexed as a typical crystalline graphite peak at plane (002). Further, a change in the m - ZrO_2 and t - ZrO_2 peaks was also evident, with slightly lower peak intensities of these phases upon the addition of the 0.5 wt%GN. The m - ZrO_2 and t - ZrO_2 amounts were also calculated to be 84% and 16% respectively. However, no clear graphitic peak was observed when 2 wt%CNTs only was added to Al_2O_3 – 10ZrO_2 (A10ZCN sample), even though the ZrO_2 phases were exhibited with relatively decreased intensities in most of their respective major peaks. 95% and 5% were the estimated m - ZrO_2 and t - ZrO_2 contents in the A10ZCN sample. The absence of the graphitic phase peak despite the addition of 2 wt%CNTs, which had relatively higher concentration than the 0.5 wt%GN could be ascribed to the easy detectability of the platelet graphene structure at plane (002) by the XRD [30]. A distinct graphitic peak was however revealed at similar diffraction angle of 26.3° when both GN and CNTs were combined in the Al_2O_3 – 10ZrO_2 structure (A10ZGCN sample). Also, the m - ZrO_2 and t - ZrO_2 phases with approximate amounts of 98% and 2% respectively, as well as the α - Al_2O_3 peak intensities were mildly decreased in the A10ZCN sample with respect to that of the monolithic Al_2O_3 and A10Z samples, but were relatively

higher when compared to that of the A10ZG and A10ZCN samples.

3.2. Mechanical properties: fracture toughness and bending strength

Grain size, morphology, structural features, and their distributions within the matrix influence the mechanical response of the prepared nanocomposites. Fig. 4 shows the trend of the Al_2O_3 matrix grain size on the micro-hardness property, with the fine-grained structures achieving higher micro-hardness values. The variation of the estimated crystallite sizes which shows similar trend as the average grain size with the measured micro-hardness (in GPa) is also shown in Fig. 4.

The results from the fracture toughness (K_{IC}) tests of the nanocomposites, as estimated from SENB and DCM methods are shown in Table 3 and Fig. 5. Schematic of the hardness test, as well as the crack extensions from indents on the samples' surface during the microhardness tests are illustrated in Fig. 5a and b. Generally, the K_{IC} values from the DCM were relatively higher than that of the SENB test for each sample measured. However, from Fig. 5c, it can be shown that similar trend in the toughness behaviour was demonstrated by both the SENB and DCM methods. For the SENB test, approximately $3.06 \text{ MPa m}^{1/2}$ was recorded for the monolithic Al_2O_3 sample. With the addition of only 10 wt% ZrO_2 to the monolithic Al_2O_3 (A10Z sample), this value increased to $4.88 \text{ MPa m}^{1/2}$, representing an increment of 60%. Sample A10ZG, with 0.5 wt%GN addition to the Al_2O_3 – 10ZrO_2 also revealed about 56% increase in the toughness values in reference to the monolithic Al_2O_3 but 4% lower than that of the A10Z sample. Therefore, addition of 0.5 wt% GN only to the Al_2O_3 – 10ZrO_2 did not necessarily improve the K_{IC} value, as compared to that of the A10Z sample with only 10 wt% ZrO_2 .

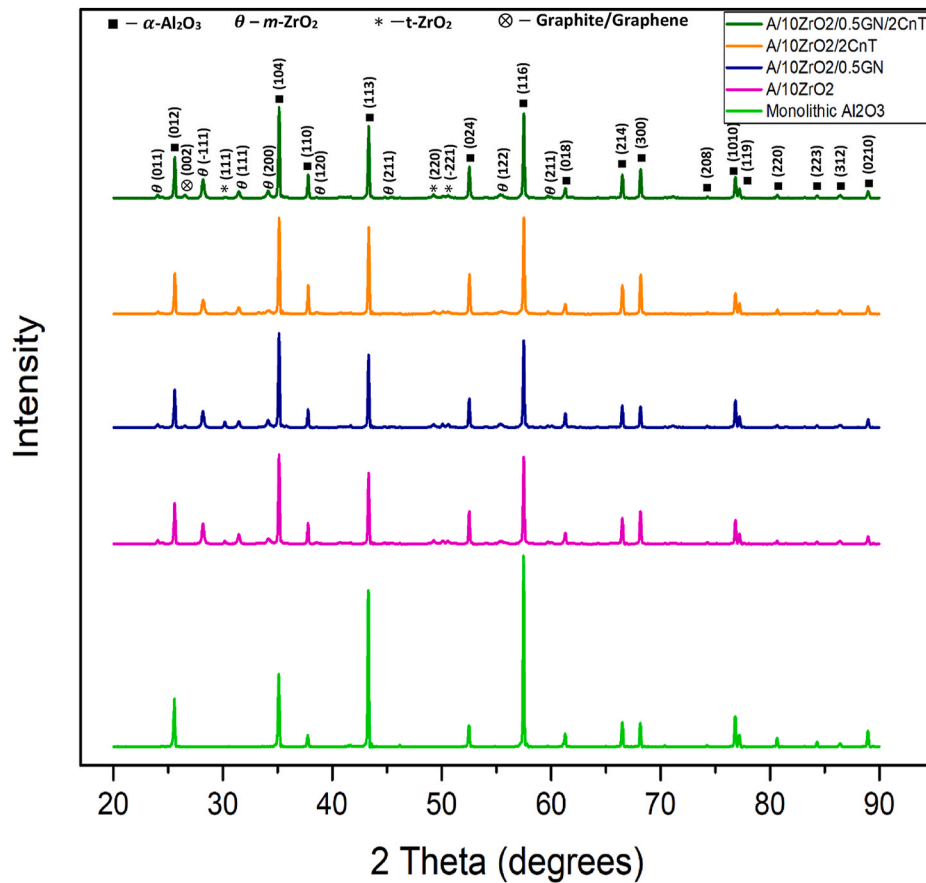


Fig. 3. XRD of the prepared monolithic Al₂O₃ and its nanocomposites depicting the ZrO₂ phases.

Table 2

Monoclinic(m) and Tetragonal (t) ZrO₂ phase contents estimated from XRD data.

Sample ID	ZrO ₂ content (wt%)	Monoclinic content (%) (V _{m-ZrO2})	Tetragonal content (%) (V _{t-ZrO2})
Pure A	0	0	0
A10Z	10	90	10
A10ZG	10	84	16
A10ZCN	10	95	5
A10ZGCN	10	98	2

However, a drastic 95% increase in the toughness with respect to the parent Al₂O₃ was realized when 2 wt%CNs was added to the Al₂O₃–10ZrO₂ (A10ZCN sample), as well as a 20% and 18% increment when compared to the A10Z and A10ZG samples respectively. A combined addition of 0.5 wt%GN and 2 wt%CNs to the Al₂O₃–10ZrO₂ yielded the highest fracture toughness value (up to 6.83 MPa m^{1/2}) representing an approximate increase of 123% with respect to the reference monolithic Al₂O₃, with approximate 43%, 40% and 14% increase in reference to the A10Z, A10ZG and A10ZCN samples respectively. Table 3 and Fig. 5 also show an increment in the respective K_{IC} values of the nanocomposites in reference to the monolithic Al₂O₃, via the direct crack measurement (DCM) method using the Niihara equation. The average DCM K_{IC} value of the monolithic Al₂O₃, which was registered as 3.39 MPa m^{1/2}, was immensely improved to 7.27 MPa m^{1/2} (increase by up to ~115%) for the A10Z sample. In addition, an enhancement of 97% and 123% respectively was recorded for the A10ZG and A10ZCN samples with DCM K_{IC} values of 6.69 MPa m^{1/2} and 7.55 MPa m^{1/2}, which was also benchmarked with that of the parent Al₂O₃. The DCM K_{IC} value for the A10ZGCN sample with the incorporation of both 0.5 wt%GN and 2 wt%CNs was also evaluated to be 8.78

MPa m^{1/2}, registering an approximate 159% increase as compared to the monolithic Al₂O₃. The evaluated toughness from the DCM values technique correlates well with that of the SENB test, with the A10ZGCN sample achieving the highest K_{IC} values in both cases.

The bending/flexural strength (σ_f) values of the fabricated nanocomposite with respect to the multi-material added was also illustrated in Table 3. Fig. 6 displays the bending strength of the nanocomposites as a function of the added ZrO₂, GN and CNTs combinations. As can be shown from Table 3 and Fig. 6, the bending strength increases from 259 MPa for the monolithic Al₂O₃ and reaches a maximum of 483 MPa for the A10ZGCN sample. Compared to the monolithic Al₂O₃, the A10Z sample exhibited a 22% increase, with a calculated bending strength value of 317 MPa. When 0.5 wt%GN was added to the Al₂O₃–10ZrO₂, an improved value strength value of 325 MPa was produced by the A10ZG sample. This shows an approximate increase of 26% and 3% with respect to the monolithic Al₂O₃ and A10Z samples respectively. However, with the addition of 2 wt%CNs to the Al₂O₃–10ZrO₂, a drastic increase of 44% in the bending strength of the A10ZCN sample was realized, as value improved to 460 MPa against the registered 259 MPa of the monolithic Al₂O₃. In comparison to the A10Z and A10ZG samples, there was a relative increase of 31% and 29% respectively. Sample A10ZGCN, having both GN and CNTs demonstrated an increase of 46%, with an approximate 34%, 33% and 5% increments in reference to the A10Z, A10ZG and A10ZCN samples respectively. Therefore, similar to the fracture toughness behaviour, the combined addition of GN and CNTs enhanced the bending strength of the nanocomposites, achieving maximum values in both cases. Also, it can be inferred that the improvements in the mechanical properties are greatly influenced by the addition of the CNTs to the Al₂O₃–10ZrO₂ more than the GN, as can be seen in Table 3 and Figs. 5 and 6.

Fig. 7 shows the FE-SEM micrographs of the fractured surfaces of the

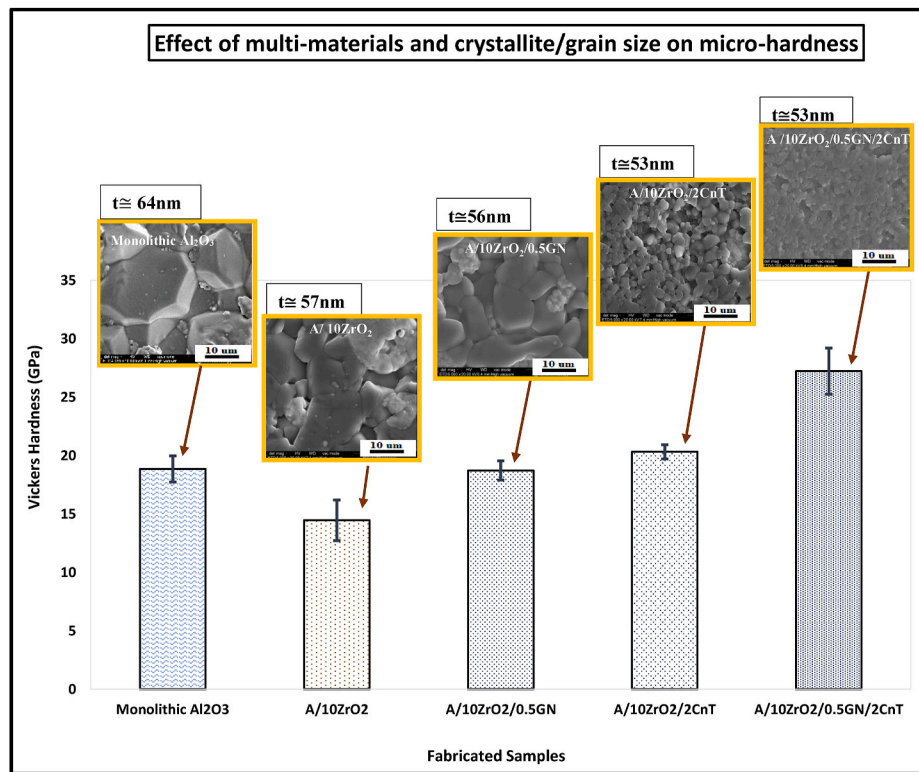


Fig. 4. Effect of grain size/crystallite size on micro-hardness of fabricated nanocomposites.

Table 3
Mechanical properties of Al₂O₃/ZrO₂ multi-material nanocomposites.

Sample ID	Fracture toughness, K_{IC} (MPa.m ^{1/2}) SENB	Fracture toughness, K_{IC} (MPa.m ^{1/2}) Niihara eqn.	Bending/flexural strength, σ_f (MPa)
Pure A	3.06 ± 0.15	3.39 ± 0.60	259 ± 14.74
A10Z	4.88 ± 0.21	7.27 ± 1.48	317 ± 32.94
A10ZG	4.78 ± 0.18	6.69 ± 1.37	325 ± 30.95
A10ZCN	5.97 ± 0.22	7.55 ± 1.29	460 ± 51.16
A10ZGCN	6.83 ± 0.19	8.78 ± 0.67	483 ± 69.22

processed nanocomposites. Details of the fracture morphology of each nanocomposite have been illustrated using both high and low magnification fractographs, which also depict the evolution of the grain size of the reference Al₂O₃ with the addition of ZrO₂, GN and CNTs. As most monolith ceramics, a typical brittle fracture mode of the reference Al₂O₃ was clearly observed (Fig. 7a). In addition, there appears to be an intergranular fracture with few micro-cracks and facets with smooth surfaces illustrating the brittle fracture behaviour of Al₂O₃. Fig. 7b also demonstrates the fracture surfaces of the A10Z samples. Both brittle and ductile fracture were identified in the A10Z sample, which also had fine and coarse ZrO₂ particles distributed within the Al₂O₃ matrix grains. The ductile fracture was observed mostly on the coarse ZrO₂ particle facets which was inspired by the transgranular fracture mode during the bending tests. Meanwhile, some of the fine globular shaped ZrO₂ particles appear to be completely removed from matrix grains leaving remnant cavities within the matrix structure. The brittle fracture of the matrix is as a result of the typical intergranular fracture of the matrix. For the fractograph of the A10ZG sample, which had both ZrO₂ and GN particle additions, a relatively finer structure was evident with smooth matrix grain surfaces and rough patches on the coarse ZrO₂ particle surfaces after fracture, confirming both brittle and ductile fractures (Fig. 7c and d). Also, the GN particles are seen dispersed on the matrix

grain boundaries, and around sites with propagating micro-cracks and micro-pores (Fig. 7d). The intergranular fracture with few transgranular ones were responsible for the removal of the matrix grains, as well as the coarse ZrO₂ particles. Fig. 7e shows the fractured surface of the A10ZCN sample depicting both intergranular and transgranular mode of fracture. Segregation of the CNTs were mostly on the matrix junctions, covering the length of the matrix grains, with others sticking out as a result of the pulling-out actions during the bending tests. Moreover, most of the ZrO₂ particles in the A10ZCN sample were relatively finer as compared to the A10Z and A10ZG samples. The uniform distribution of the CNTs were also evident in the fractured surface of the A10ZGCN sample, which was characterized with both intergranular and transgranular fractures. Even though most of the matrix grain boundaries were covered with CNTs (including the pulled-out CNTs) in the A10ZGCN sample, there were few sites with the dispersed GN particles which was fairly surrounded with grain boundary CNTs. The ZrO₂ particles showing ductile fractured surface was also observed in the A10ZGCN sample having a combined addition of ZrO₂, GN and CNTs.

3.3. Mechanical properties: toughening mechanisms

High magnification FE-SEM fractographs also demonstrate the toughening mechanisms by the reinforcement particles in the Al₂O₃ matrix. GN sheet pull-outs were observed in the fractured surfaces of the multi-material nanocomposites (Figs. 1f, 7c and 7d). Fig. 8 also demonstrates the pull-out actions by the CNTs within the matrix structure. Both short and long strands of the pulled-out CNTs were protruded mostly from the grain boundaries of the matrix (Fig. 8a-b). In addition, whilst some pulled-out CNTs appeared to be thin, other CNTs (mostly the short strands) were thicker and seem to be covered with the matrix material (Fig. 8c-d). The matrix-coated CNTs were also located on some parts of the matrix boundaries, with others glued to the matrix grains. Bridging and arrest of propagating cracks were also exhibited by both the pulled-out and glued CNTs within the multi-material nanocomposites (Fig. 8b and c).

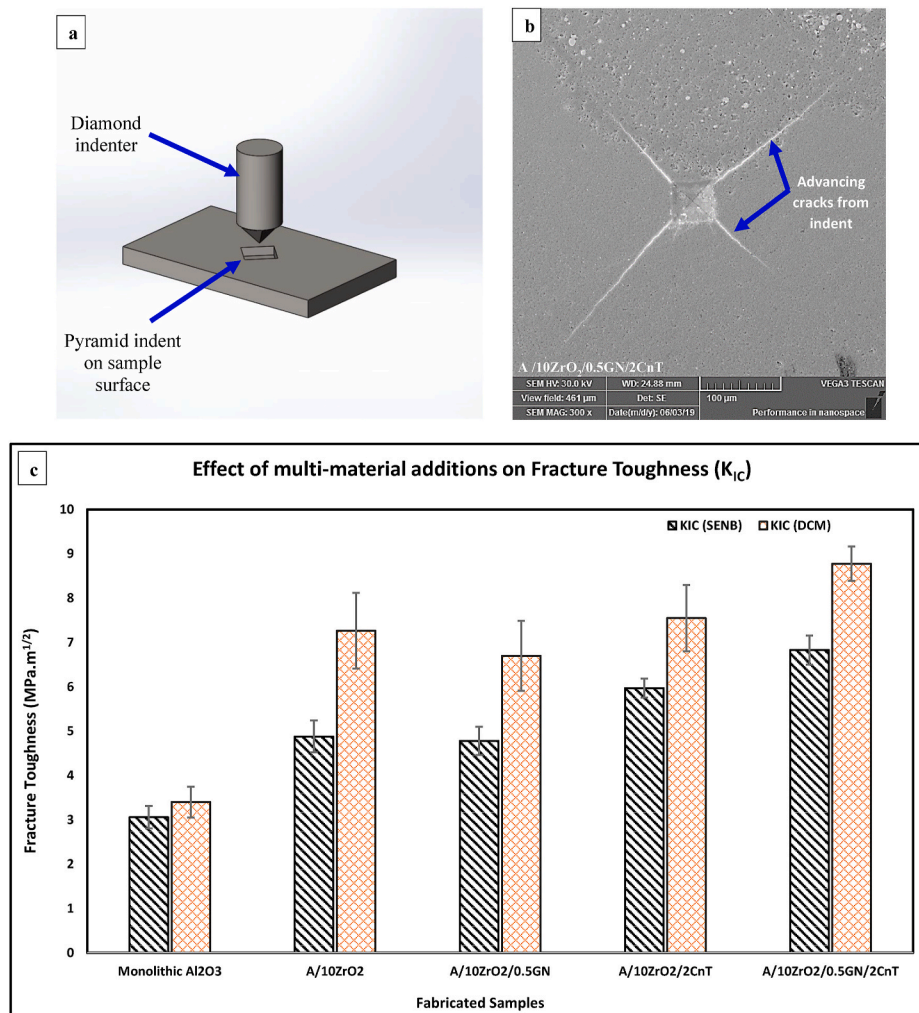


Fig. 5. (a) Vickers hardness testing illustration (b) Example of indent with emanating cracks (c) Effect of multi-material addition on fracture toughness (K_{IC}) of nanocomposites as measured by SENB and DCM methods.

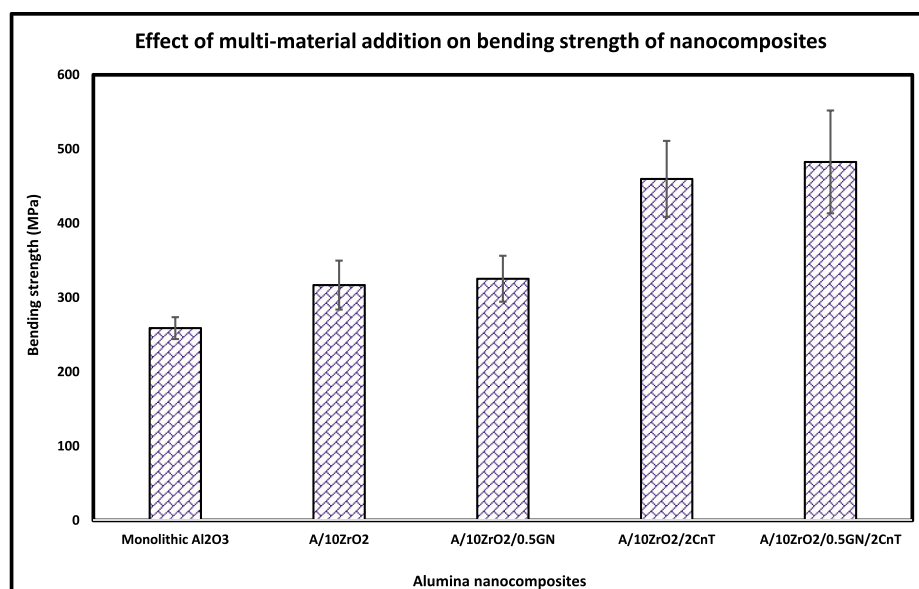


Fig. 6. Variation of the multi-material additions on the bending strength of the Al₂O₃-based nanocomposites.

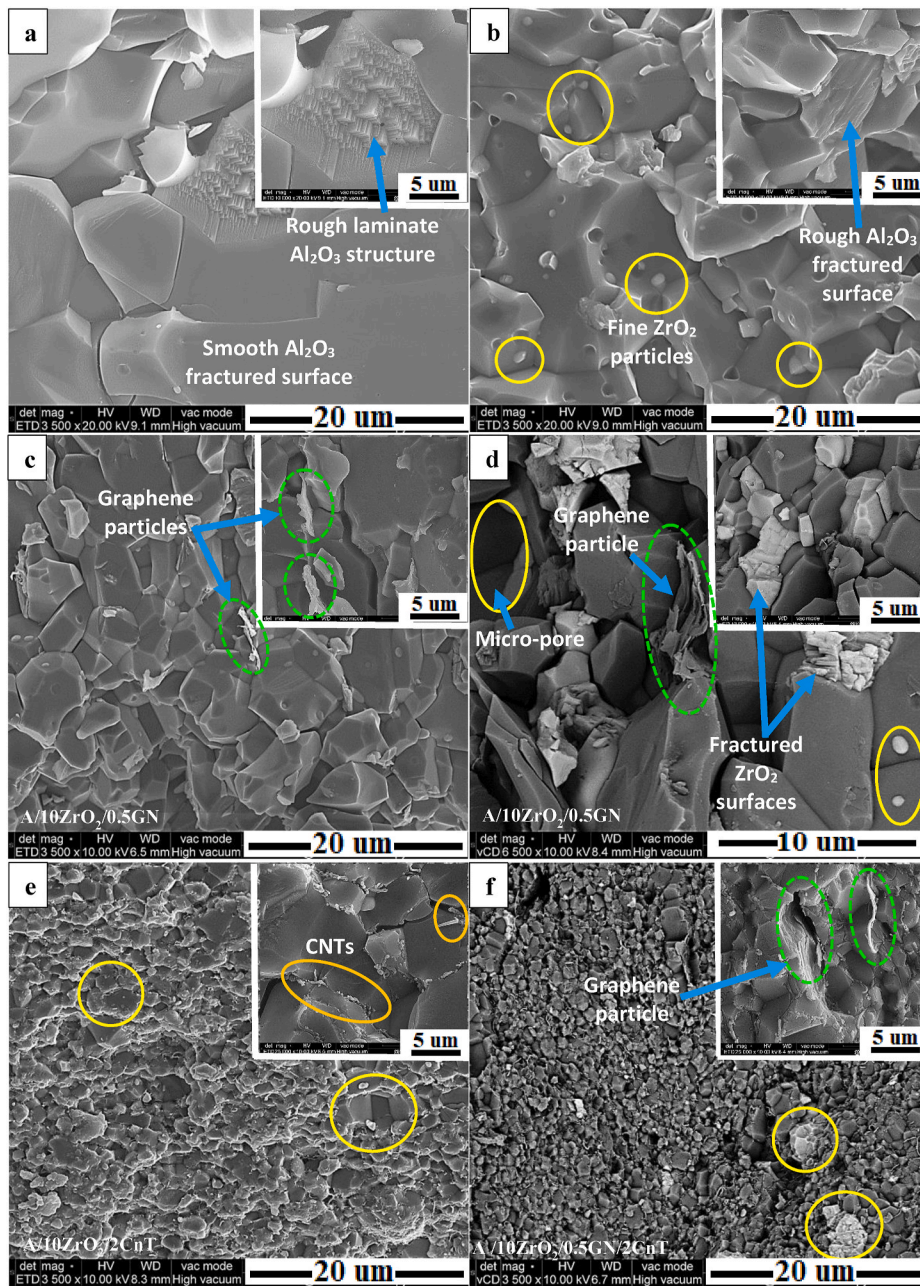


Fig. 7. SEM fractographs showing various intergranular and transgranular fracture modes predominant in (a) monolithic Al_2O_3 (b) $\text{Al}_2\text{O}_3/10\text{ZrO}_2$ (c)-(d) $\text{Al}_2\text{O}_3/10\text{ZrO}_2/0.5 \text{ GN}$ (e) $\text{Al}_2\text{O}_3/10\text{ZrO}_2/2\text{CNTs}$ (f) $\text{Al}_2\text{O}_3/10\text{ZrO}_2/0.5\text{GN}/2\text{CNTs}$ samples.

4. Discussion

4.1. Effect of ZrO_2 , GN and CNTs on grain structure

The retention of the monolithic Al_2O_3 grain structure after sintering is dependent on the selected sintering parameters including the temperature (1600 °C), applied pressure (60 MPa) and exposure time (1 h). These optimized sintering conditions generate highly dense monolithic Al_2O_3 and its nanocomposites [50,51]. Fabricating nanocomposites with densities near the theoretical value plays an ideal role in influencing the mechanical properties. The density values in Table 1 also show an overall well dispersed GN and CNT structures within the Al_2O_3 matrix. The FE-SEM fractographs also reveal the nature of dispersion of both the CNT bundles and GN particles which, were mostly residing on the matrix grain boundaries, with few within the matrix grains. Further, their distribution depicts low agglomeration of the carbonaceous particles,

especially the CNT bundles, which often render undesirable properties of the processed nanocomposites such as micro-pores, as reported by most studies [25,52,53]. The tendency for both GN and CNTs to rest on the matrix boundaries is directly responsible for the drastic grain size reduction of the monolithic Al_2O_3 matrix, as well as the added ZrO_2 grains, as previously discussed [43]. In addition, the XRD patterns also confirm the structures and phases of monolithic Al_2O_3 and the added ZrO_2 after the hot-press sintering. The XRD detection of the graphite phase at (002) plane shows that the structural integrity of the GN was not necessarily compromised during the high temperature sintering stage. The estimated crystallite sizes from the XRD patterns also depict the matrix refinement with the addition of ZrO_2 , GN and CNTs. It is perceived that this refinement is accompanied with slight broadening of the diffraction peaks according to the Scherrer's equation, which inversely relates the peak width (broadening) with the crystallite sizes, as seen in Table 1 [54,55].

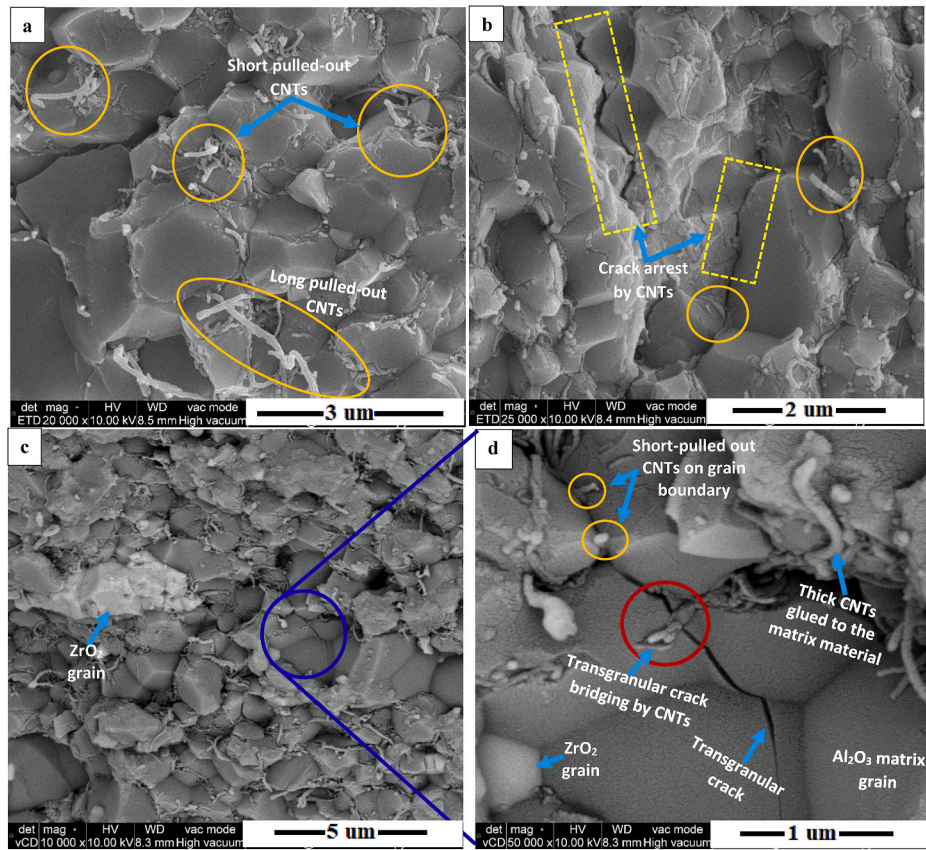


Fig. 8. FE-SEM fractographs demonstrating toughening mechanisms within multi-material nanocomposites.

4.2. Mechanical properties

4.2.1. Comparing measured SENB and DCM fracture toughness (K_{IC}) values

Fracture toughness (K_{IC}) values reported by the direct crack measurement (DCM) method were the highest, as compared to the ones by the single edge notched beam (SENB) technique. The relatively lower K_{IC} values from the SENB method were anticipated since these K_{IC} values are mostly dependent on the geometry (length, width and thickness) and the notch depth of the sample [47]. In addition, studies have also shown that the DCM method presents some restrictions and reliability issues due to the fact that the DCM fracture toughness (K_{IC}) values are obtained from indents and cracks at different locations on the fabricated nanocomposite surface. Ideally, the hot-pressed nanocomposites do not have a perfect uniform microstructure and distribution of reinforcement particles on the surface, which means there is a high tendency to indent at regions without significant reinforcement particles such as ZrO_2 , GN and CNTs. Therefore, the estimated K_{IC} values from DCM tend to have high range of errors relative to the SENB method [56–59]. For the current studies however, a fairly increasing trend in the K_{IC} values as a function of the added ZrO_2 , GN and CNTs reinforcement particles were observed for both the SENB and DCM methods (Fig. 5c). Similar trends for the SENB and DCM estimated K_{IC} values are also reported in literature for prepared Al_2O_3 -based composites, where higher values of K_{IC} were recorded by the DCM or indentation methods as compared to the conventional SENB approach (Table 4).

4.2.2. Effect of ZrO_2 , GN and CNTs on mechanical properties of nanocomposites

Grain size and hardness have a good correlation as proposed by the Hall-Petch equation. Fine-grained structures generally improve the hardness of ceramic composites due to the presence of significant

Table 4

Example of fracture toughness (K_{IC}) values of Al_2O_3 -based composites measured by SENB and DCM methods, as reported in literature.

Prepared Al_2O_3 composite	Fabrication technique	Measured fracture toughness, K_{IC} (MPa.m ^{1/2})			Literature references
		SENB method	DCM	Approximate % difference	
Monolithic Al_2O_3	HP @1600 °C for 60mins	3.06	3.39	↑ 11%	Current work Current work
Al_2O_3 /10 wt % ZrO_2		4.88	7.27	↑ 49%	
Pure Al_2O_3	HIP @ 1660 °C	3.8	3.9	↑ 3%	[60]
Al_2O_3 /10 wt % ZrO_2		4.5	5.2	↑ 16%	
Pure Al_2O_3	SPS @1400 °C for 10mins	2.8	~3.3	↑ 18%	[22]
Al_2O_3 /0.5 wt%CNTs		7.9	9.1	↑ 15%	
Pure Al_2O_3	HIP @ 1650 °C	3.75	3.72	↓ 0.8%	[61]
Al_2O_3 /10 wt % ZrO_2		4.68	5.00	↑ 7%	

NB: HP-Hot Pressing; HIP-Hot Isostatic Pressing; SPS-Spark Plasma Sintering.

amount of grain boundaries as compared to the monolithic ceramic structures [62,63]. The addition of the reinforcement particles such as GN and CNTs immensely refines the Al_2O_3 matrix with high amount of grain boundaries housing these reinforcement particles in the multi-material nanocomposite system (Figs. 2 and 5). Therefore, during Vickers micro-hardness test, the indents are mostly made on these hard-boundary structures within the refined ceramic structure, where there are significant load-transfer actions, which consequently improves

the overall hardness of the nanocomposites. It is noteworthy that the addition of only 10 wt%ZrO₂ to the Al₂O₃ matrix gave a reduced hardness value due to the soft nature (low hardness) of the relatively coarser ZrO₂ particles, as discussed in previous studies [42,43]. With the addition of GN and CNTs, the added ZrO₂ particles are equally refined with more grain boundaries that contribute to the hardness enhancement of the Al₂O₃–10ZrO₂ nanocomposites during indentation.

The relationship of grain size with fracture toughness (K_{IC}) and bending strength (σ_f) is not always obvious as compared to hardness. In addition to the refined grain structures, the individual and combined mechanical attributes of the added ZrO₂, GN and CNT particles and their mechanisms, including the effect on crack propagation directly account for the enhancement in the toughness and strength properties of the prepared multi-material nanocomposites. Typically, during bending tests, the grain boundaries of the monolithic ceramics become susceptible to crack propagation, which leads to the grain removal [64]. This intergranular crack movement causes the fractured surfaces to become very smooth since the whole grain or part of the grain structure is detached with relative ease, having little or no appreciable resistance or plastic deformation due to the absence of a tougher structures on the matrix grain boundaries (Fig. 7a). This elucidates the low fracture toughness value (K_{IC}) (up to $\sim 3.4 \text{ MPa m}^{1/2}$) reported by the hot-pressed monolithic Al₂O₃ sample, which is also corroborated by other studies [2, 22,24,25]. Illustration of a typical intergranular crack movement on the grain boundaries of the matrix is seen in the schematics of Fig. 9a–b. At another instance, some of the cracks tend to advance through the large Al₂O₃ ceramic matrix grains to cause localized fracture of the grains,

which is evidence of transgranular fracture accompanied with relatively high crack resistance as compared to the original grain boundaries. However, this was not very prevalent within the monolithic Al₂O₃ structure even though very few sites had rough patches showing signs of a transgranular fracture. In addition, the measured bending/flexural strength ($\sim 259 \text{ MPa}$) of the fabricated monolithic Al₂O₃ is also comparable to those reported by other authors [65,66]. The near-dense grain structure of after hot-press sintering Al₂O₃ can account for the inherent bending strength in Al₂O₃ [67]. Table 5 gives a summary of the mechanical properties of prepared Al₂O₃ ceramic and its composites from other studies using different fabrication routes.

Meanwhile, conventional toughening mechanisms by the ZrO₂, GN and CNTs were illustrated from the fractured surfaces, which directly account for the enhanced mechanical properties. In addition to matrix grain pinning that restricted the grain movement and yielded refined grain structures, the toughening role of the added 10 wt%ZrO₂ to monolithic Al₂O₃ was obvious in the A10Z sample. The increase in K_{IC} value can be ascribed to the transformation toughening ($t\text{-ZrO}_2$ to $m\text{-ZrO}_2$) and micro-cracking in the presence of the applied stress, which has been previously discussed [42]. The rough fractured surface of the coarse ZrO₂ particles has been attributed to crack deflection by the ZrO₂ particles which is accompanied with high fracture toughness [68]. Relative increase in the bending strength can also be ascribed to the refined grain structure in accordance to the Hall-Petch relation [67,69]. Meanwhile, the impaired K_{IC} value with the addition of 0.5 wt%GN to the Al₂O₃–10ZrO₂ (A10ZG) can be accustomed to the limited $m\text{-ZrO}_2$ content and presence of micro-pores. This can also be confirmed from

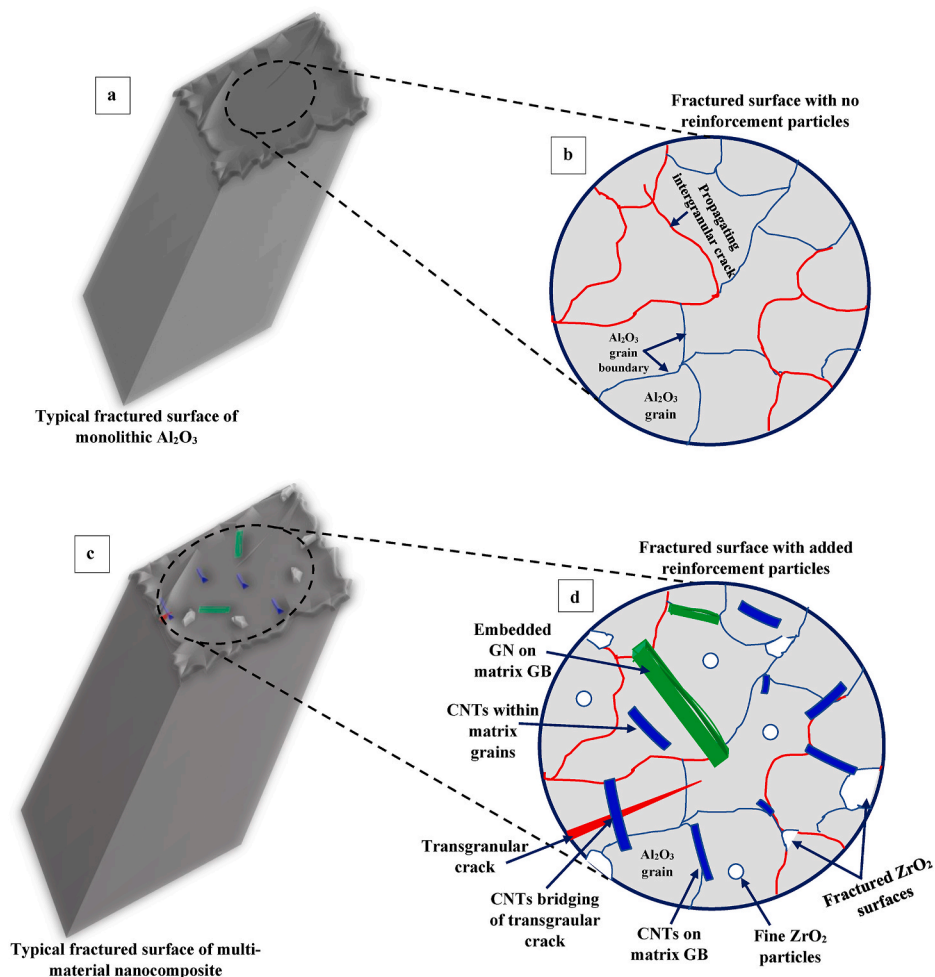


Fig. 9. Schematics of toughening mechanisms by fabricated monolithic Al₂O₃ and nanocomposites (a)–(b) fractured surface of monolithic Al₂O₃ without any reinforcement particles (c)–(d) fractured surface of nanocomposites reinforced with ZrO₂, GN and CNTs.

Table 5Reported literature values on mechanical properties of prepared Al₂O₃-based composites.

Prepared Al ₂ O ₃ composite	Fabrication technique	Reported mechanical properties			Literature references
		Hardness (GPa)	Fracture toughness (MPa.m ^{1/2})	Bending strength (MPa)	
Pure Al ₂ O ₃	HIP @ 1650 °C	18.3	3.8	—	[61]
Al ₂ O ₃ /10 wt%ZrO ₂		18.2	4.7	—	
Pure Al ₂ O ₃	PS @1600 °C for 120mins	14.3	4.2	425	[38]
Al ₂ O ₃ /20 wt%ZrO ₂		12.4	4.6	403	
Al ₂ O ₃ /10 wt%ZrO ₂ /0.5 wt%CNTs		14.5	5.1	448	
Pure Al ₂ O ₃ /ZrO ₂ (ZTA)	SPS @1550 °C for 3mins	17.5	6.5	—	[23]
ZTA/0.81 vol%GN		16.1	9.1	—	
Pure Al ₂ O ₃	HP @ 1600 °C for 60mins	16.2	3.1	—	[40]
Al ₂ O ₃ /8 vol%ZrO ₂		14.8	4.6	—	
Al ₂ O ₃ /8 vol%ZrO ₂ /4 vol%CNTs		18.3	6.7	—	
Pure Al ₂ O ₃	PS @1600 °C for 120mins	17.5	3.6	~225	[65]
Al ₂ O ₃ /0.3 vol%MWCNTs		~21	~4.5	250	
Pure Al ₂ O ₃	HP @1650 °C for 60mins	~16	3.5	~360	[30]
Al ₂ O ₃ /0.5 wt%GN		~15.8	5.5	~380	
Al ₂ O ₃ /0.5 wt%GN/1 wt%CNTs		~17	5.7	424	
Pure Al ₂ O ₃	SPS @1500 °C for 10mins	18.2	2.4	—	[28]
Al ₂ O ₃ /1 wt%CNTs		17.4	6.4	—	
Al ₂ O ₃ /1 wt%CNTs/0.5 wt%GN		16.7	8.3	—	
Pure Al ₂ O ₃	SPS @1500 °C for 3mins	16.4	4.9	~410	[26]
Al ₂ O ₃ /0.2 wt%GN/1 wt%CNTs		19.6	~6.8	767	
Al ₂ O ₃ /0.4 wt%GN/1 wt%CNTs		~15.8	~7.3	~500	
Pure Al ₂ O ₃	HP @1600 °C	16.4	3.1	—	[74]
Al ₂ O ₃ /4 wt%ZrO ₂		14.6	4.6	—	
Al ₂ O ₃ /4 wt%ZrO ₂ /0.5 wt%GN		19.3	7.9	—	

NB: PS-Pressureless Sintering; HP-Hot Pressing; HIP-Hot Isostatic Pressing; SPS-Spark Plasma Sintering.

the XRD estimations of the ZrO₂ phases which gave approximately 16% *t*-ZrO₂ with 84% *m*-ZrO₂ for the A10Z sample as compared to the 90% *m*-ZrO₂ and 10% *t*-ZrO₂ of the A10ZG (Table 2). Therefore, it can be inferred that the transformation toughening of the Al₂O₃-10ZrO₂ might be slightly restricted with the dispersion of the 0.5 wt%GN within the structure, which can hinder the expected enhancement of the fracture toughness. With the added GN having high affinity for the matrix grain boundaries, the obvious restriction to advancing cracks were eminent, which can improve the toughness value of the nanocomposites. Figs. 2(f) and 7(c) and the schematics in Fig. 9d demonstrates that both large and small pull-out GN sheets resides preferably on the boundaries to resist the intergranular crack propagation and improve the load-bearing capabilities of the A10ZG sample. This also increases the bending strength since the propagation of cracks through the grains would require more energy to overcome or bend the embedded GN particles, which demonstrate a good interfacial bonding of the matrix and the GN structures. However, the toughening mechanisms might be slightly impeded in the presence of the micro-pores (Fig. 7d) which serve as preferential sites for nucleation of cracks and propagation [25,27]. Liu et al. also related the slight decline in fracture toughness to the presence of pores due to the re-stacking behaviour of the added 1.33 vol%Graphene nanoplatelets (GNPs) to Al₂O₃ matrix [25]. The significant increase in the toughness value of the A10ZCN sample, with the addition of the 2 wt%CNTs (up to 95% for SENB and 123% for DCM relative to monolithic Al₂O₃) could be directly acclaimed to the homogeneous distribution of the CNTs, and predominant mechanisms including crack bridging and pull-outs by the CNTs. The long and short pulled-out CNTs also indicate a strong matrix-CNTs interfacial bonding even in the presence of an appreciable stress during the bending tests, which also

demonstrates the elastic deformation of the tough CNTs within the fractured surface [28,70]. Further, the CNTs which are glued to the Al₂O₃ matrix, as seen from Fig. 8d, can also serve as a source of toughening in the A10ZCN structure, since they illustrate good bonding between the matrix grains. This mechanism can therefore increase the amount of energy needed for the CNT pull-outs, and thereby improve the toughening within the structure. A mixture of intergranular and transgranular failure modes which was also observed in the fractured surface of the A10ZCN can be attributed to the crack bridging and arrest at the CNTs within the Al₂O₃ matrix grains and the grain boundaries (Fig. 8b and c). As illustrated in the schematics of Fig. 9d, the CNT-induced crack bridging limits further widening of the advancing micro-cracks within the grain to cause a transgranular fracture. This is best demonstrated by the glued and matrix-coated CNTs bridging these cracks in Fig. 8d. Crack arrest by the grain boundary CNTs also resist crack propagation along the matrix grains to cause the complete grain removal, and thus increase the amount energy to penetrate the CNT structures. Arguably, the ZrO₂ particles might also contribute to the overall increased toughness value of the A10ZCN sample. Contrary to the A10ZG sample, the addition of CNTs led to a significant *t-m* ZrO₂ transformation (~95%*m*-ZrO₂ and ~5% *t*-ZrO₂), which means toughening by the phase transformation of the ZrO₂ particles might be possible in the A10ZCN sample. Magnani demonstrated a direct correlation between the monoclinic (*m*-ZrO₂) content and the fracture toughness value of ZrO₂-based materials [71]. Therefore, a higher monoclinic content means higher rate of tetragonal phase transformation during fracture with an increase in the fracture toughness value. The improved bending strength (up to 460 MPa) of the A10ZCN sample is also due to the fine-grained structure together with the previously outlined mechanisms, which increases the overall

dissipation of energy during bending and fracture of the nanocomposite. CNTs have more effective pull-out and bridging strengthening mechanisms in ceramic structures than GN during bending [72,73], which can be directly linked to the interfacial bonding strength of the CNTs and the matrix, as can be illustrated in Fig. 8.

The drastic rise in the mechanical properties with the addition of both 0.5 wt% and 2 wt% CNTs to the Al_2O_3 -10ZrO₂ can be linked to the good coordination of the carbonaceous structures. Good dispersion of both GN and CNTs within a matrix is assumed to hold several merits on the resulting microstructure and mechanical performance such as bending/flexural strength, hardness and fracture toughness. This inspiration originates from the potential synergy and complementary effect they offer during the simultaneous dispersion and mixing of both GN and CNTs within the Al_2O_3 or ceramic matrix [27,28,30]. Yazdani suggested in his works that the CNT agglomeration and re-stacking of GN which often leads to pore formation during fabrication can be minimized by the complementary action of the carbon nanostructures, as CNTs tend to occupy GN gaps to limit the re-stacking due to their geometries [27,30]. This potentially can confer high mechanical attributes to the fabricated nanocomposites by activating a synergy between the toughening and strengthening mechanisms of the combined GN and CNTs. Therefore, the maximum values recorded for the toughness ($\sim 6.8 \text{ MP m}^{1/2}$ for SENB and $\sim 8.8 \text{ MP m}^{1/2}$) and bending strength (483 MPa) with the combined addition of GN and CNTs can be attributed to the bridging, crack arrest and pull-out mechanisms that were operative within the Al_2O_3 -10ZrO₂ structure. Fig. 9d also depicts the simultaneous toughening and consequent strengthening behaviour by the GN and CNTs structures in the presence of migrating cracks on matrix grain boundaries and within the grains. In addition, similar to the Al_2O_3 -10ZrO₂ sample, the estimated m -ZrO₂ amount was relatively higher and could participate in the overall toughening of the multi-material nanocomposite. Therefore, the complementary roles of these additives can inspire high mechanical properties of the advanced Al_2O_3 -based ceramic for high performance applications.

5. Conclusion

The mechanical and fracture behaviour of Al_2O_3 -based multi-material nanocomposites prepared with the addition of 10 wt%ZrO₂, 0.5 wt%GN and 2 wt%CNTs have been assessed in the current studies. Combination of these reinforcement materials within the Al_2O_3 structure attracts many promising attributes by refining the matrix structure and activating mechanisms for enhancing the mechanical performance of the multi-material nanocomposites. In this work, improvement in the mechanical properties were realized in the fabricated multi-material nanocomposites primarily due to the homogeneous distribution of the reinforcement structures within the matrix material and refined grained structures, coupled with active strengthening and toughening mechanisms. Summary from the studies are as follows:

1. Hot-pressed monolithic Al_2O_3 with no additives had coarse grained-structure and a typical intergranular fracture mode along the grain boundaries with a measured fracture toughness (K_{IC}) (up to $\sim 3.1 \text{ MPa m}^{1/2}$ for SENB and $\sim 3.4 \text{ MPa m}^{1/2}$ for DCM), and bending strength of 259 MPa.
2. The mechanical properties Al_2O_3 -10 wt%ZrO₂ was relatively higher with SENB and indentation (DCM) fracture toughness values of $4.87 \text{ MPa m}^{1/2}$ and $7.27 \text{ MPa m}^{1/2}$, and bending strength of 317 MPa, which represent 60%, 115% and 22% respectively, in reference to the monolithic Al_2O_3 . This was primarily dependent on the ductile nature of the ZrO₂ phases, the refined grained structure of the Al_2O_3 matrix and ZrO₂ phase transformation toughening.
3. With the addition of 0.5 wt%GN to Al_2O_3 -10 wt%ZrO₂, the mode of fracture changed from intergranular with few transgranular fracture of the matrix and the ZrO₂ grains, with a slight 4% decrease in K_{IC} against the Al_2O_3 -10 wt%ZrO₂ but up to 56% increase when

compared to that of the monolithic Al_2O_3 . The presence of micropores could hinder the anticipated rise in toughness value (up to $8.78 \text{ MPa m}^{1/2}$) even though GN pull-outs action were operative. However, the dissipated energy during GN pull-out was responsible for the increase in the bending strength ($\sim 325 \text{ MPa}$) with the addition of the 0.5 wt%GN.

4. Meanwhile, the immense enhancement in the mechanical properties such as fracture toughness (up to $7.55 \text{ MPa m}^{1/2}$) with the addition of 2 wt%CNTs to the Al_2O_3 -10 wt%ZrO₂ is ascribed to the homogeneous dispersion, fine-grained structure, as well as the toughening and strengthening mechanisms including crack bridging, crack arrest and pull-out activities of the CNTs. The fusion of the CNTs to the matrix material also depicts good interfacial bonding which accounts for the high strength in the nanocomposite up to 460 MPa.
5. In addition to refined grain structure, the complementary roles and toughening mechanisms of the combined GN and CNTs within the Al_2O_3 -10 wt%ZrO₂ nanocomposite reached an improved fracture toughness by up to 123% and 159%, as measured from the SENB and DCM respectively. This therefore displays a good coordination of the carbon nanostructures which also demonstrated the highest value in the bending strength ($\sim 483 \text{ MPa}$). The effectiveness of this addition on the overall mechanical properties of the multi-material nanocomposites is attributed to the uniform dispersion of these nanophase structures in the Al_2O_3 matrix.

CRediT authorship contribution statement

Solomon Hanson Duntu: Conceptualization, Methodology, Software, Data curation, Writing – original draft, Investigation, Writing – review & editing. **Kenneth Hukpati:** Data curation, Writing – review & editing. **Iftikhar Ahmad:** Conceptualization, Methodology, Supervision. **Mohammad Islam:** Validation, Supervision. **Solomon Boakye-Yiadom:** Funding acquisition, Conceptualization, Supervision, Validation, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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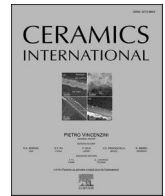
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Paper V: Combined Effect of Low ZrO₂ Content and Carbon Nanostructures on Mechanical and Wear Properties of Hot-Pressed Al₂O₃/ZrO₂ Hybrid Nanocomposites

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Combined effect of low ZrO₂ content and carbon nanostructures on mechanical and wear properties of hot-pressed Al₂O₃/ZrO₂ hybrid nanocomposites

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ABSTRACT

Al₂O₃/ZrO₂ systems with higher ZrO₂ amounts (≥ 20 wt%) are known to offer improved properties such as fracture toughness, but are restricted in their hardness, wear and strength performances. The incorporation of a third phase carbon nanostructure (such as CNTs and GN) to Al₂O₃/ZrO₂ reinforced with low ZrO₂ content (≤ 5 wt %) has emerged as a novel process to overcome this property trade-off by exploring the remarkable mechanical properties of these hybrid nanocomposite systems. Therefore, in the current work, colloidal mixing followed by hot-pressing process (@ 1600°C) were used to consolidate monolith Al₂O₃, Al₂O₃/ZrO₂, Al₂O₃/ZrO₂/CNTs and Al₂O₃/ZrO₂/GN nanocomposite structures using low ZrO₂ content (4wt%) and optimum amounts of CNTs (2wt %) and GN (0.5wt%) as the hybrid reinforcement phases. Microhardness, fracture toughness and flexural strength properties were improved from 19GPa, $\sim 3\text{MPa}\cdot\text{m}^{1/2}$ and $\sim 260\text{MPa}$ up to 24GPa, $\sim 7\text{MPa}\cdot\text{m}^{1/2}$ and $\sim 374\text{MPa}$ respectively, with hybrid additions of ZrO₂/CNTs and ZrO₂/GN to the monolith Al₂O₃. The primary source of the property enhancement in the hybrid nanocomposites was due to reduction in the matrix and ZrO₂ grain sizes (decreased up to $\sim 78\%$), good interaction between reinforcing phases and combined mechanisms such as crack bridging and deflection, matrix grain wrapping and grain gluing by CNTs and GN. The wear rate of the parent Al₂O₃ was also improved from $9.71 \times 10^{-5} \text{mm}^3/\text{N}\cdot\text{m}$ up to $0.81 \times 10^{-5} \text{mm}^3/\text{N}\cdot\text{m}$ (showing $\sim 92\%$ decrease) with ZrO₂/CNTs and ZrO₂/GN hybrid inclusions, which was attributed to the overall enhanced mechanical properties and wear resistant mechanisms during the dry sliding.

1. Introduction

In the last decades, the fabrication, microstructural design and properties of advanced ceramic-based composites have shown considerable interest in areas including biomedical and structural engineering [1,2]. A widely used structural ceramic-based composite is the Alumina-Zirconia or Zirconia Toughened Alumina (ZTA), which are designed to have a unique combination of a base alumina (Al₂O₃) matrix with dispersed zirconia (ZrO₂) phases. This is done as an attempt to improve the brittle nature of low density alumina ceramics [2,3]. The engineering perks of these composites including high strength, hardness, chemical inertness and resistance to abrasion properties, which make

them suitable for cutting tools and wearing parts, are further enhanced with an improvement in fracture toughness (K_{IC}) attributes derived from the distributed ZrO₂ reinforcements [4,5]. It has been shown that the addition of ZrO₂ can offer fracture toughness values up to $12\text{MPa}\cdot\text{m}^{1/2}$ and higher, as compared to that of the parent Al₂O₃ matrix material (estimated at $\sim 3\text{MPa}\cdot\text{m}^{1/2}$) [6,7]. These blends of mechanical properties make Al₂O₃/ZrO₂ composites relevant structural materials for biomedical applications including knee and hip joint prosthesis, as well as other high temperature engineering applications [8]. For Al₂O₃/ZrO₂ system, the overall mechanical performance is a function of the ZrO₂ content and their nature of distribution within the Al₂O₃ matrix. With the Al₂O₃ matrix contributing hardness and strength to the composite,

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the substantial improvement in the toughness is determined by the homogeneous dispersion and toughening mechanisms of ZrO_2 when optimal amount is added to the matrix [8–10]. Several studies have highlighted micro-cracking and phase transformation as the major mechanisms of toughening by the ZrO_2 inclusions. The tetragonal ($t\text{-ZrO}_2$) to monoclinic ($m\text{-ZrO}_2$) phase transformations are mostly inspired under mechanical stress when the ZrO_2 particles are fairly dispersed within the matrix phase [10]. This martensitic transformation is also accompanied with a volume expansion (about 3%) which tend to exert compressive stress on the parent Al_2O_3 matrix grains to minimize crack expansion, thereby improving the toughness of the composite structure [7,11]. This mechanism, coupled with the micro-cracking phenomenon in the presence of applied stress contribute to the overall toughness of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites.

For the remarkable mechanical attributes of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite systems to be fully experienced, an optimum concentration of the nano ZrO_2 particles are needed to reinforce the matrix material. Studies however have shown that, regardless of the toughening effect of ZrO_2 , the hardness and wear properties are sometimes deteriorated when larger amounts of the ZrO_2 ($\geq 20\text{wt}\%$) are included within the parent Al_2O_3 matrix [12,13]. For instance, it has been demonstrated that increasing the ZrO_2 content ($\geq 20\text{wt}\%$) results in thickening of the ZrO_2 grains rather than refining the Al_2O_3 matrix grains, thus rendering the refining capabilities of ZrO_2 all but ineffective [5]. Furthermore, the quest to create a tougher composite structural material by reinforcing with large amount of ZrO_2 phases often comes at the expense of the desired strength, which can limit potential engineering applications of the fabricated $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite materials [14]. For instance, microcracking toughening, which is inspired when large inclusions of ZrO_2 is added in ZTA generates tougher composite structures whilst restricting the strength properties [7,9]. Also, inhomogeneous ZrO_2 phase distributions within the parent Al_2O_3 material, as a result of the processing techniques contribute to the decline in the wear, hardness and other mechanical properties of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites [15–17]. Rao et al. showed in their recent studies that mechanical properties such as hardness decreased from 17.45 GPa to 15 GPa (representing an approximate decline of 14%) when 10wt% ZrO_2 was added to the monolithic Al_2O_3 , regardless of the drastic 70% increment in the fracture toughness value [5]. In a more recent work by Gafur et al. both the microhardness and flexural strength of conventionally mixed and sintered $\text{Al}_2\text{O}_3\text{--ZrO}_2$ composites fairly declined with increasing ZrO_2 inclusions (from 5vol% to 20vol%), despite the increase in the fracture toughness. A decrease in hardness from 17.35 GPa to 12.98 GPa and flexural strength (from ~ 496 MPa to ~ 455 MPa) with the higher content of ZrO_2 ($\geq 10\text{vol}\%$) was ascribed to coarsening of the ZrO_2 grains and pore formation in the composite [18]. In similar studies with fabricated $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites, it was demonstrated that the wear resistance also diminishes with higher ZrO_2 contents due to the formation of defects on composite surface [19]. These trade-off in properties therefore suggest a need to further explore various research methods that can simultaneously enhance the bulk hardness, wear and strength properties of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ and ZTA composite systems for various advanced engineering applications.

The desire to improve ZTA and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite systems without depleting the strength, hardness and wear properties has sprouted new research approach. Particularly, via microstructural tailoring and design, new multiphase composites have been developed to counter these shortcomings and improve the overall mechanical performance of the dual-phase $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite systems [2,20]. This normally involves the inclusion and dispersion of other third phase nanoparticulate materials to $\text{Al}_2\text{O}_3/\text{ZrO}_2$ to form a hybrid or multi-phased nanocomposites [2,21]. Carbon nanostructures such as graphene (GN) and carbon nanotubes (CNTs) exhibit various inherent physical and mechanical properties that can be further explored in ceramic-based composites. The unique structure and geometry of these carbon nanostructures (2D-graphene and 1D-CNTs) credit them with

numerous remarkable attributes such as specific surface area, high tensile strength, thermal and electrical properties, and make them suitable for fabricating a stronger, tougher and wear resistant $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite systems [22,23]. The addition of these carbon nanostructures is known to directly influence the grain structures of both the matrix and the reinforced ZrO_2 phases, and immensely enhance the fracture toughness and strength properties by activating several combined mechanisms within the composite [24,25]. Also, several studies have explored the lubricating properties of both graphene and CNTs when used as a reinforcing phase in ceramic-based hybrid composite systems [26,27]. The effective interaction of the reinforced particles in a multi-phased hybrid composite depends on their amounts and homogeneous distributions within the matrix material, which consequently influence the structure and the bulk mechanical properties [28,29]. Literature works suggest that the improvement in the mechanical properties is most evident when low contents of the carbon reinforcing phase are utilized in the ceramic-based composites [30,31]. An attempt by Echeberria et al. to illustrate the effect of MWCNTs (0.01wt%) on ZTA hybrid composite (having 2wt% ZrO_2) fabricated using hot isostatic pressing (HIP) resulted in an increase in both the hardness (up to $\sim 17\%$) and fracture toughness (up to $\sim 37\%$) properties [24]. Despite these promising outcomes, only few studies have been conducted on the mechanical and tribological effect of these carbon additives on $\text{Al}_2\text{O}_3/\text{ZrO}_2$ and ZTA composites.

The addition of a third-phase nanostructure to a ZTA or $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite has the potential to surpass both conventional and novel attributes of alumina-zirconia systems, with the augmentation of properties including toughness, strength and wear. However, the scarcity of results demands further studies in the microstructural, mechanical properties and tribological performance of these novel engineering structures. Thus, in the current investigation, low ZrO_2 amount (4wt%), with optimum amounts of carbon nanotubes (2wt% CNTs) [32] and graphene (0.5wt% GN) [33] were used to prepare $\text{Al}_2\text{O}_3/4\text{wt}\%\text{ZrO}_2/2\text{wt}\%\text{CNTs}$ and $\text{Al}_2\text{O}_3/4\text{wt}\%\text{ZrO}_2/0.5\text{wt}\%\text{GN}$ hybrid nanocomposite systems using colloidal processing and hot-pressing technique. These third phase amounts were selected based on literature studies to yield the best structural and mechanical attributes of the hybrid nanocomposites [32,33]. The influence of the hybrid additions of these nanostructures on the microstructure, mechanical and wear performance of the consolidated nanocomposites were also examined and detailed in this study.

2. Experimental procedure

2.1. Hybrid nanocomposite fabrication

Nanopowders of $\alpha\text{-Al}_2\text{O}_3$ and ZrO_2 with average particle size of approximately $\leq 50\text{nm}$ and $\leq 80\text{nm}$ respectively, were acquired from commercial sources (Sigma-Aldrich, UK). Graphene (GN) and carbon nanotubes (CNTs) were also procured and processed, as detailed previous work [25,34,35]. Low content of ZrO_2 powders (4wt%) were colloiddally mixed with the Al_2O_3 matrix powder and subsequently added to the prepared 0.5wt% GN and 2wt% CNTs suspensions whilst stirring continuously to form the $\text{Al}_2\text{O}_3\text{--}4\text{wt}\%\text{ZrO}_2\text{--}0.5\text{wt}\%\text{GN}$ and $\text{Al}_2\text{O}_3\text{--}4\text{wt}\%\text{ZrO}_2\text{--}2\text{wt}\%\text{CNTs}$ hybrid nanocomposite powder mix slurry. The slurries were then dried constantly on a hot plate heating at a temperature from 120°C up to 150°C . The dried powder mix obtained were then milled to fine nanocomposite powders, which was followed by consolidation and high temperature sintering, as detailed in previous works [35–37]. Hot-pressing of the final powder mix was conducted using a 60MPa uniaxial pressure and a sintering temperature of 1600°C in a graphite die for a duration of 1hr to ensure highly dense bulk samples. A $10^\circ\text{C}/\text{min}$ rate of heating was used during the sintering, within an argon (Ar) controlled atmosphere. The rectangular consolidated nanocomposites having dimensions of $50\text{mm} \times 40\text{mm} \times 2\text{mm}$ were further sectioned for various physical, microstructural, mechanical and tribological characterizations. Both the monolith Al_2O_3 and $\text{Al}_2\text{O}_3\text{--}4\text{wt}\%\text{ZrO}_2$

Table 1
Structural and mechanical attributes of hot-pressed Al₂O₃/ZrO₂ nanocomposites.

Compositions	Sample Label	Measured ZrO ₂ grain size (μm)	Monoclinic ZrO ₂ amount (%)	Tetragonal ZrO ₂ amount (%)	Estimated Young's Modulus (GPa)	Critical Energy Release Rate, G _{IC} (J/m ²)
Alumina (A)	A	—	—	—	383	21.85 ± 3.97
A+4wt%ZrO ₂	AZ ₄	4.23 ± 0.3	84	16	378	29.83 ± 9.22
A+4wt%ZrO ₂ +2wt% CNTs	AZ ₄ CN	1.31 ± 0.1	94	6	396	122.13 ± 19.48
A+4wt%ZrO ₂ +0.5wt %GN	AZ ₄ G	3.07 ± 0.17	86	14	384	87.58 ± 21.30

nanocomposite were also fabricated for reference purposes using similar processing conditions, as detailed in Table 1.

2.2. Physical and structural characterization of nanocomposites

Apparent densities of the sintered hybrid nanocomposites, as well as the parent Al₂O₃ samples were measured using the Archimedes principle, with distilled water as the immersion liquid. Theoretical densities of the prepared monolith Al₂O₃, Al₂O₃-4wt%ZrO₂, Al₂O₃-4wt%ZrO₂-0.5wt %GN and Al₂O₃-4wt%ZrO₂-2wt%CNTs samples were estimated using rule of mixtures, with literature density values of the Al₂O₃, ZrO₂, CNTs and GN assumed as 3.97g/cm³, 5.87g/cm³, 1.85g/cm³ and 2.21g/cm³ respectively [28,38]. The relative densities were then calculated by dividing the apparent densities by the estimated theoretical densities of the nanocomposites. Sections of the sintered nanocomposite samples were cut from their bulk pieces using a diamond wire-saw, and prepared for microstructural studies using routine metallographic procedures, involving grinding and polishing up to 0.05μm finish. The prepared surface of each sample was then observed in a field emission scanning electron microscope (FE-SEM, Quanta 3D), operating at an accelerated voltage of 10KV, in order to document the grain morphology and distributions, as well as structural features of the nanocomposites.

The Al₂O₃ matrix grain size and distributions within the sintered nanocomposites were also estimated from the SEM micrographs via the linear intercept method, in conjunction with image J software. At least 5 different micrographs were used for each sample and the mean grain size value recorded. The ZrO₂ grains were also measured for each Al₂O₃-ZrO₂ nanocomposites using similar technique described above.

2.3. Crystallite phase identification of nanocomposites

Phase analysis of the hot-pressed monolith Al₂O₃ and the hybrid nanocomposites was carried out using the X-ray diffraction (Rigaku Miniflex 600 XRD) attached with Cu-Kα radiation λ = 1.54056 Å. Patterns from each sample were detected and collected by the XRD system from 5 to 110° at a range of 2θ, with a scanning rate of 1.4°/min. The ZrO₂ phase transformation from tetragonal to monoclinic (*t-m*) in the Al₂O₃-ZrO₂ hybrid nanocomposites was also quantified using the crystal planes (111) and ($\bar{1}\bar{1}\bar{1}$) of *m*-ZrO₂, and (111) of *t*-ZrO₂. The corresponding intensities of the phase peaks in conjunction with known equations were then used to approximate the amounts of *t-m* ZrO₂ phases in the hybrid nanocomposite samples [39,40]:

$$V_m = \frac{1.311X_m}{1 + 0.311X_m} \quad (1)$$

$$X_m = \frac{[I_m(\bar{1}\bar{1}\bar{1}) + I_m(111)]}{[I_m(\bar{1}\bar{1}\bar{1}) + I_m(111) + I_t(111)]} \quad (2)$$

where V_m denotes the volume fraction of *m*-ZrO₂ and X_m represents the integrated intensity. Volume fraction of the *t*-ZrO₂ phase was also estimated using the relation: $V_t = 1 - V_m$.

2.4. Characterization of mechanical properties

2.4.1. Vickers hardness measurement

The microhardness of the hot-pressed samples was measured using the Vickers microhardness tester (METLAB, Canada) under a 9.81N load for 15s. The diagonals of the diamond shaped indents on each sample surface were then measured with an attached microscope coupled to the microhardness system. At least 10 indentations were made on each sample at a fairly spaced distances, and their diagonals recorded. The applied load and measured diagonals were used to calculate the Vickers microhardness value of each indent in GPa using Equation (3) [41]. Average microhardness (Hv) value in GPa was then documented for each sample.

$$H_v = 0.0018544 \times \left(\frac{L}{x^2} \right) \quad (3)$$

with L and x denoting the indentation load (N) and average diagonal length from indent (m) respectively.

2.4.2. Flexural strength and fracture toughness measurements

The hot-pressed nanocomposites were subjected to three-point bending tests at room temperature to measure the flexural strength using a Hybrid Rheometer (Discovery 3), with a bending frame accessory. Sectioned rectangular test samples with approximate dimensions of 50mm (length) × 2mm (width) × 2mm (thickness) were used on the three-point test frame with a span length of 40mm and crosshead speed of 0.05mm/min. Three test specimens were prepared for each nanocomposite, and the flexural strength measured using Equation (4) [42]:

$$F.S = \frac{3 \times L \times S}{2 \times b \times h^2} \quad (4)$$

where L is the breaking point load, S , b and h represent the span length, sample width and sample thickness respectively.

The fracture toughness (K_{IC}) of the nanocomposites was determined using bending test (Single edge notched beam, SENB) and indentation method. The SENB test was conducted on a 30mm (length) × 2mm (width) × 2mm (thickness) specimen using the three-point bending frame (Discovery Hybrid Rheometer), with a loading speed and span length of 0.05mm/min and 25mm respectively. Three similar test specimens with cut notches at the centre were used for each fabricated nanocomposite sample, with their toughness values evaluated using Equation (5) [43,44]:

$$K_{IC} = \left(\frac{3 \times P \times S}{2 \times b \times h^{3/2}} \right) \times \alpha^{1/2} \times Y \quad (5)$$

$$Y = \frac{1.99 - \alpha(1 - \alpha)(2.15 - 3.93\alpha + 2.7\alpha^2)}{(1 + 2\alpha)(1 - \alpha)^{3/2}} \quad (6)$$

where P is the fracture load applied during bending, S is the bending span, b and h denotes the width and thickness of the test specimen respectively, a is the notch depth, α is the notch depth to thickness ratio

Table 2
Summary of wear properties of hot-pressed Al₂O₃/ZrO₂ nanocomposites.

Sample Label	Surface Roughness (nm)	Brittleness Index ($\mu\text{m}^{1/2}$)	Average Friction Coefficient (COF)	Wear Volume (mm ³)	Wear Rate ($\times 10^{-5}$ mm ³ /N.m)
A	59.15 ± 3.66	6.18 ± 0.93	0.65 ± 0.21	0.243 ± 0.05	9.71 ± 0.87
AZ ₄	71.61 ± 6.78	6.05 ± 0.71	0.76 ± 0.19	1.345 ± 0.12	47.14 ± 3.59
AZ ₄ CN	18.89 ± 1.41	3.89 ± 0.99	0.59 ± 0.17	0.027 ± 0.01	1.08 ± 0.28
AZ ₄ G	45.11 ± 2.68	4.00 ± 0.42	0.71 ± 0.19	0.021 ± 0.01	0.81 ± 0.21

(a/h), and Y is the geometrical compliance function.

Microstructures of the fractured surfaces were also studied to identify the fracture modes and toughening mechanisms by the hybrid reinforcement phases within the matrix material.

Fracture toughness from indentation was also estimated by directly measuring the cracks (DCM method) originating from the indents during the Vickers hardness testing under the 9.8N load. The crack lengths were used together with Niihara [45] Equation (7) to calculate the indentation fracture toughness of the nanocomposites

$$K_{IC} = 0.203 \times \left(\frac{c}{a}\right)^{-1.5} \times H \times a^{0.5} \quad (7)$$

where H is the microhardness value (GPa), c is the radial crack length (mm) and a is the half of the length of Vickers indent diagonal (mm).

2.4.3. Critical energy release rate (G_{IC})

The critical energy release rate parameter (G_{IC}), which is a function of the fracture toughness was also estimated for the prepared hybrid nanocomposites. For crack movement through the ceramic nanocomposite structures, the G_{IC} value mathematically quantifies the energy dissipated during crack propagation, which is calculated using the theoretical equation (8) [46]:

$$G_{IC} = K_{IC}^2 \times \left(\frac{1 - \nu^2}{E}\right) \quad (8)$$

where K_{IC} is the fracture toughness value, ν denotes the Poisson's ratio of Al₂O₃ (assumed as 0.21 [47]), and E represents the Young's modulus of the hot-pressed nanocomposites which is calculated from the rule of mixture, with the known mass fractions and literature values of Al₂O₃, ZrO₂, CNTs and GN taken as 383 GPa [48], 205 GPa [49], 800 GPa [50] and 1000 GPa [51] respectively. The estimated E and G_{IC} values are also presented in Table 1.

2.5. Wear analysis of nanocomposites

Tribological properties of the hot-pressed monolith Al₂O₃ and the hybrid nanocomposites were also evaluated at ambient temperature using the UMT Tribolab (Bruker Tribometer, Canada). A linear reciprocating sliding wear test configuration was used, with the polished flat surfaces of the nanocomposites sliding against a 9.5mm Si₃N₄ spherical ball, in accordance with the ASTM-G133 protocol. The stationary counter-ball with a constant contact force of 25N was pressed against the oscillating nanocomposite samples, at a predefined stroke length of 10mm and stroking velocity of 0.1m/s (0.5Hz). Three tests were conducted for each prepared nanocomposite at different locations on the samples' surface, and the average friction coefficient recorded (Table 2). The surface roughness (S_a) of the polished samples prior to the wear test was also measured using an optical profilometer (Bruker Contour GT), and documented in Table 2. Post-wear testing analysis of each sample

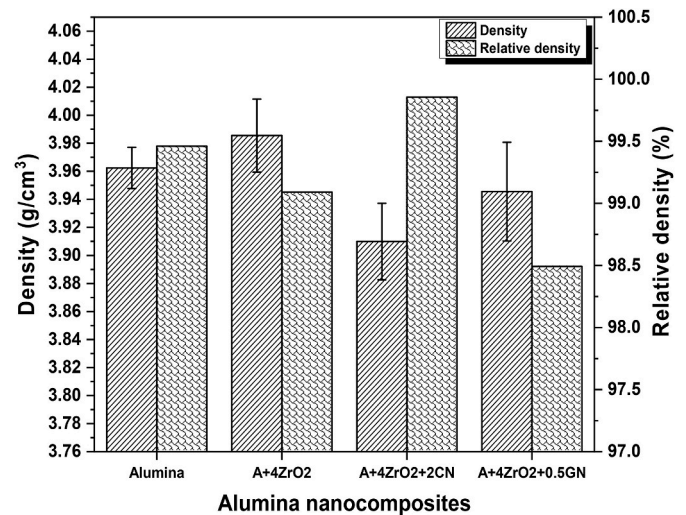


Fig. 1. Measured bulk density (g/cm³) and densification (%) of hot-pressed nanocomposites.

having wear tracks were carried out to determine the volume loss and consequent wear rate of each sample. The optical profilometer was utilized to generate the 2D and 3D wear track profiles in order to measure their wear width and depth. Prior to these measurements, the tracks covered with debris were thoroughly cleaned and dusted using air pressure to reveal the true depth and width for accurate measurements. The wear rate (W_R) was calculated using the relation in Equation (9) [52].

$$W_R = \frac{V}{F \times L} \quad (9)$$

with V as the volume loss (mm³), F represents the applied load (N) and L is the total sliding distance (m). The worn surfaces and wear debris of each nanocomposite were also studied after the wear test using the FE-SEM, to determine various wear mechanisms during the dry sliding tests.

Brittleness Index (BI): The wear properties of the hot-pressed ceramic nanocomposites were also quantified using the brittleness index parameter given in Equation (10) [53]:

$$BI = \frac{Hv}{K_{IC}} \quad (10)$$

where Hv is the Vickers hardness (GPa) and K_{IC} is the fracture toughness value of the nanocomposites.

3. Results

3.1. Density and microstructure

Fig. 1 shows the variation of the sintered densities and the relative densification (as computed from the theoretical densities of the matrix and reinforcement phases) of the hot-pressed Al₂O₃ and hybrid nanocomposites. A near density value of 3.96g/cm³ and 3.98g/cm³ was recorded for both the monolith Al₂O₃ and Al₂O₃-4wt%ZrO₂ (designated as AZ₄ sample), with approximate relative densities of 99.5% and 99.1% respectively. From Fig. 1, it can also be deduced that the addition of CNTs and GN to Al₂O₃-4wt%ZrO₂ led to relatively lower densities, with the Al₂O₃-4wt%ZrO₂-2wt%CNTs (designated as AZ₄CN sample) registering 3.91g/cm³ density, whilst a density value of 3.95g/cm³ was obtained for Al₂O₃-4wt%ZrO₂-0.5wt%GN (designated as AZ₄G sample). For both AZ₄CN and AZ₄G samples, respective densification of approximately 99.8% and 98.5% was realized. Thus, good sinter densities ($\sim 99\%$) was achieved via the hot-pressing processing route for both the monolith Al₂O₃ and its nanocomposites.

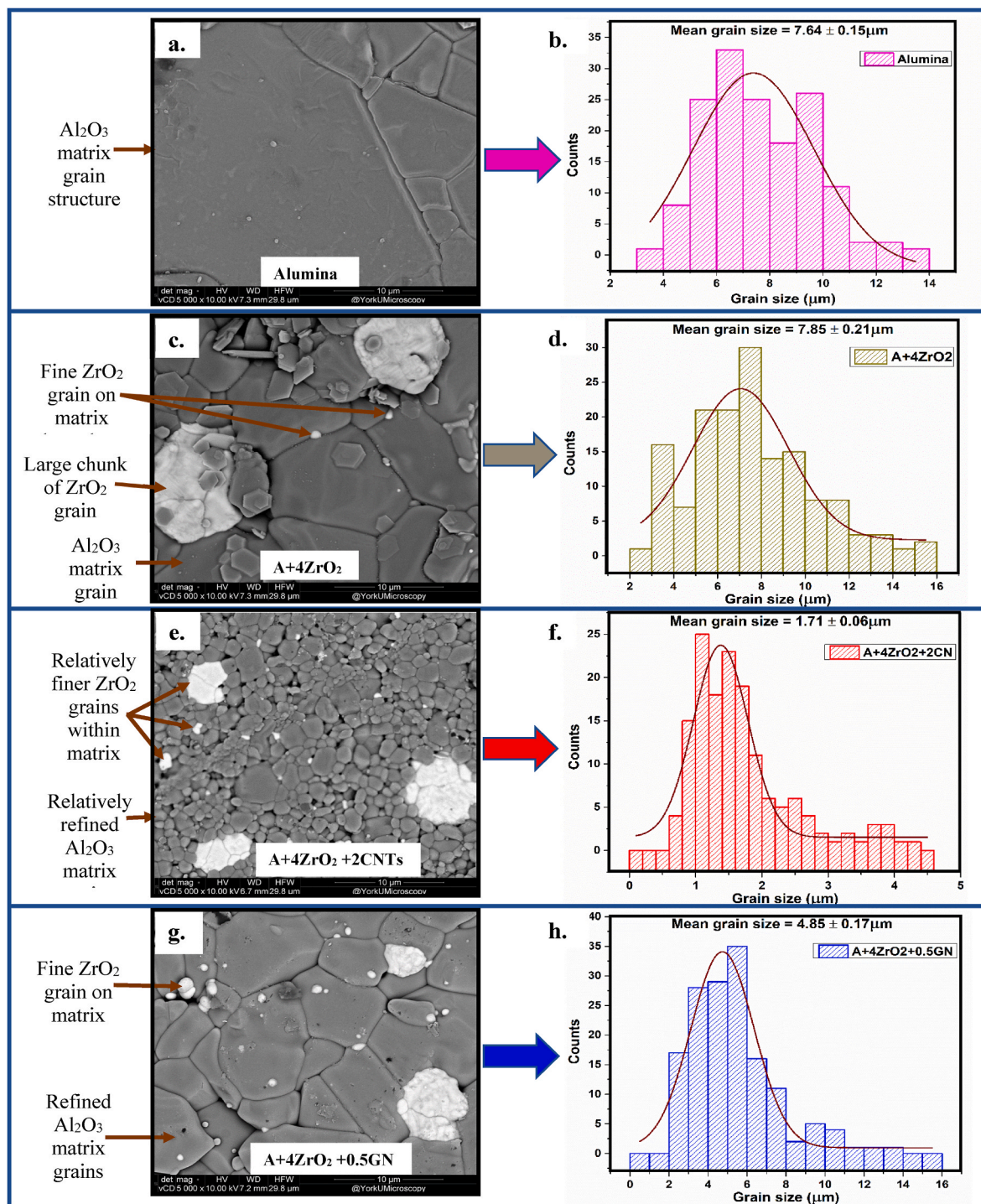


Fig. 2. FE-SEM micrographs and grain size distributions of sintered nanocomposites (a) monolith Al_2O_3 (b) Al_2O_3 -4 ZrO_2 (c) Al_2O_3 -4 ZrO_2 -2CNTs (d) Al_2O_3 -4 ZrO_2 -0.5GN.

Fig. 2 illustrates the grain structure and grain distributions of the sintered Al_2O_3 -based hybrid nanocomposites as examined via the FE-SEM. The grains of the monolith Al_2O_3 sample with an average grain size of $7.64\mu\text{m}$ (Fig. 2a–b), exhibited both fine and coarse structures, as observed in previous studies [36,37]. A slight increase of $\sim 3\%$ in the grain size was realized with the addition of only 4wt% ZrO_2 in the AZ_4 sample (measured grain size of $7.85\mu\text{m}$), which also displayed fairly coarse grain structure (Fig. 2c–d). The added ZrO_2 phases were distinct within the Al_2O_3 matrix structure, with both huge chunks and very fine globular-like ZrO_2 particles dispersed within the parent matrix. An

average ZrO_2 grain size of $4.23\mu\text{m}$ was also estimated for the sintered AZ_4 sample, as seen from Table 1. The grain size of the Al_2O_3 matrix structure was hugely refined (up to $1.71\mu\text{m}$) in the AZ_4CN sample, having the hybrid additions of 4wt% ZrO_2 and 2wt% CNTs (Fig. 2e–f). About $\sim 77\%$ and $\sim 78\%$ reduction in the grain size was achieved in reference to the monolith Al_2O_3 and AZ_4 samples respectively. Similar to the AZ_4 sample, the added ZrO_2 particles in the hybrid AZ_4CN sample were also insoluble within the matrix grain structure, having both coarse and fine distributions within the matrix. The measured ZrO_2 grain size was averaged as $1.31\mu\text{m}$, which demonstrates an approximate reduction

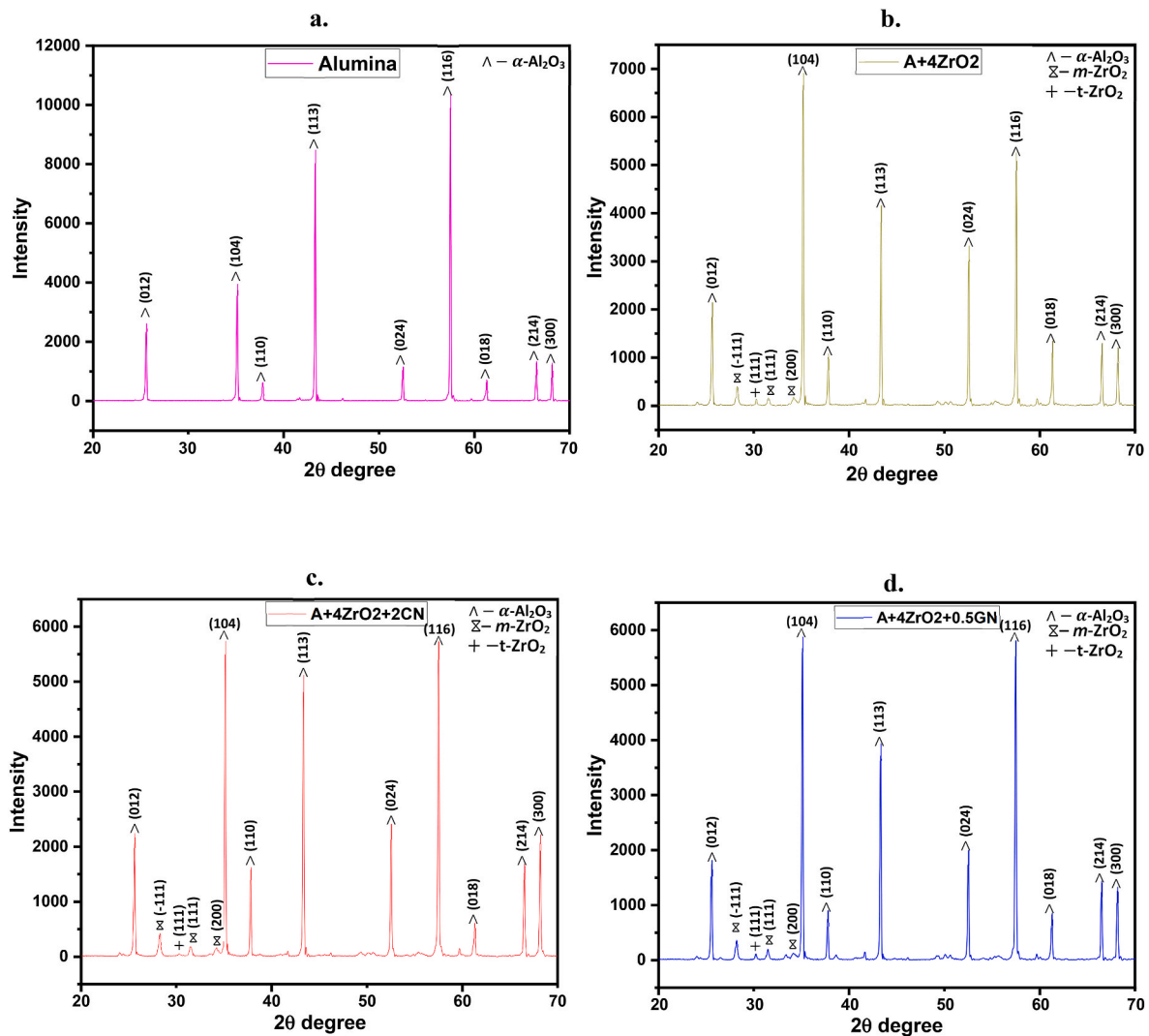


Fig. 3. X-ray diffraction (XRD) patterns showing crystalline phases of hot-pressed nanocomposites.

of 69% when compared to the ZrO_2 grains in the AZ_4 sample. This therefore illustrates the refinement capabilities of the added 2wt% CNT nanostructures on both the Al_2O_3 matrix and the ZrO_2 inclusions. With the combined additions of both 4wt% ZrO_2 and 0.5wt% GN, the AZ_4G hybrid nanocomposite also exhibited about $\sim 37\%$ and $\sim 38\%$ drop in the grain size relative to the monolith Al_2O_3 and the AZ_4 samples respectively, with an average grain size of $4.85\mu\text{m}$ (Fig. 2g–h). The AZ_4G grain size was however estimated to be about $\sim 65\%$ higher when compared to the AZ_4CN sample, having the co-additions of 4wt% ZrO_2 and 2wt% CNTs. The dispersed ZrO_2 particles were also marginally refined up to about $3.07\mu\text{m}$, which represents an estimate of $\sim 27\%$ decrease with respect to the AZ_4 sample having only 4wt% ZrO_2 . Although both additions of CNTs and GN showed a refinement in the ZrO_2 grain size relative to the Al_2O_3 -4wt% ZrO_2 , the AZ_4CN hybrid nanocomposite demonstrate a more finer structure with about $\sim 57\%$ lower ZrO_2 grain size when compared to that of the AZ_4G hybrid nanocomposite.

3.2. Phase compositions and crystalline structure

The features of the crystallite phases are shown in the XRD patterns of the hot-pressed nanocomposites in Fig. 3. Typical phases of the monolith Al_2O_3 as previously discussed [36,54] is illustrated in the XRD spectra in Fig. 3a, which depicts the starting α - Al_2O_3 crystalline phase.

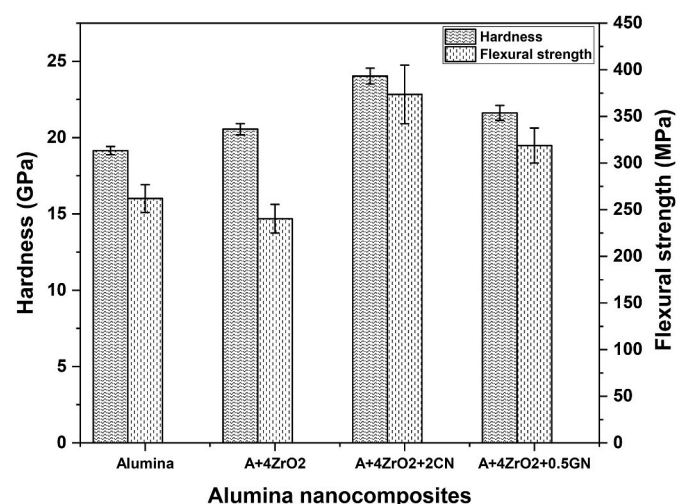


Fig. 4. Hardness and Flexural strength properties of nanocomposites.

However, Fig. 3b, 3c and 3d illustrate the extra diffraction peaks with the various hybrid additions of 4wt% ZrO_2 , 2wt% CNTs and 0.5wt% GN. With the emergence of the additional peaks, the major peak intensities

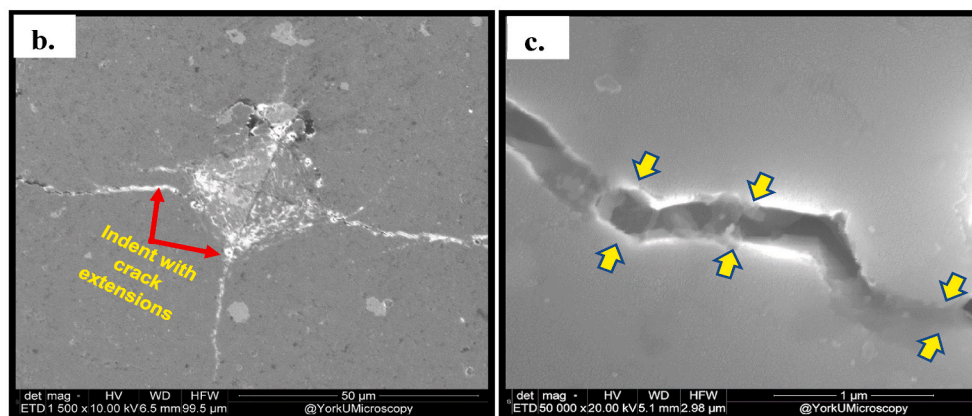
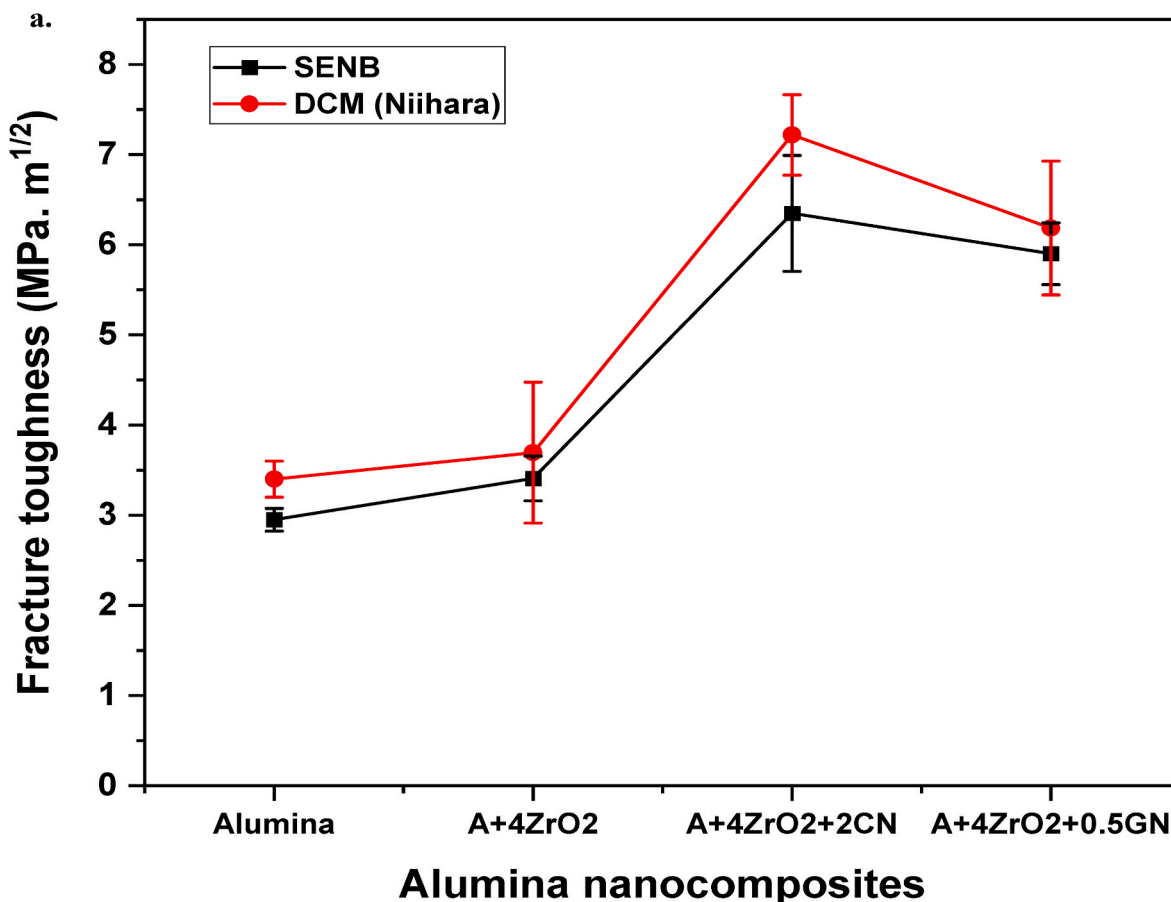


Fig. 5. (a) Fracture toughness variations in Al_2O_3 -based nanocomposites (b) Vickers indent with originating cracks (c) crack bridging and deflection in hybrid nanocomposite.

of the reference Al_2O_3 were relatively decreased in samples AZ₄, AZ₄CN and AZ₄G. The additional peaks in the hot-pressed $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanocomposites were identified as monoclinic (*m*- ZrO_2) phases, which were indexed at approximate diffraction angles of 28.2°, 31.5° and 35.2°, with the tetragonal (*t*- ZrO_2) phase indexed at approximate diffraction angle of 30.2° (Fig. 3b–d). Table 1 also presents the estimated *m*- ZrO_2 and *t*- ZrO_2 amounts (%) in the hybrid $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanocomposites. Variations in the *m*- ZrO_2 and *t*- ZrO_2 contents which had 4wt% ZrO_2 additions suggests the effect of carbon nanostructures (CNTs and GN) during the colloidal mixing of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanocomposites. For instance, it has been demonstrated that the addition of GN can sometimes hinder the *m*- ZrO_2 amount in the nanocomposite structure [55].

3.3. Mechanical performance of hybrid nanocomposites

Fig. 4 illustrates the microhardness values (Hv) of the hot-pressed nanocomposites determined from indentation. An enhancement in the hardness values with the hybrid additions of ZrO_2 , CNTs and GN in the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanocomposites were depicted, with the AZ₄CN hybrid nanocomposite recording the highest Hv value of ~24.0 GPa, revealing about 26%, 17% and 11% increment as compared to the monolith Al_2O_3 (Hv of ~19 GPa), AZ₄ (Hv of ~20.5 GPa) and AZ₄G (Hv of ~21.6 GPa) respectively. An improvement of about 14% and 5% was also realized upon the addition of GN in the AZ₄G sample, with reference to the parent Al_2O_3 and AZ₄ samples respectively. It is noteworthy that the addition of

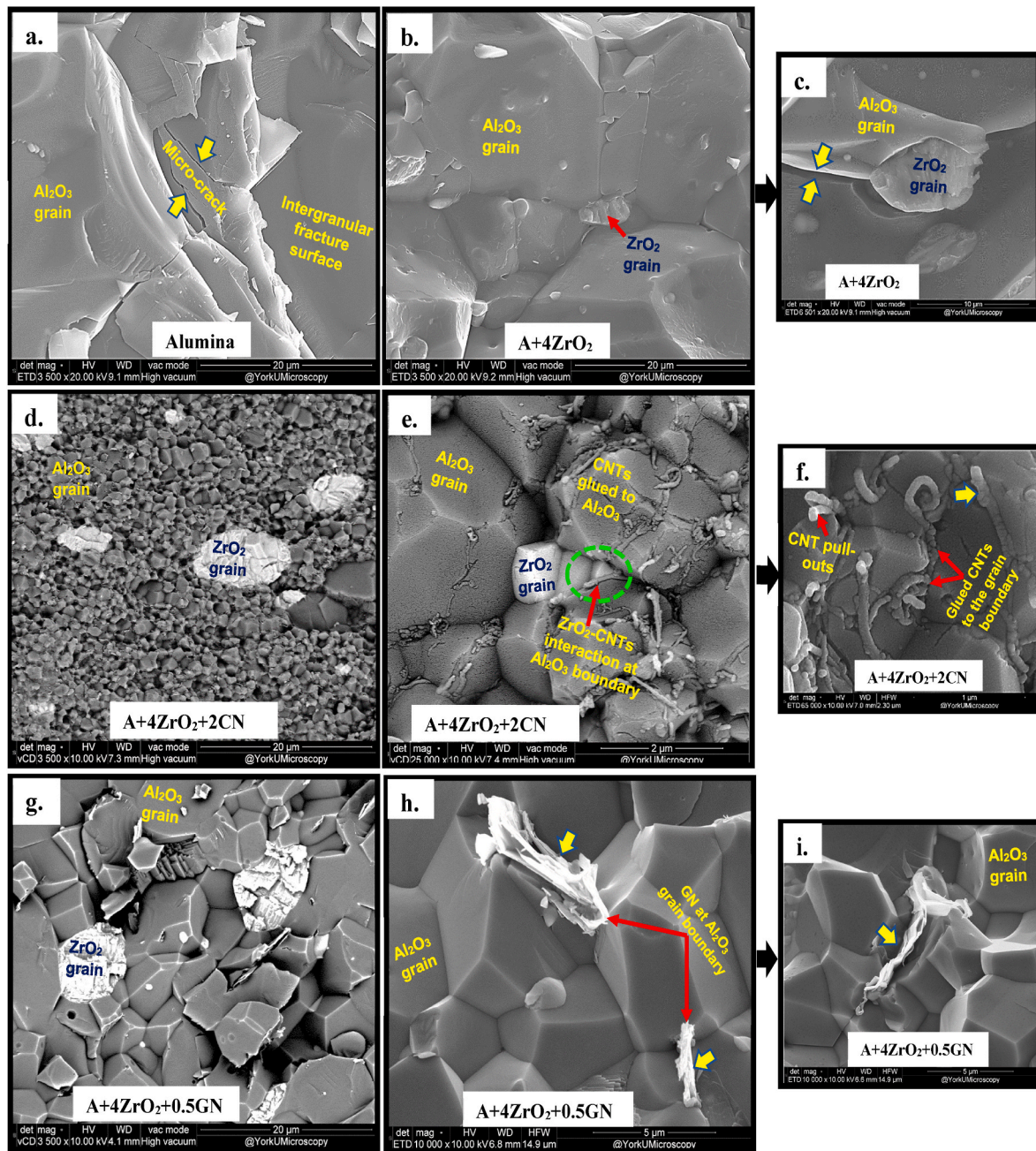


Fig. 6. Fracture modes and mechanism of toughening by ZrO₂, CNTs and GN within nanocomposites (a) monolith Al₂O₃ (b)–(c) Al₂O₃-4wt%ZrO₂ (d)–(f) Al₂O₃-4wt%ZrO₂-2wt%CNTs (g)–(i) Al₂O₃-4wt%ZrO₂-0.5wt%GN.

low amount of ZrO₂ (4wt%) to the monolith Al₂O₃ resulted in an increase in the microhardness value (~8% increment), whereas higher amounts (up to and above 10wt%) tend to yield significant drop in the hardness value, as demonstrated in previous studies [5,36,54].

Fig. 4 also shows the relative improvement in the flexural strength of the nanocomposites, which were calculated from the three-point bending tests. The flexural strength of the parent Al₂O₃ which was determined in previous studies to be 260MPa [54] reached a maximum value of ~374MPa (44% increment) with the hybrid additions of 4wt% ZrO₂ and 2wt%CNTs. However, the single addition of 4wt%ZrO₂ (AZ₄ sample) recorded about 8% drop in the strength value, which was estimated to be ~240MPa. With the combined additions of 4wt%ZrO₂ and 0.5wt%GN, the AZ₄G sample yielded strength value of ~319MPa, which represents about 23% and 33% increase over the monolith Al₂O₃ and AZ₄ samples respectively. Compared to the AZ₄ and AZ₄G samples, an

approximate increase of 55% and 17% respectively, was realized in the flexural strength when hybrid reinforcements of ZrO₂/CNTs was included within Al₂O₃ matrix structure (AZ₄CN sample).

Single edged notched beam (SENB) and direct crack measurement (DCM) fracture toughness (K_{IC}) values of the hot-pressed Al₂O₃ and Al₂O₃/ZrO₂ hybrid nanocomposites are also illustrated in Fig. 4. Regardless of the method used, the hybrid addition of ZrO₂/CNTs (AZ₄CN sample) recorded the maximum K_{IC(SEN)} and K_{IC(DCM)} values of up to 6.3MPa.m^{1/2} and 7.2MPa.m^{1/2} respectively, which was 115% and 118% higher as compared to that of the parent Al₂O₃, having respective K_{IC(SEN)} and K_{IC(DCM)} values of ~3MPa.m^{1/2} [54] and ~3.3MPa.m^{1/2}. As can be seen from Fig. 5a, the indentation toughness values were higher than that from the conventional bending tests, which is also demonstrated in other works [56–58]. In both methods however, the single addition of 4wt%ZrO₂ (AZ₄ sample) exhibited a slight rise in the

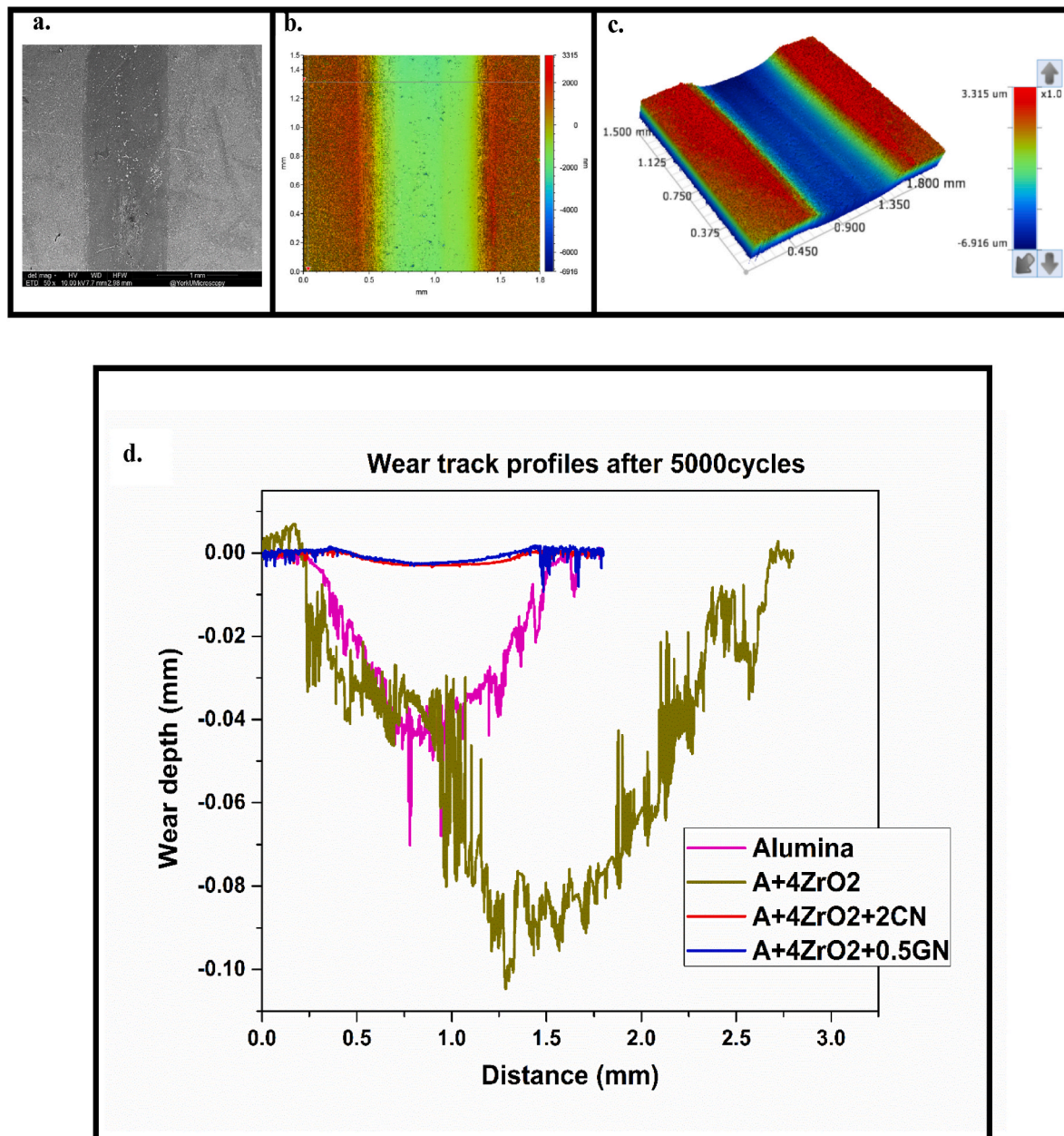


Fig. 7. (a)–(c) Sample worn surface with 2D and 3D wear track profile after wear test (d) Wear width and depth variations obtained from worn grooves of nanocomposites after 5000 sliding cycles.

toughness of the parent Al_2O_3 , registering $K_{\text{IC(SEN)}}$ and $K_{\text{IC(DCM)}}$ values of $\sim 3.4 \text{ MPa.m}^{1/2}$ ($\sim 13\%$ increase) and $3.7 \text{ MPa.m}^{1/2}$ ($\sim 12\%$ increase) respectively. Relative to the reference Al_2O_3 , the addition of ZrO_2 and GN (AZ₄G sample) also indicated about 97% and 88% increase in the fracture toughness, with $K_{\text{IC(SEN)}}$ and $K_{\text{IC(DCM)}}$ values of $5.9 \text{ MPa.m}^{1/2}$ and $6.2 \text{ MPa.m}^{1/2}$ respectively. The FE-SEM micrographs shown in Fig. 5b–c demonstrate the emerging cracks induced by the indentation, as well as bridging mechanisms by the carbon nanostructures. Fig. 6 also illustrates the post-fracture surfaces of the nanocomposites which depicts their fracture modes and toughening mechanisms. A mixture of transgranular and intergranular fracture can be observed, indicated by the smooth and rough fractured surfaces. Typical intergranular fracture with micro-cracks are seen in the parent Al_2O_3 sample (Fig. 6a). Fig. 6b–c also demonstrate the intergranular mode of fracture for the AZ₄ sample, which also displayed fine and coarse ZrO_2 phases trapped at Al_2O_3 matrix grain junctions. For the AZ₄CN hybrid nanocomposite (Fig. 6d–f), both ZrO_2 and CNT nanostructures were apparent on

intergranular-fractured grain surfaces. Trapped ZrO_2 particles were also surrounded by the dispersed CNTs glued to the Al_2O_3 matrix grains, as well as the grain boundaries (Fig. 6e). Pull-out strands of the CNTs were also evident, which illustrates toughening effect of the added CNTs. The fractured surface morphology of the AZ₄G hybrid nanocomposite was also characterized with smooth and rough surfaces of the Al_2O_3 and ZrO_2 grains, indicating both intergranular and transgranular fractures (Fig. 6g–i). Evidently, the presence of the dispersed GN nanostructures at the matrix grain boundaries contributed to the fracture mode of the surrounding grains.

Table 1 also summarizes the estimated Young's modulus (E) and critical energy release rate (G_{IC}) of the prepared nanocomposites. From Table 1, it is shown that the E value increased from 383 GPa for the parent Al_2O_3 to a maximum of 396 GPa for the AZ₄CN hybrid nanocomposite, which was about 3.4% higher. The calculated modulus from Table 1 also showed a relatively lower E value for the AZ₄ sample (decreased by 1.3%), whilst a comparable E value was realized in the

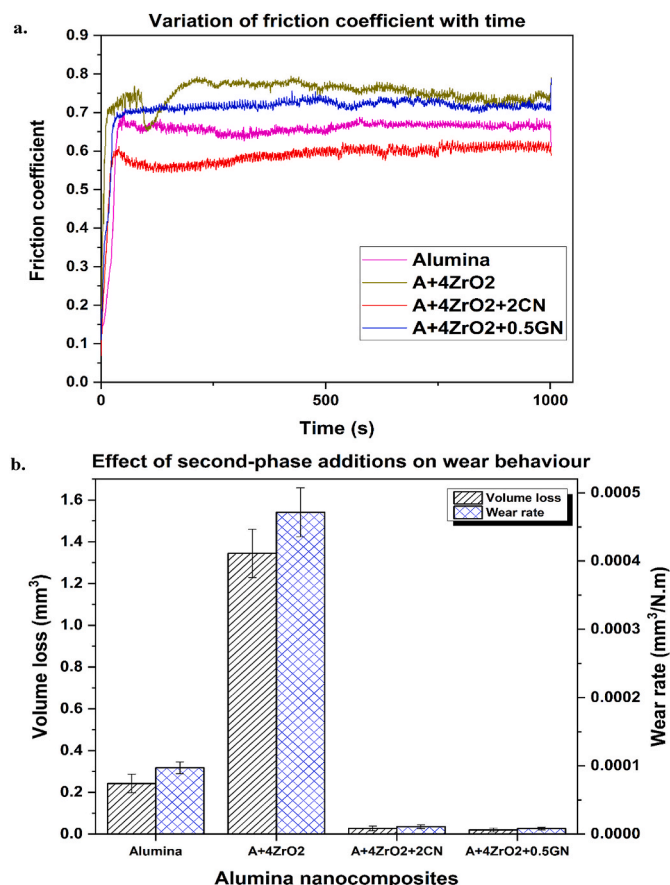


Fig. 8. Friction coefficient as a function of the sliding time (1000s) during the wear test (b) Volume loss and wear rate as a function of the hot-pressed nanocomposites.

AZ₄G hybrid nanocomposite. The energy release rate (G_{IC}) values of the nanocomposites were also computed to be $\sim 22 \text{ J/m}^2$ for the parent Al_2O_3 , which was immensely increased up to 122 J/m^2 (up to 458% higher) with the hybrid addition of ZrO_2 and CNTs (AZ₄CN sample). The calculated G_{IC} value of the monolith Al_2O_3 was comparable to those obtained in literature [46]. For the AZ₄ and AZ₄G samples, there was approximately 37% and 300% increase in the G_{IC} values over that of the reference Al_2O_3 (Table 1).

3.4. Wear performance of hybrid nanocomposites

The wear resistance behaviour of the hot-pressed nanocomposites was also analysed after subjecting samples to dry sliding reciprocating test for 1000s. Table 2 and Figs. 7–10 illustrates the performance of both the monolith Al_2O_3 and $\text{Al}_2\text{O}_3\text{-ZrO}_2$ nanocomposites after the sliding tests. The surface roughness of each polished sample was also compared prior to each wear experiment, as summarized in Table 2, with the AZ₄CN sample showing the lowest S_a value of $\sim 19 \text{ nm}$. Fig. 7 shows the 3D wear track profile and depth variations of each nanocomposite after 5000cycles. From Fig. 7b, it can be shown that the AZ₄ sample had the largest depth and width, which were estimated to be more than $\sim 70\mu\text{m}$ and $\sim 2300\mu\text{m}$ respectively. The monolith Al_2O_3 also exhibited fairly larger wear track profile but was relatively lower than that of the AZ₄ sample. However, the hybrid additions of ZrO_2 , CNTs and GN resulted in lower depth and width wear tracks, which was estimated to be up to $\sim 3\mu\text{m}$ and $\sim 950\mu\text{m}$ respectively. Friction coefficient (COF) was determined after the sliding cycles from the COF trends in Fig. 8a. The mean COF value for each nanocomposite was also estimated from the trend and presented in Table 2. The COF of the reference Al_2O_3 dropped from

0.65 to 0.59 in the AZ₄CN nanocomposite. For the AZ₄ and AZ₄G samples, the mean COF values computed to be 0.76 and 0.71 respectively, were slightly higher when compared to the reference Al_2O_3 sample. The wear properties of the nanocomposites were further characterized by the volume loss and wear rate using Equation (9), which was also plotted in Fig. 8b. Wear volume, which corresponds to the direct measure of material lost after the dry sliding test reached a maximum value of $\sim 1.35\text{mm}^3$ for the AZ₄ nanocomposite, which was $\sim 463\%$ higher than the monolith Al_2O_3 , with recorded volume loss of $\sim 0.24\text{mm}^3$. Meanwhile, as shown in Table 2 and Fig. 8b, the AZ₄CN and AZ₄G hybrid nanocomposites produced the minimum volume loss of up to $\sim 0.03 \text{ mm}^3$, which was approximately $\sim 90\%$ and $\sim 98\%$ lower when compared to the Al_2O_3 and AZ₄ samples respectively. The wear resistance of the hot-pressed monolith Al_2O_3 nanocomposite also showed drastic improvement from $9.71 \times 10^{-5} \text{ mm}^3/\text{N.m}$ up to $0.81 \times 10^{-5} \text{ mm}^3/\text{N.m}$ (up to $\sim 92\%$ decrease in wear rate) for the AZ₄CN and AZ₄G hybrid nanocomposites. However, the individual addition of 4wt% ZrO_2 (AZ₄ sample) rather led to poor wear resistance, recording an estimated $\sim 385\%$ higher wear rate relative to the reference Al_2O_3 . Thus, the additions of 4wt% ZrO_2 with 2wt%CNTs and 0.5wt%GN enhanced the wear performance of Al_2O_3 matrix and $\text{Al}_2\text{O}_3/4\text{wt}\%\text{ZrO}_2$ nanocomposite. Table 2 also summarizes the brittleness index (BI) calculated for the parent Al_2O_3 and the $\text{Al}_2\text{O}_3\text{-ZrO}_2$ nanocomposites. The brittleness index as a combined parameter can be used to assess the wear resistance behaviour better than the individual mechanical parameters such as hardness and fracture toughness. A lower BI value corresponds to an enhanced wear resistance, as demonstrated in several studies [26,59,60]. The reported BI values in Table 2 reflects this trend, with the AZ₄CN and AZ₄G hybrid nanocomposites exhibiting up to $\sim 37\%$ lower brittleness index value, as compared to the monolith Al_2O_3 and AZ₄ samples.

Fig. 9 also shows the FE-SEM analysis of the wear tracks and wear debris, which illustrates the scratch and groove morphology of the worn surfaces on the samples' surfaces. Wear texture of the monolith Al_2O_3 , as shown in Fig. 9a–c, demonstrates material pull-outs and large grooves which corroborates the volume loss and wear rate results in Table 2 and Fig. 8b. The groove morphology of the AZ₄ sample is more severe as a result of the intense Al_2O_3 matrix and ZrO_2 grain pull-outs (Fig. 9d–f). This was also evident in the large worn-out particles (Fig. 9f), which suggests higher wear rate within the AZ₄ sample during the dry sliding. Fig. 9g–i also depicts the worn surface of the AZ₄CN hybrid nanocomposite with distributed minor scratch grooves and micro-cracks, as well as few smooth regions devoid of the mild pull-outs. The relatively finer wear debris of the AZ₄CN sample also portrays the lower rate of wear and material loss, as seen in Fig. 8b. Similar to the AZ₄CN sample, the wear morphology of the AZ₄G nanocomposite was also characterized with minimum pull-out grooves, and more smooth regions after the dry sliding (Fig. 9j–l). The fine debris of the AZ₄G sample also indicates a less severe wear and fracture of the matrix and ZrO_2 grains. The mechanisms of the wear resistance by ZrO_2 phases and carbon nanostructures including crack bridging, deflection and arrest within the worn surfaces are also illustrated in Fig. 10.

4. Discussions

The prepared monolith Al_2O_3 and the $\text{Al}_2\text{O}_3\text{-4wt}\%\text{ZrO}_2$ hybrid nanocomposites achieved a near-density structure ($\sim \geq 98\%$) after the high temperature sintering. The low densities ($\sim \leq 3.98\text{g/cm}^3$) of the nanocomposites after the hybrid additions of the nanostructures in their low amounts (4wt% ZrO_2 , 2wt%CNTs, and 0.5wt%GN) also suggest the lightweight properties of the consolidated ceramic structure were maintained. Low concentration of the added reinforcements are known to offer optimum structural and mechanical properties to ceramics [32,33]. The distribution of the carbon nanostructures (CNTs and GN) is also illustrated in fractured surfaces of the $\text{Al}_2\text{O}_3\text{-4wt}\%\text{ZrO}_2$ hybrid nanocomposites. Both CNTs and GN phases have high affinity for the Al_2O_3

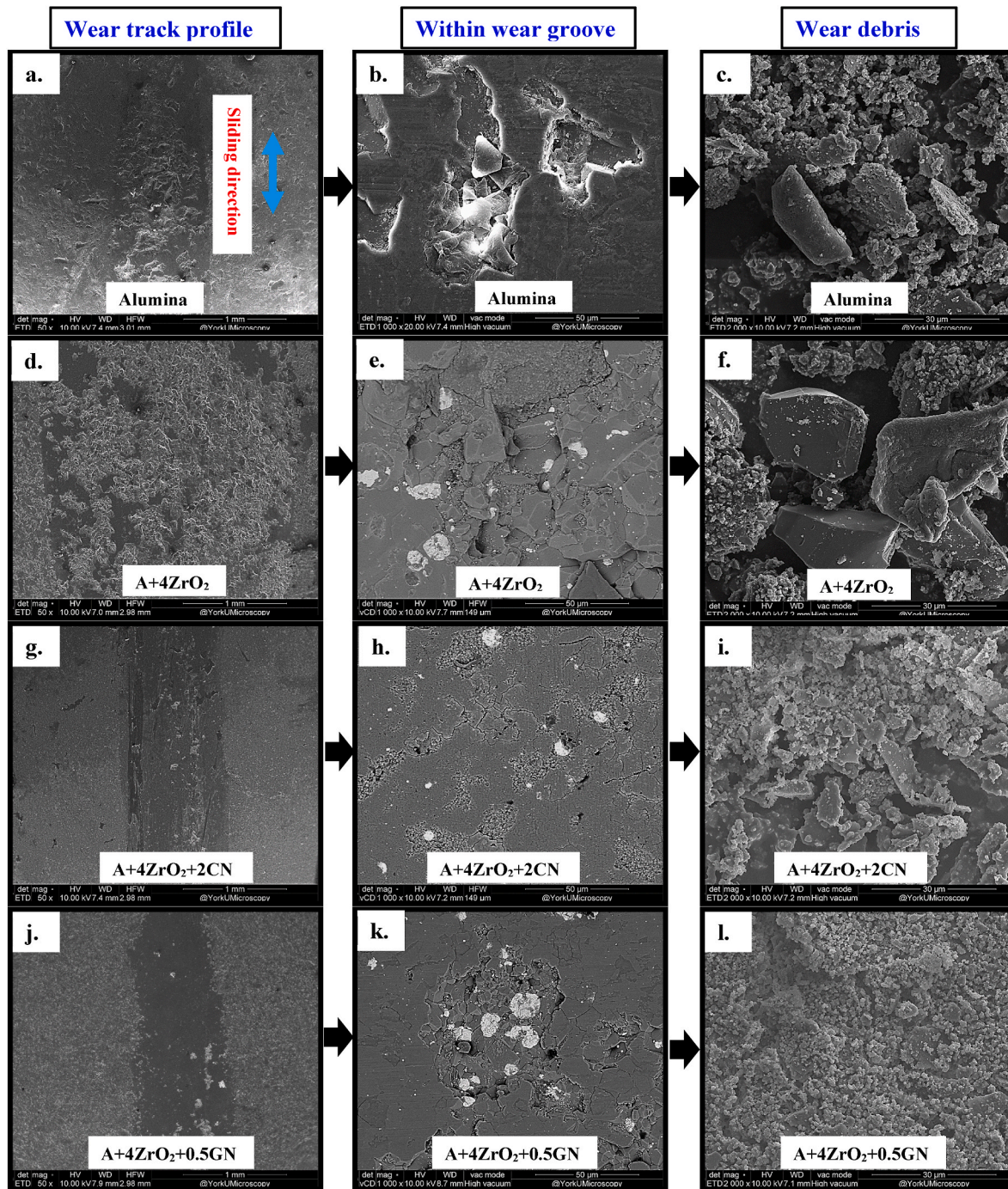


Fig. 9. Wear morphologies showing wear track profiles, worn surface and nature of wear debris particles of each nanocomposite after wear test.

matrix grain boundary, as illustrated in Fig. 6, as well as the schematics in Fig. 11a. This binding characteristics of the CNTs and GN at the matrix grain boundary have also been demonstrated by other studies [23, 27–29]. Some bundles of the CNTs however tend to attach themselves on and within the grains rather than the boundaries (Figs. 6 and 11a). The location of the carbon nanostructures within the matrix structure immensely contributes to the grain refinement by hindering their growth during sintering [29,61]. With the additions of ZrO_2 /CNTs and ZrO_2 /GN, the refinement of the grains (both Al_2O_3 and ZrO_2 grains) in the hybrid nanocomposite is more apparent due to the coordination of reinforcement phases. An example of this is seen in Fig. 6e, and demonstrated in Fig. 11a, where there is an evident of simultaneous interaction and pinning activities of ZrO_2 with CNTs, as well as ZrO_2 and

GN structures on the Al_2O_3 grain junctions. However, as observed in Al_2O_3 -4wt% ZrO_2 nanocomposite, the single addition of only 4wt% ZrO_2 gave comparable grain size as the parent Al_2O_3 , as illustrated in previous reports [36]. This could suggest that adding only low amounts of ZrO_2 is not enough to restrict the matrix grain growth during sintering, despite achieving a dense structure [62].

The mechanical performance of Al_2O_3 and the Al_2O_3 -4wt% ZrO_2 hybrid nanocomposites were dependent on the grain structure and the reinforcement particles. The trade-off in mechanical properties such as hardness against toughness, which were otherwise realized with high concentration of ZrO_2 ($\geq 10\text{wt}\%$) within Al_2O_3 - ZrO_2 and ZTA ceramic structures were minimized with the inclusions of low content ZrO_2 particles (4wt%), and optimized amount of carbon nanostructures (2wt

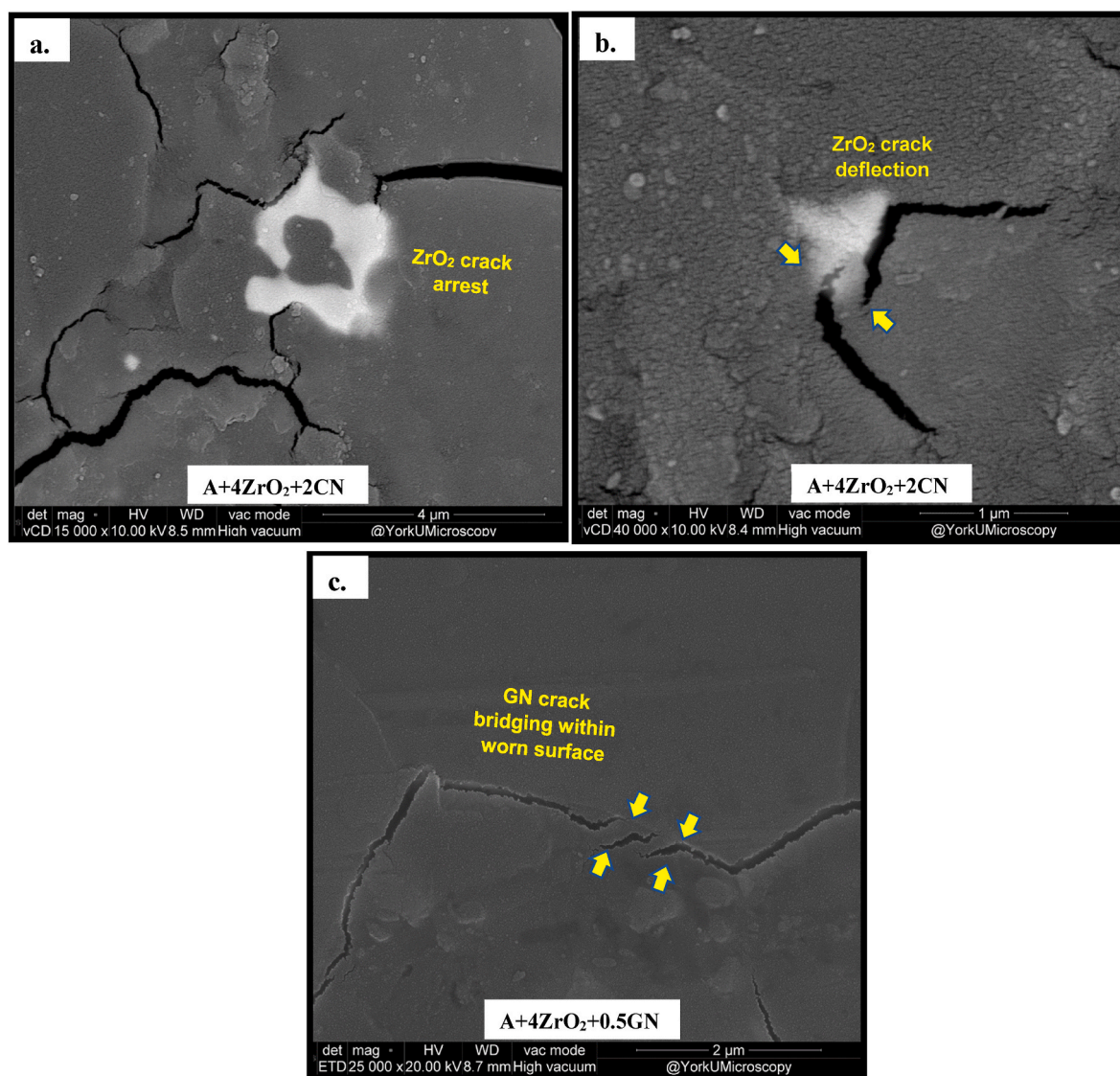


Fig. 10. Example of wear resistant activities within wear track including (a)–(b) crack arrest and deflection by ZrO₂ (c) GN crack bridging and deflection.

%CNTs and 0.5wt%GN) [5,32]. In addition, there was a simultaneous rise in the toughness and flexural strength properties, which can be ascribed to the relative grain refinement, combined interaction and mechanisms of the reinforcement phases within the Al₂O₃ matrix. Crack bridging and deflection of CNTs and GN were observed as the primary toughening and strengthening mechanisms as a result of the hybrid interaction between ZrO₂ and CNTs, as illustrated in Figs. 6 and 11a. The deviation of crack paths and crack inhibition by ZrO₂ and carbon nanostructures during bending and indentation is accompanied with high amount of energy which translates into their load-bearing and strength capabilities. This therefore corroborate the estimated energy release rate (G_{IC}) values which demonstrated high value (122 J/m²) for the AZ₄CN nanocomposite due to the large network of CNTs on the matrix boundaries and within the grains. Also, CNT gluing to the matrix grains, as seen in Fig. 6e–f signifies a stronger CNTs-matrix bonding and interactions, which essentially contributes to the improved mechanical properties [2,46]. For the AZ₄G sample, the embedment and wrapping of the GN particles accord the increase in the strength and toughness properties (Fig. 6h–i). Fig. 11a also highlights the coordination of the ZrO₂ and GN structure at matrix boundary in the presence of propagating cracks, which further depicts toughening capabilities in addition to the grain refinement effect by the hybrid additions. The refinement of

the ZrO₂ grains by the carbon nanostructures in the AZ₄CN and AZ₄G samples also contributed to their overall mechanical performance including hardness and strength. However, it is perceived that the finer ZrO₂ grains tend to restrict the *t-m* ZrO₂ phase transformation in the presence of applied stress [63,64]. Therefore, the ZrO₂ phase transformation toughening in the AZ₄CN and AZ₄G samples could be limited to the relatively larger ZrO₂ grains [65] and the active mechanisms by the carbon inclusions.

The grain structure and mechanical properties also influenced the tribological performance of the hot-pressed nanocomposites during interaction with the hard Si₃N₄ counter-surface. The relatively lower wear volume and wear rate of the AZ₄CN and AZ₄G hybrid nanocomposites (up to 0.81×10^{-5} mm³/N.m) can be ascribed to the finer grains, dispersion and presence of CNTs and GN within matrix grains and grain boundaries, as well as the specific mechanical attributes of the carbon nanostructures which consequently improved the wear performance of the nanocomposites [26,33,60]. The higher rate of wear with large removal of grain materials of the parent Al₂O₃ and the AZ₄ samples are due to the plastic deformation during the continuous sliding against the harder counter-body. This induces stresses and causes cracks to propagate on the top surface, that promotes chipping, delamination and pull-out of the matrix grains [66,67]. Fig. 11b illustrates the contact

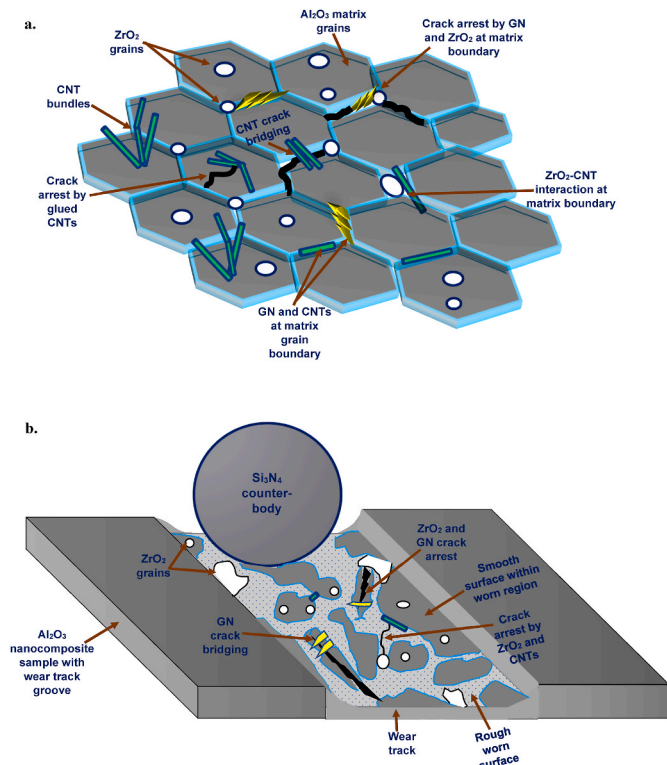


Fig. 11. Schematic illustrations of (a) interaction of ZrO₂, CNTs and GN within matrix structure (b) wear resistant activities in wear grooves.

surface interaction of the counter-body with nanocomposite, as well as the crack propagations and wear mechanisms within the wear track. With the hybrid addition of ZrO₂ and the carbon nanostructures, the crack paths are impeded during the oscillatory movements of the counter-body, and thereby limits the rate of grain pull-outs to cause the large wear grooves and volume loss. Fig. 10a–c also demonstrates the crack bridging, deflection and arrest capabilities of the fine and ductile ZrO₂ particles within the wear track of the AZ₄CN nanocomposite, which hinders the progress of surrounding cracks along the matrix grains during the sliding wear. This resistant mechanism was identified as a unique behaviour of the ZrO₂ particles amidst the moving cracks during the dry sliding tests. The bridging of the crack paths is also seen within the worn surface of the AZ₄G sample, which is a predominant wear resistant activity when lower GN content (≤ 0.5 wt%) is added to ceramic composite structures [33]. Therefore, the addition of optimum amount of carbon nanostructures can drastically enhance the wear resistance of Al₂O₃-4wt%ZrO₂ systems via these combined wear resistant mechanisms.

5. Conclusion

In this work, ceramic Al₂O₃ and Al₂O₃/ZrO₂ nanocomposite systems reinforced with low content ZrO₂ (4wt%) and optimum amounts of CNTs (2wt%) and GN (0.5wt%) were mixed using colloidal process and hot-pressed to form hybrid nanocomposite structures designated as: Al₂O₃-4wt%ZrO₂, Al₂O₃-4wt%ZrO₂-2wt%CNTs and Al₂O₃-4wt%ZrO₂-0.5wt% GN. The correlation between the grain structure, mechanical and tribological properties of the processed nanocomposites under similar experimental conditions were thoroughly investigated. The following conclusions were drawn from this study:

1. The addition of CNTs and GN as a third phase to Al₂O₃-4wt%ZrO₂ showed a good dispersion of the reinforcement structures within the Al₂O₃ matrix after sintering and consolidation.

2. Though the addition of only 4wt%ZrO₂ yielded comparable grain sizes to the Al₂O₃ matrix, there was however a significant refinement of the matrix grains with the hybrid inclusions of ZrO₂/CNTs and ZrO₂/GN within the matrix, with up to 78% and 38% grain size reduction observed for the Al₂O₃-4wt%ZrO₂-2wt%CNTs and Al₂O₃-4wt%ZrO₂-0.5wt%GN hybrid nanocomposites respectively. The ZrO₂ grains were also refined up to 69% and 27% with the respective additions of ZrO₂/CNTs and ZrO₂/GN hybrid reinforcements to the Al₂O₃/ZrO₂ nanocomposite structures.
3. Hybrid additions of ZrO₂/CNTs and ZrO₂/GN also increased the fracture toughness and flexural strength of the parent Al₂O₃ from $\sim 3\text{MPa}\cdot\text{m}^{1/2}$ and $\sim 260\text{MPa}$ up to $\sim 7\text{MPa}\cdot\text{m}^{1/2}$ and $\sim 374\text{MPa}$ respectively. This was due to the finer grain structure, and the combined presence and interaction of the reinforcement nanostructures precipitating within the matrix grains and grain boundaries, simultaneous toughening and strengthening mechanisms including crack bridging and deflection by GN and CNTs, GN grain wrapping, CNT pull-outs and grain gluing which illustrated good CNT-matrix bonding.
4. The wear resistance also improved from $9.71 \times 10^{-5}\text{mm}^3/\text{N}\cdot\text{m}$ up to $0.81 \times 10^{-5}\text{mm}^3/\text{N}\cdot\text{m}$ with the additions of ZrO₂/GN and ZrO₂/CNTs, which was accustomed to the enhanced mechanical properties and the wear resistant mechanisms such as crack arrest, bridging and deflection by the reinforcement phases.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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