

## Preparation and Properties of Nanoparticle-enhanced Composite Phase Change Material with Ceramic Porous Media

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**Abstract** - Nanoparticle-enhanced tailing-paraffin composite phase change material (NCPCM) is fabricated by spontaneous melt infiltration. Industrial waste-iron tailing is used as raw material to prepare ceramic porous carrier with a foam-gel casting method. By adjusting the fabrication parameters, optimal NCPCM properties are obtained with paraffin content of 70%~88% and thermal conductivity of 0.351~0.490 W/(m·K), which is nearly 200% the thermal conductivity of paraffin wax. After 25 melting/solidification cycles, the nanoparticles remain well dispersion with overall stability in the composite phase change material, and the thermal conductivity slightly decreased from 0.349 to 0.317 W/ m·K. With multiple melting and solidification cycles, a low weight loss of 2.3~7.8 wt.% is demonstrated. The strength of ceramic frame is found to have a direct effect on the weight loss. Compared with existing nanoparticle-enhanced phase change material, the new NCPCM shows significantly improved thermal conductivity and better nanoparticle stability due to its ability to prevent nanoparticles from disposition.

**Keywords:** *Nanoparticle; Phase Change Materials; Ceramic Porous Media; Thermophysical Properties; Dispersion.*

### I. INTRODUCTION

Energy storage plays an important role in meeting the growing global energy demand. Phase change materials (PCMs), with high storage density and isothermal process in phase change process, are often applied in latent heat energy storage systems where energy is stored in the form of latent heat during melting and recovered during solidification of the PCMs [1].

Paraffin wax is a reliable option for PCM in various engineering applications, such as storage of solar thermal energy, industrial waste heat recovery and insulation building material [2]. But the low thermal conductivity of paraffin causes low heat transfer rate during charging and discharging cycles [3]. Therefore, efforts have been made to enhance the rate of melting/freezing by utilizing different methods. An effective method of improving the melting/freezing rate is to add highly thermal conductive nanoparticles inside the PCM.

This nanoparticle-enhanced phase change material (NePCM) has been studied in a shell-and-tube thermal energy storage system [4]. Khodadadi and Hosseinizadeh [5] observed that NePCM exhibits higher heat release rate when compared to the conventional PCM partly due to the simultaneous increase of the thermal conductivity and reduction of the latent heat. Although nanoparticles can improve the thermal conductivity of the PCM, the stability issue presents a major challenge. It's very difficult to achieve long term uniform dispersion of nanoparticles in paraffin wax since nanoparticle sedimentation is almost unavoidable [1].

Another heat transfer enhancing technique involves composite phase materials (CPCM) incorporating porous ceramics. This technique can efficiently improve the thermal conductivity and maintain original shape of the PCM even when the wax is melted. Several authors reported the thermal enhancement of CPCMs. Zhao et al.[6] performed an experimental investigation to characterize the phase change processes (both melting and solidification) of paraffin wax inside copper metal foam. The porous materials, through capillary and surface tension forces, keep the PCM in stable shape at liquid phase [7]. Qian, et al. [8] fabricated shape-stabilized composite phase change material (ss-CPCM) based on SiO<sub>2</sub> materials. SiO<sub>2</sub> acts as the carrier matrix to provide structural strength and prevent the leakage of melted PCM. Their results show that the use of porous medium enhances the melting/solidification process faster than pure PCM without a porous medium.

NCPCM is a new way that combines the advantages of NePCM and CPCM. Although the transport processes of nanofluids in a porous medium have been studied in recent years, the fabricating technology and thermal properties of NCPCM were barely reported. The key point is that the ceramic must have micron-sized pores and high porosity, good wettability and chemical stability with NePCM. Iron ore tailings (IOT) have been generated in steel production as an industrial waste all over the world, which caused economic, environmental and health-related problems [9]. Using IOT as a carrier to fabricate NCPCM is an efficient method for improving thermal properties, keeping the shape of melted paraffin, reducing industrial pollution and drastically

decreasing the manufacturing cost. This paper presents the preparation and analyzes the thermal conductivity of NCPCM.

## II. MATERIALS AND PROCEDURE OF PREPARATION

### A. Preparation of Tailing Porous Ceramic Media

Tailing was obtained from iron mines of Miyun area in Beijing. Tailing porous ceramics were fabricated by a foam-gel casting method. First, iron tailing slurries with a solid loading of 45 wt.% were prepared by mixing ball-milling IOT powders, deionized water, Acrylamide, N,N'-Methylenebisacrylamide and ammonium polyacrylate for 15h. After that, Sodium dodecyl sulfate and lauryl alcohol were added into the slurries, followed by high-speed stirring to acquire foamed slurries. Tetraacetythylenediamine and Ammonium persulfate were slowly added to the foamed slurries and mixed adequately. Then the slurries were poured into molds and gelled in the air for 10 min to get green porous bodies. Finally, the green bodies were dried and sintered at different temperatures of 1070, 1080, 1090, 1100, 1110 and 1120 °C for 7 h.

### B. Preparation of NCPCM

Technical grade paraffin wax with melting temperature 56 °C and graphene nanoplatelets were supplied by Sigma-Aldrich Canada. The porous ceramic and 99g paraffin were heated to 150°C and 90°C, respectively. Then 1g of graphene nanoparticles were added into the melted paraffin and the mixture was stirred for 30 min.

The mixture is under ultrasonic treatment for 5min after stirring to prevent nanoparticles from aggregation. Then, the porous ceramics were put into a beaker full of melted paraffin to make sure that the melted paraffin covers the ceramics. The infiltration process needs 5min. After that, the beaker is let to cool down to 60 °C and the samples are taken out to dry in the air. Figure 1 shows pictures of samples of the porous ceramic, CPCM and NCPCM. Due to the black color of graphene nanoparticles, the color of NCPCM is much darker than the other samples.



Figure 1. Pictures of porous medium (a), CPCM (b) and NCPCM (c)

## III. PROPERTIES OF POROUS CERAMIC AND NCPCM

### A. Properties of Ceramic and Infiltration Result

The porosity of porous ceramic is a key property to decide NePCM content in NCPCM which is measured by the Archimedes method in distilled water. Compressive strength was measured by a WDW-100E testing machine with a crosshead loading speed of 0.5 mm/min, using cylindrical

specimens with a diameter of 20 mm and a height of 20 mm. Phase composition of the sintered materials was identified by X-ray diffraction (D/MAX-III, Rigaku, Japan). Eight specimens were used to acquire average property. Pore size distribution was analyzed by the mercury intrusion method in an Auto Pore IV 9510 instrument.

Physical properties of the tailing porous ceramics sintered at different conditions are listed in Table 1, and the effects of sintering temperature on the compress strength are shown in Fig.2. Six samples were tested for each temperature point.

Table 1 PROPERTIES OF THE TAILING POROUS CERAMICS

Sintering temperature (°C)	Bulk density (g/cm <sup>3</sup> )	Apparent Porosity (%)	Shrinkage (%)
1070	0.39±0.01	88.8±0.1	3.81±0.43
1080	0.38±0.01	87.4±0.4	5.59±0.31
1090	0.36±0.01	87.0±0.8	8.20±1.42
1100	0.29±0.02	85.5±0.1	9.46±0.23
1110	0.48±0.01	82.6±0.2	10.74±0.31
1120	0.76±0.01	71.6±0.4	20.67±0.45

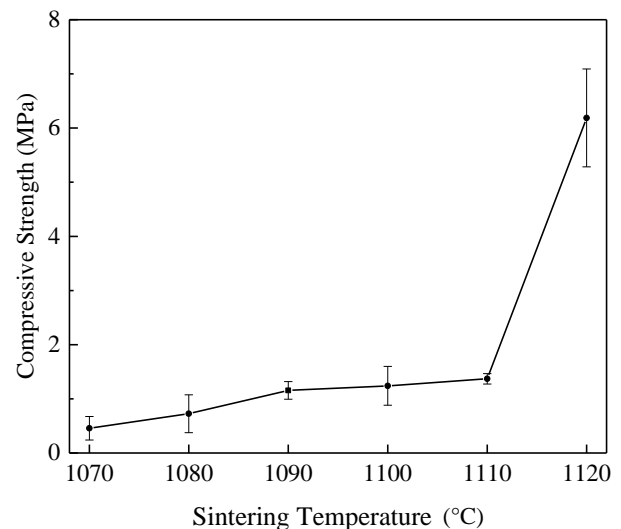


Figure 2. Relationship between sintering temperature and compressive strength

As temperature increased from 1070 to 1120 °C, bulk density and shrinkage of ceramic increased from 0.39 to 0.76 g/cm<sup>3</sup> and 3.81 to 20.67 % respectively, and the porosity decreased from 89% to 71%. With the increase of sintering temperature, atomic diffusion kinetic energy increases, which enhances the sintering activity and makes the tailings particles closer. 1110 °C is likely a point where liquid phase is significantly generated, while higher temperatures lead to drastic shrinkage of the samples, resulting in increased porosity of the porous ceramics. Higher porosity of porous ceramics means bigger energy storage density of the NCPCM.

As we can see in Fig 2, with higher sintering temperatures, the compressive strength of porous ceramics increased due to the much stronger interconnection among quartz grains and framework of more glass phase generated in higher

temperature. Based on the Gibson equation, the following relationship between porosity and strength was correlated from the experimental data:

$$\sigma_1 = 129 \times (1 - \Gamma)^{2.53} \quad (1)$$

where  $\Gamma$  is porosity,  $\sigma_1$  is compression strength of porous ceramics.

When sintering temperature reached 1080 °C and held for 3 hours, porosity, bulk density and compression strength were 86.6 %, 0.31 g/cm<sup>3</sup> and 0.75 MPa respectively, which can satisfy the needs of NCPCM.

Figure 3 shows the phase composition of tailing porous ceramics sintered at 1080 °C. The mineralogical composition of the porous samples determined by X-ray Diffraction (XRD) shows main crystalline phases like quartz (SiO<sub>2</sub>), diopside (CaMgSi<sub>2</sub>O<sub>6</sub>), augite (Ca(Mg,Fe,Al)(Si,Al)<sub>2</sub>O<sub>6</sub>). Anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) were identified. This phase has good erosion resistance and forms the main mineral framework of the tailing porous ceramics, which are responsible for the physical properties and mechanical strength of porous ceramics.

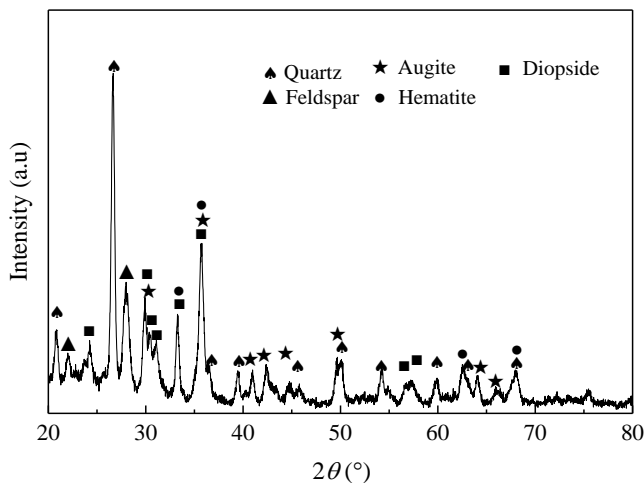


Figure 3. XRD patterns of porous ceramics sintered at 1080 °C

Figure 4 shows the pore size distribution of porous tailing ceramics sintered at 1080 °C for 3 hours. It shows a bimodal distribution of the pore size of the porous tailing ceramic, with a weak peak at about 1.4 μm and a strong peak at 45 μm, while the pore diameter was mainly in the range of 20-80 μm. According to previous work, when the radius of pores is smaller than 100 μm, the capillary force is larger than that from atmospheric pressure, which helps to eliminate air from the samples in the infiltration process. Also, when the pore radius is 3~35 μm, the differential pressure  $\Delta P$  changes from 6 MPa to 1 MPa, which efficiently prevents the melted paraffin from leaking out of the porous medium.

Table 2 shows filling fractions of the prepared CPCM and NCPCM. The values indicate percentage of pores that are occupied by liquid paraffin (which has a density of 0.74 g/cm<sup>3</sup>) and liquid nanoparticle enhanced paraffin (which has a density of 0.73 g/cm<sup>3</sup> due to the low density of graphene nanoparticles).

As we can see in Table 2, different sintering temperatures lead to different pore sizes of the samples, which causes variation in capillary forces and therefore changes in the infiltration efficient. Compared with the CPCM, adding graphene nanoparticles didn't seem to change the wettability of paraffin on the surface of the ceramics.

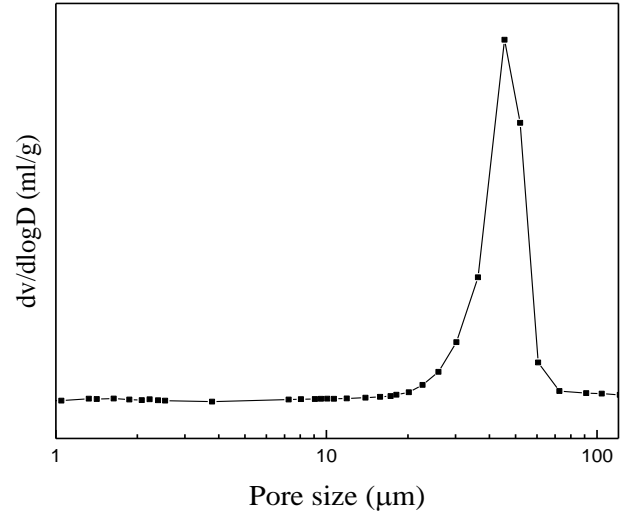


Figure 4. Pore size of sample sintered at 1080 °C

Table 2 INFILTRATION OF CPCM AND NCPCM

Sintering Temperature (°C)	Porosity of Porous Ceramic (%)	Filling Fraction of CPCM (%)	Filling Fraction of NCPCM (%)
1070	89	98.08	99.21
1090	86	98.91	99.08
1110	82	98.13	97.30

### B. Thermal Conductivity

The thermal conductivities of iron ore tailing were measured on 5×5×3 mm<sup>3</sup> machined specimens at room temperature, using the Thermal Transport Option (TTO) of Physical Properties Measurement System (PPMS, Model 6000, Quantum Design, USA). The NCPCMs, i.e., tailing ceramic/NePCM composite materials, were measured with a KD2 Pro Thermal Properties Analyzer (Decagon Devices, USA). The thermal conductivity of the tailing ceramic and the NePCM is 1.41 W/m·K and 0.282 W/m·K, respectively.

Figure 5 shows thermal conductivities of NCPCM, CPCM, NePCM and the base PCM (paraffin wax). With combined advantages of CPCM and NePCM, the new NCPCM shows a significant increase of thermal conductivity to 0.428 W/m·K, as compared to 0.229 W/m·K of the base PCM. It was confirmed that the micron-sized pores can prevent nanoparticles from deposition. Also, the tailing ceramic has higher thermal conductivity than paraffin, which also helps improve the thermal properties.

### C. Multiple Melting Solidification Cycles

Weight loss of samples was tested after 1, 5, 10, 15, 20 and 25 melting / solidification cycles. Figure 6 shows cross-

sectional view of a sample after these cycles. As we can see in Fig. 6, there is no observable color change in the cross-sectional view of the NCPCM, suggesting that the nanoparticles were still well dispersed in the PCM without deposition (otherwise there will be dramatic change of color gradient with dark colored area from nanoparticle deposition). These results demonstrate that the NCPCM technique can effectively prevent the nanoparticles from disposition.

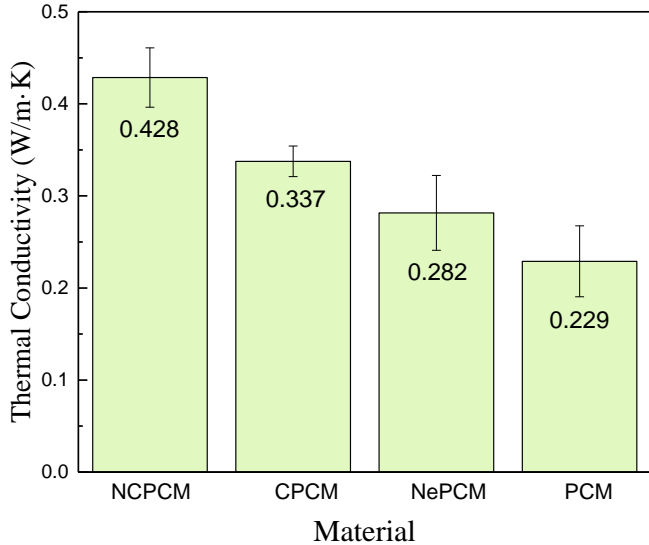


Figure 5. Thermal conductivities of NCPCM, CPCM, NePCM and pure PCM

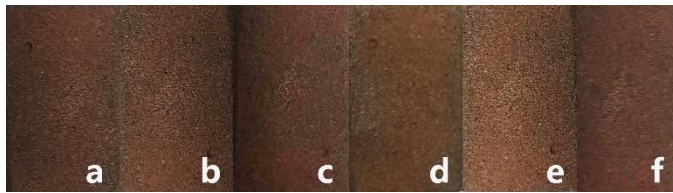


Figure 6. The section of sample after 1(a), 5(b), 10(c), 15(d), 20(e) and 25(f) times of melting / solidification cycles

Figure 7 shows weight losses of two NCPCM samples after 1, 5, 10, 15, 20 and 25 melting / solidification cycles respectively.

As the number of melting/ solidification cycles increased, the mass of samples slightly decreased. With air fills into the sample after paraffin leaking, the thermal conductivity decreased from 0.349 to 0.317 W/ m·K. This can be explained by evaporation and leak of paraffin. Comparing the two curves in the Figure 7, one can find that the leakage and weight loss are greatly affected by the porosity. As the porosity increases, more and more glass phase forms on internal walls of the ceramics promoting the strength of samples. Stronger wall of the pores can decrease the impact from liquid paraffin in melting and solidification and prevent the paraffin from leaking.

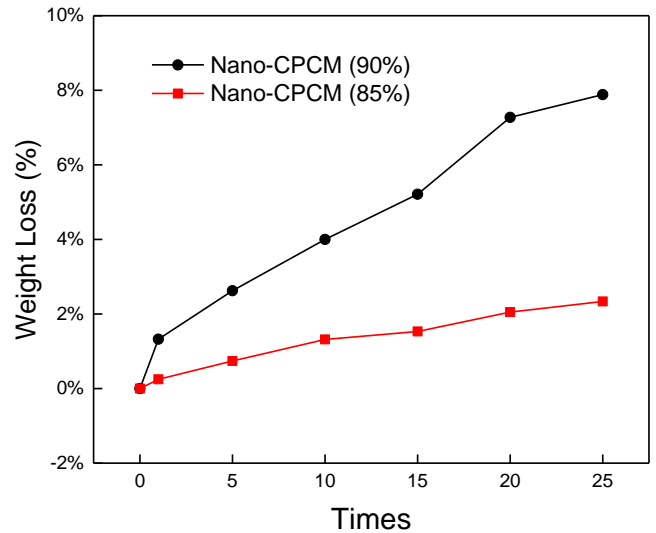


Figure 7. NCPCM Sample material weight loss with 90% and 85% porosity after multiple melting / solidification cycles

#### IV. CONCLUSIONS

Nanoparticle enhanced tailing-paraffin composite phase change material (NCPCM) was successfully prepared using iron ore tailing, graphene nanoparticles and paraffin as raw materials with a foam-gel casting method and spontaneous infiltration technique. With higher sintering temperature, the porosity of ceramic decreased from 89% to 71% and the bond between particles become stronger as well. It was found that paraffin dispersed with graphene nanoparticles has good wettability with the tailing ceramic. It efficiently prevents leaking of the melted paraffin out from the porous medium. NCPCM significantly increases the thermal conductivity of PCM from 0.229 W/m·K to 0.428 W/ m·K. In addition, the porosity of the ceramic porous media has a significant effect on weight loss which was only 2.3wt.% when porosity is smaller than 85%. NCPCM with tailing porous ceramic demonstrates good mechanical integrity, with significantly improved and controllable thermal properties.

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