Research Article

Influence of Nanoparticles and Graphite Foam on the Supercooling of Acetamide

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Acetamide is a promising phase change materials (PCMs) for thermal storage, but the large supercooling during the freezing process has limited its application. In this study, we prepared acetamide-SiO₂ composites by adding nano-SiO₂ into acetamide. This modified PCM was then impregnated into the porous graphite foam forming acetamide-SiO₂-graphite foam form-stable composites. These composites were subjected to melting-solidification cycles 50 times; the time-temperature curves were tracked and recorded during these cycles. The time-temperature curves showed that, for the acetamide containing 2 wt. % SiO₂, the supercooling phenomenon was eliminated and the material's performance was stable for 50 cycles. The solidification temperature of the acetamide-SiO₂-graphite foam samples was 65°C and the melting temperature was lowered to 65°C. The samples exhibited almost no supercooling and the presence of SiO₂ had no significant effect on the melting-solidification temperature. The microscopic supercooling of the acetamide-SiO₂ composite was measured using differential scanning calorimetry (DSC). The results indicated that when the content of SiO₂ was 1 wt. to 2 wt. %, the supercooling could be reduced to less than 10°C and heat was sufficiently released during solidification. Finally, a set of algorithms was derived using MATLAB software for simulating the crystallization of samples based on the classical nucleation theory. The results of the simulation agreed with the experiment results.

1. Introduction

Among the available techniques suitable for storing thermal energy and for controlling temperature in systems subjected to periodic heating, the use of latent heat thermal storage technology has attracted considerable attention. In a latent heat thermal storage system, thermal energy is stored/controlled by using phase change materials (PCMs) in which a large amount of heat is absorbed or released during the phase change processes with only small temperature variations. This process allows for periodic heating, the conversion of temperature oscillations into melting interface oscillations and significant damping of the thermal perturbations. Phase change materials (PCMs), such as acetamide (C₂H₅NO), exhibit desirable properties, such as high latent heat of fusion and suitable melting temperature, which offer potential for thermal storage applications. The melting point of acetamide is 78°C and it can be expected to store waste energy from heat sources with temperatures over 70°C. However, one feature of most PCMs is the supercooling characteristic and acetamide

is no exception. It possesses a large degree of supercooling which was 39.3°C and which has been found by DSC testing. In acetamide PCMs, solidification does not occur at the melting point and the material assumes the supercooled state over a relatively wide temperature range. This seriously affects the subsequent endothermic melting process and causes failure in phase change thermal control applications. To initiate the solidification of the supercooled PCMs, nucleation induction procedures are needed including the addition of nucleation catalysts, application of mechanical vibration, or ultrasonic irradiation [1–4]. Of these techniques, addition of nucleating agents is the most convenient, reliable, and economical one.

Many studies have shown that employing nanoparticles dispersed into the PCMs as a nucleating agent can significantly suppress supercooling. Mo et al. [5] investigated the supercooling of TiO₂-water nanofluids and DI water and showed that the nanoparticles reduce the supercooling of the water by heterogeneous nucleation. In Lu et al. study [6], the effect of several nanomaterials (AlN, Si₃N₄, ZrB₂, SiO₂, BC₄,

and SiB_6) as nucleating agents for sodium acetate trihydrate (SAT) was investigated. The results showed that addition of 5 wt.% or 4 wt.% Si_3N_4 , 10 wt.% ZrB_2 , 5 wt.% AlN dispersed in SAT helped eliminate the supercooling of SAT. Specifically, 2 wt.% ultrasonic dispersed nano- SiO_2 , premixed by magnetic stirring in the melted SAT, eliminated the supercooling of the SAT. Using three different types of SiO_2 nanoparticles as the antisupercooling agents, Wu et al. [7] investigated the surface effect of the interaction between nanoparticle and hydrate salts during the phase changing process. Aerosol SiO_2 exhibited the most effective and stable performance as nucleators for hydrate salts. Supercooling of hydrate salts was found to be easily suppressed by the nanoadditives, which have high specific surface area and strong polar hydroxyl bonds on the surface.

Most of the current studies have focused on hydrate salt PCMs and have ignored the organic PCMs. However, hydrate salts PCMs are inferior to the organic PCMs, because the former are easy to phase-separate in the phase change process [8]. In this paper, the supercooling of acetamide PCMs was researched. And the acetamide- SiO_2 composites were prepared by adding nano- SiO_2 into acetamide. Then, the acetamide- SiO_2 composites were impregnated into porous graphite foam to form acetamide- SiO_2 -graphite foam samples (a type of thermal energy storage application [9]). The phase change properties of these materials were then established. Finally, we simulated the crystallization process of the experimental samples using MATLAB and found that the model agreed well with the experimental results.

2. Experimental

2.1. Materials and Methods. Acetamide ($\text{C}_2\text{H}_5\text{NO}$) with purity of 99% was used as the target material. SiO_2 nanoparticles with the average diameter of 30 nm were chosen as the additive to be dispersed in acetamide. The melted acetamide and SiO_2 were combined and magnetically stirred for 30 min with magnetic stirrer and then sonicated for 3 h to obtain a well-dispersed suspension. The acetamide- SiO_2 composites were solidified at the room temperature and were used for this study. The graphite foam with porosity of 85% and average pore diameter of 400 μm (prepared using the template method, details references [10]) was infiltrated with the melted acetamide- SiO_2 for 20 min to form acetamide- SiO_2 -graphite foam. In this way, we prepared the samples with a content of SiO_2 of 0 wt.%, 0.5 wt.%, 1 wt.%, 2 wt.%, and 5 wt.%, respectively.

2.2. Melting-Solidification Experiments. The thermal cycling behavior of each sample was determined using the apparatus shown in Figure 1. Testing was accomplished by placing the identical quantities of each sample in a beaker, a thermocouple was connected to the center of these samples, and a data acquisition module collected temperature data to a computer in real time. Samples were solidified at room temperature and then placed in the incubator at 110°C to melt them. This procedure was repeated for 50 cycles.

FIGURE 1: Schematic of melting-solidification experiments.

2.3. Results and Discussion

2.3.1. Melting-Solidification Experiments. Figure 2 shows the thermal analysis curves of the acetamide- SiO_2 samples. The percentage in the figure's legends represents the mass fraction of SiO_2 in samples. All samples were melted at 78°C in the heating process. In cooling process, some of the curves exhibited two fluctuations in temperature, the first of which was nucleation and the second was grain boundaries adjustment. Between these two fluctuations, there was a flat region which was the crystal nuclei growth. It can be seen that the supercooling of acetamide existed not only in the beginning of nucleation but also in crystal growth process. In this experiment, supercooling degree of pure acetamide in nucleation and crystal growth process was 14 and 11°C , respectively.

The solidification temperature of the acetamide-0.5 wt.% SiO_2 sample was less than that of pure acetamide, as can be seen in Figure 2(a). This reflected the fact that when the content of SiO_2 was too short (0.5 wt.%), the SiO_2 could not work as a nucleator, and they would work as an impurity, hindering the crystallization process of the PCM. With the increase in thermal cycles, the cooling curves of the two samples became consistent, indicating that the SiO_2 had failed to cause any reaction, as shown in Figures 2(b) and 2(c).

As shown, 1 wt.%, 2 wt.%, and 5 wt.% SiO_2 particles appeared to eliminate the supercooling of acetamide in the initial few cycles. This indicated that the supercooling of acetamide could be eliminated with moderate content of SiO_2 . However, the supercooling of the acetamide-1 wt.% SiO_2 gradually increased with the increase of the cycle numbers as shown in Figure 2(b). At the end of the cycles, the cooling curve of the acetamide-1 wt.% SiO_2 sample was close to that of pure acetamide and the supercooling of the acetamide-5 wt.% SiO_2 sample also increased slightly. Only the 2 wt.% SiO_2 appeared to efficiently suppress the supercooling during all the cycles; the performance showed almost no change after 50 cycles, indicating that the performance of the acetamide-2 wt.% SiO_2 sample is the most stable.

Figure 3 shows the thermal analysis curves of the acetamide- SiO_2 -graphite foam samples. In Figure 3(a), it can be seen that the sample began to crystallize at 65°C and that the temperature of crystal nuclei growth was 67°C . The fluctuations seen in the 2% and 5% curves which indicated a sudden increase to the melting temperature were caused by grain boundaries adjustment. Notably, the melting temperature of the samples in which grain boundaries adjustment occurred upon cooling was normal (78°C) while the others were reduced to 67°C as can be seen in Figures 3(a), 3(b), and

FIGURE 2: Time-temperature curves of acetamide-SiO₂ samples: (a) 1st cycle; (b) 25th cycle; (c) 50th cycle.

3(c). During the first three cycles, the occurrence of the grain boundaries adjustment is random. With the increase in the number of cycles, from the forth cycle to the end, the curves no longer reflect boundaries adjustment. The solidification temperature and melting temperature of samples were 65°C and 67°C, respectively, so that the supercooling of the samples was essentially eliminated. The addition of SiO₂ particles produced no apparent effect on the melting-solidification properties of the acetamide-SiO₂-graphite foam samples.

In the solidification process, acetamide generated a large number of grain boundaries. Part of the energy released by the solidification was preserved in the grain boundaries so that solidification latent heat would be reduced [11]. The grain boundaries could be reduced by spontaneous adjustment which would allow further the energy release. But the pore

structure of the graphite foam severely limited grain boundaries adjustment precluding reduction in the number of grain boundaries. The chemical potential energy stored in the molecular van der Waals attractions is a major factor in the latent energy of materials [12]. A large number of grain boundaries would reduce the intermolecular forces (van der Waals force) that the materials need to overcome during the melting process, so that the melting temperature and latent heat are reduced. This is the reason why the melting point of acetamide-SiO₂-graphite foam was lower than normal (78°C). These conclusions can be confirmed by DSC results.

2.3.2. DSC Results. Figure 4 shows the DSC results for the acetamide and acetamide-1 wt.% SiO₂ samples. In the DSC

FIGURE 3: Time-temperature curves of acetamide-SiO₂-graphite foam samples: (a) 1st cycle; (b) 2nd cycle; (c) 3rd cycle; (d) 4th cycle; (e) 50th cycle.

TABLE 1: The DSC results of acetamide-SiO₂ samples.

Samples	Melting point (°C)	Solidification point (°C)	Melting latent heat/(J·g ⁻¹)	Solidification latent heat (J·g ⁻¹)
0%	80.3	41	280.3	224.1
0.5%	79.8	39.5	278.6	219.8
1%	79.8	72.1	278.2	270.5
2%	79.9	70.9	272.6	266.8
5%	79.8	57.6	270	248.2

FIGURE 4: DSC curves of acetamide and acetamide-1 wt.% SiO₂ samples: (a) acetamide; (b) acetamide-1 wt.% SiO₂.

curve of acetamide sample, the first melting, first solidification, and second melting temperatures were 80.3°C, 41°C, and 69.2°C and the corresponding latent heat was 280.3 Jg⁻¹, 204.1 Jg⁻¹, and 223.5 Jg⁻¹, respectively. As can be seen, the latent heat of solidification was much smaller than that of melting, indicating that the grain boundaries were not adjusted, so that the second melting temperature was lower than the first. The solidification temperatures and latent heat of the acetamide-1 wt.% SiO₂ sample were 72.1°C and 270.5 J · g⁻¹, showing that the SiO₂ particles reduced the degree of supercooling and the number of grain boundaries so that more latent heat was released and the second melting curve is consistent with the first.

The DSC results of acetamide-SiO₂ samples are given in Table 1 and Figure 5. The supercooling of 0%, 0.5%, 1%, 2%, and 5% samples occurred at 39.3°C, 40.3°C, 77°C, 9.0°C, and 22.2°C and the solidification enthalpies for these events were 56.2 J·g⁻¹, 58.8 J·g⁻¹, 77 J·g⁻¹, 5.8 J·g⁻¹, and 21.8 J·g⁻¹ which are each lower than the melting latent heat. The larger

FIGURE 5: DSC curves of acetamide-SiO₂ samples.

supercooling and smaller solidification latent heat of the 0% and 0.5% samples indicate that no effective grain boundaries adjustment had occurred. In contrast, 1% and 2% samples which exhibited smaller supercooling and larger solidification enthalpies indicated that these samples had fewer grain boundaries. The process of grain boundaries adjustment could be seen in the cooling curve of the 5% sample, which possessed two exothermic peaks. One peak was associated with nucleation with a latent heat of 200 J·g⁻¹ and the other was indicative of grain boundaries adjustment with a latent heat of 48.18 J·g⁻¹.

Notably, the sample quantities used for the DSC and melting-solidification experiments were 5 mg and 10 g, respectively. The degree of the supercooling decreased when the mass of the specimen was increased from 5 mg to 10 g. This could be due to the increase in the nucleation catalyst in molten acetamide as a result of the increase in the mass of the specimen [13]. Therefore, the supercooling measured by DSC was the extreme case and the results of cycling experiment were more in line with the actual applications.

3. Simulation Study

3.1. Classical Nucleation Theory. The traditional theory of nucleation [14, 15] is based on the Gibbs theory [16] which is described as the generation of new phase within a uniform

FIGURE 6: The initial state of different samples in simulations: (a) acetamide; (b) acetamide-graphite foam; (c) acetamide-SiO₂; (d) acetamide-SiO₂-graphite foam.

single-phase system. We have successfully employed this theory to explain many of the experiments phenomena.

The surface free energy of spherical particles is

$$\Delta F_s = 4\pi r^2 \sigma. \quad (1)$$

ΔF_s is the change of surface free energy; σ is solid and liquid interface energy. The solid-liquid phase change process provides the change of free energy, for spherical particles; that is,

$$\Delta F_v = -\frac{4}{3}\pi r^3 \Delta F_v, \quad (2)$$

where ΔF_v is the free energy change with the formation of a new phase; ΔF_v is the free energy change with the formation of a new phase per unit volume. For spherical particles, the change of net free energy is

$$\Delta F = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \Delta F_v. \quad (3)$$

ΔF reaches a maximum value at r_k , where r_k is the critical radius of the crystal nuclei. For a spontaneous process, the free energy is always reduced. When the size of the grain is smaller than the critical size, the grains are melted on their own; when the grain size is greater than the critical size, the crystal nuclei will grow spontaneously. Calculating the

derivative of (3), the critical radius of the spherical particles is obtained when the ΔF is maximum:

$$r_k = \frac{2\sigma}{\Delta F_v}. \quad (4)$$

ΔF_v is proportional to the supercooling:

$$\Delta F_v = \alpha \Delta T, \quad (5)$$

where α is a constant and the ΔT is the degree of supercooling. Placing (5) into (4), we obtain

$$r_k = \frac{2\sigma}{\alpha \Delta T}. \quad (6)$$

It is clear that as ΔT increases, r_k will decrease and nucleation will be facilitated.

The nucleation process also includes heterogeneous nucleation. Heterogeneous nucleation occurs on the surface of other materials, such as impurity particles or vessel bumps. The degree of supercooling by heterogeneous nucleation is very small. In this paper, the additives of SiO₂ were assumed to be the heterogeneous grain, prompting acetamide heterogeneous nucleation, which significantly reduced the degree of supercooling.

3.2. Solidification Simulation. Based on the classic nucleation theory, the solidification process of acetamide, acetamide-SiO₂, acetamide-graphite foam, and acetamide-SiO₂-graphite

foam samples was simulated using MATLAB software. The simulation used a matrix of 1000×1000 to represent the samples. In this matrix, the numbers 0, 1, and 2 represented the liquid samples, the solid samples, and the graphite foam skeleton, respectively. The different crystal nuclei used different numbers which are greater than 2. The crystal nuclei radius is represented by the number of connected “solid” nodes; the critical radius of the crystal nuclei was represented by $A/\Delta T$, where A is a constant obtained by comparing the simulated and DSC results and ΔT is the degree of supercooling. The so-called “crystal nuclei” is the general term used for connected “solid” nodes whose number is larger than the critical size. In the large 1000×1000 matrix, several small matrices with sizes of 4×4 were randomly selected to simulate the SiO_2 particles randomly dispersed in acetamide.

Figure 6 was the initial states of simulation in various cases. The schematic of molten acetamide, acetamide-graphite foam, acetamide- SiO_2 , and acetamide- SiO_2 -graphite foam was shown in Figures 6(a)–6(d), respectively. In Figure 6(b), the gray frame represents the graphite foam skeleton, the entire sample was divided into 100 cells by “skeleton,” and all cells were in communication with each other just like the interconnected pores of graphite foam. In Figure 6(c), the white point was SiO_2 particles, one hundred randomly distributed “ SiO_2 particles” were throughout the whole region. This figure was a partially enlarged view. In Figure 6(d), the sample was divided into 100 cells by “graphite foam skeleton” and one hundred randomly distributed “ SiO_2 particles” throughout the whole region; this figure is a partially enlarged diagram.

The rules of the program were as follows: (1) if the state of the node was “graphite foam,” “ SiO_2 ” or “crystal nuclei,” then it remained unchanged; (2) if (1) was false and a “crystal nuclei” was adjacent to the node, then the state changed to the “crystal nuclei”; (3) if (1) and (2) were false, the node could change to “solid” with the probability of P and with the probability of $1 - P$ into “liquid.”

The main program flow chart is shown in Figure 7.

3.3. Results and Discussion. In the simulations, the supercooling degree of four samples was 39.20°C , 40.02°C , 9.10°C , and 10.20°C in turn. It can be seen that SiO_2 significantly reduced the degree of supercooling; the crystal nuclei of acetamide- SiO_2 and acetamide- SiO_2 -graphite foam samples were generated by heterogeneous nucleation on the surface of SiO_2 particles.

In Figures 8 and 9, the samples had many crystal nuclei and grain boundaries with a large degree of supercooling. After adding the graphite foam, many grain boundaries were forcibly separated by the graphite foam skeleton, increasing the total number of grain boundaries. Moreover, the grain boundaries which were separated by the graphite foam skeleton could not be eliminated by grain boundaries adjustment. This part of the grain boundaries was termed “permanent grain boundaries.” Figures 10 and 11 show that the number of crystal nuclei and grain boundaries was significantly reduced by SiO_2 particles, but the presence of the graphite foam still produced large numbers of grain boundaries.

FIGURE 7: The main program flow chart.

Table 2 lists the number of grain boundaries and the crystal nuclei in the simulations. Acetamide had many grain boundaries, so that grain boundaries adjustment was difficult and the heat release was small. The total numbers of crystal nuclei and grain boundaries of the acetamide- SiO_2 were the least so that the more heat was released, which was consistent with the DSC results (refer to Figure 4). In the simulation of acetamide-graphite foam and acetamide- SiO_2 -graphite foam samples, the grain boundaries were more complex and difficult to adjust, due to the presence of graphite foam, which was consistent with the conclusion of the melting-solidification experiments (see Figure 5).

4. Conclusions

Acetamide- SiO_2 composite has been prepared, by adding SiO_2 particles to acetamide and this composite was then impregnated into the graphite foam to form a new type of

FIGURE 8: Acetamide crystallization simulation: (a) the initial state; (b) being crystallization; (c) crystallization completed.

FIGURE 9: Acetamide-graphite foam crystallization simulation: (a) the initial state; (b) being crystallization; (c) crystallization completed.

FIGURE 10: Acetamide-SiO₂ crystallization simulation: (a) the initial state; (b) being crystallization; (c) crystallization completed.

FIGURE 11: Acetamide-SiO₂-graphite foam crystallization simulation: (a) the initial state; (b) being crystallization; (c) crystallization completed.

TABLE 2: The number of crystal nuclei and grain boundaries in the simulation.

Samples	The numbers of crystal nuclei	Total grain boundaries (node)	Permanent grain boundaries (node)
Acetamide	103	21336	0
Acetamide-Graphite foam	98	35037	17360
Acetamide-SiO ₂	6	4303	0
Acetamide-SiO ₂ -Graphite foam	6	21300	17360

form-stable phase change material. Each sample was subjected to 50 melting-solidification cycles and the acetamide-SiO₂ samples were tested using DSC. Based on the classical nucleation theory, the crystallization process of these samples was simulated using MATLAB. The conclusions of this work are as follows.

In melting-solidification experiments, the crystallization supercooling degree of acetamide was 14°C; the supercooling of crystal nuclei growth was 11°C. The supercooling of acetamide could be eliminated by adding SiO₂ with a mass fraction of 1% to 5%. The performance of the acetamide-2% SiO₂ was very stable with no change after 50 cycles. The acetamide-SiO₂ samples were impregnated into the graphite foam, the melting temperature of the acetamide-SiO₂-graphite foam samples was reduced to 67°C, and the solidification temperature was reduced to 65°C. At the same time, the supercooling degree of the samples was essentially eliminated, but a little heat storage capacity was lost. The presence of SiO₂ did not have a significant impact on the supercooling of these samples.

DSC results showed that the grain boundaries of acetamide could not be effectively adjusted, so that the heat release was low during the cooling process. In the second melting process, the large numbers of boundaries in acetamide caused the melting point and melting latent heat to be lower than normal. Addition of SiO₂ with the content of 1 wt.% and 2 wt.% reduced the supercooling of acetamide to less than 10°C and improved the heat release. In the first and second melting process, the melting points and latent heat of the samples were equal.

The simulation results showed that the presence of SiO₂ could significantly reduce the number of grain boundaries. On the contrary, the presence of graphite foam could significantly increase the number of grain boundaries and make the grain boundaries more difficult to adjust. The simulation also explained the reason, from the microscopic point of view, why the degree of supercooling was reduced. This was attributed to be heterogeneous nucleation which occurred along the SiO₂ particles in the crystallization process.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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