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Phase change performance of sodium acetate trihydrate with AlN nanoparticles and CMC

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ABSTRACT

Sodium acetate trihydrate (SAT), which has high energy storage density and high thermal conductivity, is an important phase change material (PCM) for thermal storage. But it suffers from serious supercooling and phase segregation during the solidification process, and therefore its application requires the use of effective nucleating and thickening agents. In this study, AlN nanoparticles were proposed as the nucleating agent and carboxyl methyl cellulose (CMC) was selected as the thickener for SAT. The phase change temperature and the latent heat of SAT with the addition of AlN nanoparticles and CMC were measured. The results show that AlN nanoparticles can prevent supercooling of SAT significantly. For SAT with 5 wt% AlN nanoparticles and 4 wt% CMC, no supercooling phenomenon occurs, and its phase change temperature and latent heat are 52.5 \degree C and 227.54 kJ/kg, respectively. AlN nanoparticles and CMC additives also can improve the dehydration temperature according to the results of TG–DTA. Size distribution of AlN nanoparticles was measured by means of light scattering method. The size range is 95–300 nm, which is confirmed by environmental scanning electron microscope. The radial needle-like crystals growth process was also observed and recorded by an optical microscope.

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1. Introduction

Solar energy is a renewable, clean but unstable energy source. Therefore, its thermal utilization requires an efficient thermal storage so that the excess heat can be collected and stored for later use during the hours without solar irradiation. Many other heat energy utilization systems, such as industrial waste heat recovery system, refrigeration and heat pump system and distributed combined cooling, heating and power (CCHP) system may also need thermal storage technique to improve system performances. Because of having large latent heat and constant phase change temperatures, phase change materials (PCMs) are considered as the promising mediums for thermal storage applications. Some good reviews [\[1–4\]](#page--1-0) provide overviews of research on PCMs and their applications.

Sodium acetate trihydrate (SAT), which has high energy storage density and high thermal conductivity, is one of the important PCMs for thermal storage. It has a phase change temperature of 58 \degree C, and is therefore suitable for hot water supplying by storing low temperature thermal energy. But SAT suffers from serious supercooling and phase segregation during the solidification process, and therefore, suitable nucleating agents and thickeners are necessary for its applications. Some previous studies proposed several nucleating agents. Kimuraa

and Kaia [\[5\]](#page--1-0) reported that mixtures of SAT and 10 wt% NaBr - 2H2O or NaHCOO 3H₂O were very stable on repeated phase change (over 1000 cycles) in a heat cycle test (60–30 \degree C), while SAT deteriorated rapidly under similar experimental conditions (70–40 \degree C). They also presented a pressed mixture of anhydrous NaCH₃COO, Na₂HPO₄ and polyethylene powder as nucleating agent. Naumann et al. [\[6\]](#page--1-0) indicted that nucleation efficiency of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ for the crystallization of SAT is not stable over long periods. Ryu et al. [\[7\]](#page--1-0) reported that the supercooling of thickened SAT with more than 1 wt% $K₂SO₄$ and Na₂P₂O₇ \cdot 10H₂O were reduced to 0–2 \degree C and 0–3 \degree C, respectively. But Choi et al. [\[8\]](#page--1-0) used 2 wt% K_2SO_4 as a nucleating agent for SAT, and the degree of supercooling was still about 6–10 °C. Li et al. [\[9\]](#page--1-0) also indicated that K_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ could reduce the supercooling of SAT but were unstable for long term usage. $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}_6$ $\text{Na}_4\text{P}_2\text{O}_7$ \cdot 10H $_2$ O and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ were recommended as effective nucleaing agents for SAT with thickener gelatin by Li et al. [\[9\].](#page--1-0) Mao et al. [\[10\]](#page--1-0) investigated the performances of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}_4$ $Na₃PO₄ \cdot 12H₂O$, $Na₂CO₃ \cdot 10H₂O$, $Na₂SiO₃ \cdot 9H₂O$ and $Na₂B₄O₇ \cdot 10H₂O$ as nucleating agents for SAT, their results showed that $Na₂HPO₄$. 12H2O cooperated with thickener carboxyl methyl cellulose (CMC) and gelatin can reduce the supercooling of SAT and maintain thermal storage capacity. In conclusion, the proposed nucleating agents are almost hydrated salts, instability themselves may affect the phase change performance of SAT.

Aluminum nitride (AlN) has a hexagonal crystal structure and is an inorganic ceramic material with high thermal conductivity and low thermal expansion coefficient. It has stable physical and

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chemical properties in large temperature range, and its nanoparticles have large specific surface area and high surface activity. If dispersed into SAT with a proper size distribution, AlN nanoparticles may act as nucleating cores for SAT. Compared with the traditional hydrated salts nucleating agents, AlN nanoparticles take advantage of stability. But till now, usage of AlN nanoparticles or other nanoparticles as nucleating agents for SAT or other hydrated salts are rarely reported publicly. Therefore, it is proposed as the nucleating agent for SAT in this study.

To prevent the phase segregation of SAT, CMC is used as an effective thickener according to the work of Cabeza et al. [\[11\],](#page--1-0) which also can prevent aggregation and sedimentation of AlN nanoparticles suspended in SAT.

2. Materials

SAT (analytical reagent grade, purity $>$ 99%) and CMC (with high viscosity of 300–800 mPa s in 20 g/L aqueous solution) were offered by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). AlN nanoparticles, with purity higher than 99.0% and an average size of 50 nm, was provided by Kaier Nanometer Energy & Technology Co., Ltd. (Hefei, China).

3. Experimental work

The content of AlN nanoparticles was varied from 3 to 5 wt%. The content of CMC was fixed at 4 wt%. All the materials were weighted using a precision electronic balance (SL1002N, Shanghai Minqiao Precise Science Instrument Co., Ltd., China, precision 0.01 g) and mixed together into a mortar with a pestle. Then the finely ground sample was filled into a stainless steel test-tube. To avoid water evaporation during the melting process, samples were sealed by paraffin wax with phase change temperature of about 47 \degree C. The temperature was measured by a T-type thermocouple with 0.1 ° C accuracy and an Agilent 34970A (Agilent Technologies, Inc., USA) was employed as the data acquisition apparatus. To melt samples, hot water with temperature 70° C was supplied by a thermostat (DC-4006, Sunny Hengping Scientific Instrument Co., Ltd., China).

4. Results and discussion

Fig. 1 is the freezing curve of pure SAT with phase change temperature of 58 $^{\circ}$ C. It is obvious that the pure SAT exhibits a significant degree of supercooling about 17 \degree C. Fig. 2 is the freezing curve of $SAT+3$ wt% AlN nanoparticles $+4$ wt% CMC. The degree of supercooling is reduced to 2.4 \degree C. Fig. 3 is the freezing curve of $SAT+4$ wt% AlN nanoparticles + 4 wt% CMC. The degree of supercooling is further reduced to only about 1 \degree C. [Fig. 4](#page--1-0) is the freezing curve of $SAT+5$ wt% AlN nanoparticles +4 wt% CMC. It shows that no supercooling occurs. Therefore, AlN nanoparticles can be an effective nucleating agent for SAT. According to the measurement results shown in Figs. 1–4, it is also obvious that the phase change temperature of SAT is reduced along with the increasing content of AlN nanoparticles.

The phase change temperature and the latent heat of pure SAT and $SAT+5$ wt% AlN nanoparticles +4 wt% CMC were measured by DSC (DSC-60, Shimadzu, Japan). Scans were made at 10 °C/min and nitrogen purge gas at 20 ml/min was used. [Fig. 5](#page--1-0) is the DSC melting curve of pure SAT. Its phase change temperature (onset temperature) is 58 °C and the latent heat is 238.54 $\frac{1}{g}$. [Fig. 6](#page--1-0) is the DSC melting curve of $SAT+5$ wt% AlN nanoparticles $+4$ wt% CMC. The phase change temperature is decreased to 52.5 °C, and the latent heat is decreased to 227.54 J/g. The results indicate

Fig. 2. Freezing curve of $SAT+3$ wt% AlN nanoparticles + 4 wt% CMC.

Fig. 3. Freezing curve of SAT+4 wt% AlN nanoparticles +4 wt% CMC.

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