



Research Paper

Effects of additives on the subcooling behavior of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ phase transition

Ying Ma, Binyi Lei, Yicai Liu*, Tong Wu

School of Energy Science and Engineering, Central South University, Changsha 410083, China

HIGHLIGHTS

- We discuss the reaction mechanism between additive nano-TiO₂ and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.
- We discuss the reaction mechanism between additive gelatin and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.
- The subcooling temperature decreased to 3.1 °C with specific additives.

ARTICLE INFO

Article history:

Received 1 August 2015

Accepted 29 December 2015

Available online 21 January 2016

Keywords:

 $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

Phase-change material

Subcooling behavior

Cooling curve

Nano-TiO₂

Deionized water

ABSTRACT

An experimental device for studying subcooling behavior was fabricated, and the subcooling curves of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were drawn. The effects of nucleating agent, interface modifier agent, and deionized water addition were studied, and the mechanism was discussed. The results showed that the subcooling temperature of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ decreased to 3.1 °C with 1.5% nano-TiO₂ (20 nm), 2% gelatin, and 10% deionized water.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The unprecedented pressure of energy saving has prompted extensive studies on phase-change energy storage [1]. However, no effective method of recovering waste heat at around 70–100 °C is available. Crystalline hydrated salts are some of the most important phase-change materials for energy storage at medium to low temperature range [2]. Among these materials, sulfate with a phase-change temperature of 90 °C can satisfy application requirements. However, crystalline hydrated salts have the disadvantage of high subcooling temperature and less nucleation during melt–freeze process, which significantly limits their practical application [3]. Telkes [4], Cantor [5], and Liu and Chung [6] studied the improved energy-storage properties of $\text{Al}_2(\text{SO}_4)_3$ solution with added borax. Yang et al. [7] and Ding et al. [8] studied the crystallization kinetics of $\text{Al}_2(\text{SO}_4)_3$ solution, the nucleation behavior of thermal-

storage hydrated salt material, and the impact of different nucleating agents on the subcooling behavior of $\text{Al}_2(\text{SO}_4)_3$ solution [9,10].

The present study focused on the selection of type and dosage of nucleating agent, which lead to less research on the subcooling decreasing mechanism of hydrated salt materials. Therefore it is particularly important to conduct subcooling temperature experiments based on the exploration of phase change mechanism and surface modifiers, as well as the mechanism of additives on the subcooling behavior of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

2. Relationship of liquid–solid interfacial tension to the subcooling temperature of metal salt

According to the classical nucleation theory [11], insoluble impurities could be nucleation substrate during solidification, and the solid crystal nucleus adheres to the substrate as heterogeneous nucleation. Fig. 1 illustrates that the solid crystal nucleus has a single-ball coronal shape with radius r and contact angle θ between the solid phase and substrate, as well as liquid–solid, liquid–substrate, and solid–substrate surface tension values σ_{SL} , σ_{LM} , and σ_{SM} , respectively. When the surface tension achieves balance, then

* Corresponding author. Tel.: 0086 731 88876111; fax: 0086 731 88879863.
E-mail address: lyccsu@csu.edu.cn (Y. Liu).

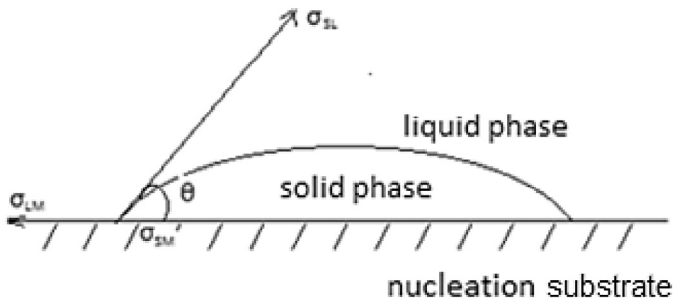


Fig. 1. Heterogeneous nucleation.

$$\sigma_{SM} + \sigma_{SL} \cos \theta = \sigma_{LM} \quad (1)$$

The variation in system free-energy is

$$\Delta G_N = V_S \Delta G_V + A_{SL} \sigma_{SL} + A_{SM} (\sigma_{SM} - \sigma_{LM}) \quad (2)$$

where ΔG_N is the free-energy variation of the heterogeneous nucleation system, V_S is the volume of solid crystal nucleus, ΔG_V is the per-volume free-energy difference between liquid and solid, and A_{SL} and A_{SM} are the liquid–solid and liquid–substrate interfacial areas, respectively.

According to geometry,

$$V_S = \frac{\pi r^3}{3} (2 - 3 \cos \theta + \cos^3 \theta) \quad (3)$$

$$A_{SL} = 2\pi r^2 (1 - \cos \theta) \quad (4)$$

$$A_{SM} = \pi r^2 \sin^2 \theta \quad (5)$$

When Eqs. (3)–(5) are substituted into Eq. (2),

$$\Delta G_N = \left(\frac{4\pi r^3}{3} \Delta G_V + 4\pi r^2 \sigma_{SL} \right) + \left(\frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right) \quad (6)$$

Let $\frac{d\Delta G_N}{dr} = 0$, then

$$\Delta G_V = -\frac{2\sigma_{SL}}{r_N^*} \quad (7)$$

where r_N^* is the critical core radius of the heterogeneous nucleation.

Therefore, ΔG_V increases with decreased σ_{SL} .

The relationship of per-volume free-energy difference of liquid–solid, i.e., the nucleation driving force ΔG_V , to subcooling temperature ΔT is

$$\Delta G_V = -L_V \left(\frac{\Delta T}{T_0} \right) \quad (8)$$

where L_V is the latent heat of phase transition and T_0 is the critical temperature of phase transition.

When Eqs. (7) and (8) are set as simultaneous equations, then

$$\Delta T = \frac{-2T_0 \sigma_{SL}}{L_V r_N^*} \quad (9)$$

For phase-change materials, T_0 , L_V , and r_N^* are certain. Therefore, the subcooling temperature ΔT of phase-change materials will decrease with decreased liquid–solid interfacial tension σ_{SL} .

3. Mechanism of intensifying crystallization and the energy-storage process of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ with additives

3.1. Nanomaterial nucleation

As is verified by a lot of research works, the surface of TiO_2 is full of surface hydroxyl group [12]. When the reaction temperature is lower than 227 °C, surface hydroxyl group stably exists on top of the TiO_2 (011) surface, where the adsorption capacities of trough and bridge position are relatively weak [13]. The temperature of this experimental system is much lower than 227 °C; hence, aluminum ion with positive charges from the $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ molecule may firmly bond to Ti–OH groups belonging to TiO_2 surface hydroxyl and can form stable Ti–O–Al bonds. Therefore, TiO_2 particles may act as nucleation substrate, and the surface hydroxyl groups act as nucleation points that can pull the $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ molecule together. Subsequently, a dense and continuous cladding layer forms around TiO_2 . This layer is both a physical cladding and a stable chemical bond because of the presence of surface hydroxyl, which can effectively accelerate the crystallization of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

In addition, the radius and coordination number of Al^{3+} are close to those of Ti^{4+} ; hence, Al^{3+} may easily replace Ti^{4+} to penetrate the interstitial void [14], which is conducive for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ to aggregate around TiO_2 . The nanomaterial also has a large specific surface area, which translates to a strong ability to mitigate the increased system surface energy. Therefore, the nucleation effect of nano- TiO_2 is very good [15] and can effectively reduce the system subcooling temperature.

3.2. Surface modification of gelatin

Gelatin molecule contains a large number of amino acids, with hydrophilic polar and lipophilic nonpolar groups simultaneously existing. Thermodynamic analysis indicates that gelatin decreases the surface tension between the seeded out solid $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and liquid $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. As mentioned in the first part of this paper, as gelatin can reduce the surface tension between seeded out solid $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and liquid $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, it may directly decrease the subcooling temperature. Consequently, for the ability to reduce the surface tension between solid nano- TiO_2 and liquid $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, the particles become better dispersed in the system, and agglomeration is prevented.

Electrochemical analysis indicates that TiO_2 surface has negative charges for the surface hydroxyl group. According to the Stern electric double layer model, the Al^{3+} of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is strongly attracted and firmly bonds to the TiO_2 surface to form a fixed adsorption layer in the region with one to two-molecule-thick distance from the TiO_2 surface. Al^{3+} also forms a diffusion layer beyond the adsorption layer, i.e., the formation of the electric double layer. After adding gelatin to the system, the electric double layer is compressed and the Zeta potential of the system is lowered, which renders $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ crystallization process much easier because gelatin molecule has a large number of groups with positive charges.

In summary, the additive TiO_2 and gelatin may reinforce the crystallization of aluminum sulfate hydrous salt. The experimental results help to explain this conclusion.

4. Effects of additives on the liquid–solid interfacial tension of metal salt

4.1. Materials and methods

The following test materials were used: 35g analytical-grade $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ as phase-change material, industrial-grade anatase-

Download English Version:

<https://daneshyari.com/en/article/644671>

Download Persian Version:

<https://daneshyari.com/article/644671>

[Daneshyari.com](https://daneshyari.com)