

Experimental investigation of crystallization process of nanofluid by DSC

Chen Ying Jia Lisi Mo Songping

(Faculty of Material and Energy, Guangdong University of Technology, Guangzhou 510006, China)

Abstract: A water-TiO₂ nanofluid with a weight fraction of 5% and an average particle size of 75 nm is used to investigate the effect of TiO₂ nanoparticles on the crystallization and melting behaviors of deionized water by using differential scanning calorimetry (DSC) at four different cooling rates, 3, 5, 7, 9 °C/min. The DSC experimental results show that the water-TiO₂ nanofluid has a lower supercooling degree and a faster crystallization rate than the deionized water. With the increase in the cooling rate, the influence of the TiO₂ nanoparticles on the supercooling degree of the deionized water becomes greater, but on the crystallization rate it turns lower. During the melting process, compared with the deionized water, the water-TiO₂ nanofluid has a lower melting temperature, a less latent heat and a higher melting rate.

Key words: water-TiO₂ nanofluid; nucleation; supercooling degree; differential scanning calorimetry

An ice storage air-conditioning system is an important element of many energy conservation programs in industrial and commercial applications. Water is widely used as the phase change material (PCM) for ice storage because of such advantages as high latent heat, stable chemical property, low costs and easy acquisition, no environmental pollution concerns and compatibility with the material of air-conditioning equipment. However, freezing does not occur until the temperature of the water is below its freezing point. Therefore, it is necessary to lower the evaporation temperature of the chiller unit during the ice storage process. As a result, it apparently causes a decline in the coefficient of performance (COP) of the chiller unit. Therefore, it is very important to prevent or reduce the supercooling degree of the water.

There are many studies on the supercooling phenomenon of water in enclosed containers. Arnold^[1] investigated the nucleation phenomenon of water in spherical capsules and indicated that the nucleation temperature of water was affected by the cooling rate and the amount of nucleation. Lee et al.^[2] studied the supercooling phenomenon of pure water in horizontal cylinders and developed a correlation of the supercooling period as a function of the cooling rate and the nucleation temperature. Many experiments have also been conducted to investigate the nucleation behaviors of water droplets. Bigg^[3] studied the freezing process of water droplets with different diameters suspended by two insoluble liq-

uid layers and indicated that the mean nucleation temperature was higher when the cooling rate decreased. Vail and Stansbury^[4] investigated the nucleation behaviors of water droplets at a constant cooling rate and the results were similar to those reported by Bigg. The release of supercooling can be improved by the addition of nucleating agents. Vonnegut^[5] used silver iodide and lead iodide as the nucleating agents and found that these agents greatly reduced the supercooling degree of small water droplets.

The most widely adopted method by previous experiments was analyzing temperature curves due to the simplicity. DSC is a professional technique to study the dynamics of crystallization and melting behaviors of materials, and it has been widely applied in the fields of polymer composites and metallic alloys. However, there have been limited studies focusing on the crystallization and melting behaviors of water by using this instrument.

In this paper, the crystallization and melting properties of a water-TiO₂ nanofluid and deionized water are investigated by means of DSC. TiO₂ nanoparticles are chosen as additives due to their good hydrophilic properties and wetting characteristics.

1 Materials and Method

1.1 Materials

A water-TiO₂ nanofluid is purchased from Sigma-Aldrich Chemical Co., Ltd., USA, with a weight fraction of 5%, an average particle size of 75 nm and a density of 1.07 g/mL at 25 °C and is used as received.

1.2 Calorimetric measurements

In this paper, DSC (NETZSCN-STA 449C) equipped with a cooler is used. All experiments are carried out under a nitrogen purge with a flow rate of 20 mL/min. 10 to 15 mg samples are first heated from room temperature to 30 °C and held in the state for 5 min to eliminate the influence of thermal history. Then the samples are cooled to -30 °C at various cooling rates ranging from 3 to 9 °C/min. After being maintained at -30 °C for 5 min, the samples are heated to 30 °C again with a heating rate of 5 °C/min. The thermograms are recorded for later data analysis.

From the thermograms, some useful parameters such as the onset temperatures of crystallization and melting ($T_{c, onset}$, $T_{m, onset}$), the exothermic and endothermic peak temperatures ($T_{c, peak}$, $T_{m, peak}$), and the end temperatures of crystallization and melting ($T_{c, end}$, $T_{m, end}$) can be obtained^[6]. The crystallization enthalpy H_c is calculated by integrating the DSC thermograms from $T_{c, onset}$ to $T_{c, end}$, which can be expressed as^[7]

$$\Delta H_c = \int_{T_{c, onset}}^{T_{c, end}} \left(\frac{dH}{dT} \right) dT \quad (1)$$

Received 2009-11-18.

Biography: Chen Ying (1969—), female, doctor, professor, chenying@gdut.edu.cn.

Foundation item: The National Natural Science Foundation of China (No. 50876022).

Citation: Chen Ying, Jia Lisi, Mo Songping. Experimental investigation of crystallization process of nanofluid by DSC [J]. Journal of Southeast University (English Edition), 2010, 26(2): 359 – 363.

where dH is the crystallization enthalpy in the infinitesimal temperature section dT .

The crystallization kinetics under non-isothermal conditions is analyzed in this paper. X_t is the relative degree of crystallinity at time t and can be calculated by^[8]

$$X_t = \frac{\int_{T_{c, \text{onset}}}^T \left(\frac{dH_c}{dT} \right) dT}{\int_{T_{c, \text{onset}}}^{T_{c, \text{end}}} \left(\frac{dH_c}{dT} \right) dT} \quad (2)$$

The half crystallization time ($t_{1/2}$) is the time required for 50% crystallization. A smaller value of $t_{1/2}$ means a faster crystallization rate^[9].

The degree of supercooling is defined as^[10]

$$\Delta T = T_{m, \text{onset}} - T_{c, \text{peak}} \quad (3)$$

In non-isothermal crystallization, the relationship between the crystallization time scale t and the temperature T can be evaluated as

$$t = \frac{T_{c, \text{onset}} - T}{\Phi} \quad (4)$$

where Φ is the cooling rate.

2 Results and Discussion

2.1 Crystallization behaviors

The non-isothermal crystallization thermograms of the deionized water and the water-TiO₂ nanofluid at various cooling rates ranging from 3 to 9 °C/min are shown in Fig. 1. It can be seen that with the increase of the cooling rate, the crystallization peaks of the two fluids become sharper and the onset and peak crystallization temperatures move towards lower values. Compared with the deionized water, the

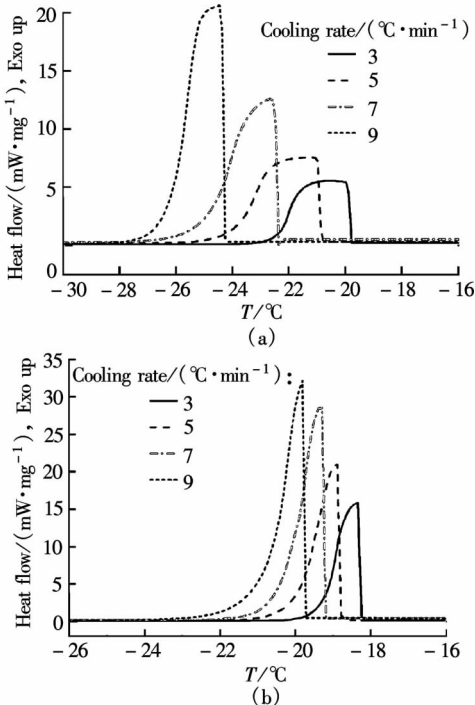


Fig. 1 DSC thermograms of nonisothermal crystallization at different cooling rates. (a) Deionized water; (b) Water-TiO₂ nanofluid

curve of the water-TiO₂ nanofluid is sharper and the crystallization temperature is higher.

The variation of the onset and peak temperatures of crystallization at different cooling rates for the deionized water and the water-TiO₂ nanofluid are shown in Fig. 2. It is obvious that the onset and peak temperatures of the water-TiO₂ nanofluid are higher than those of the deionized water at any given cooling rate. This phenomenon can be explained by the heterogeneous nucleation effect of TiO₂ nanoparticles on water. Water molecules can easily attach to the surfaces of the TiO₂ nanoparticles, which makes the crystallization of the deionized water occur at a high temperature. It is also shown in Fig. 3 that the differences in the crystallization temperatures of the deionized water and the water-TiO₂ nanofluid increases with the increase in the cooling rate. As we know, the homogeneous nucleation of a material spontaneously occurs below the melting point and requires a long time. But the heterogeneous nuclei might be formed as soon as the material reaches its crystallization temperature. Therefore, the heterogeneous nucleation needs less time at the same cooling temperature. The cooling rate has a greater influence on the heterogeneous nucleation than on the homogeneous nucleation. Moreover, the nucleation effect of the TiO₂ nanoparticles is observed to be much greater at the higher cooling rates in our experiments.

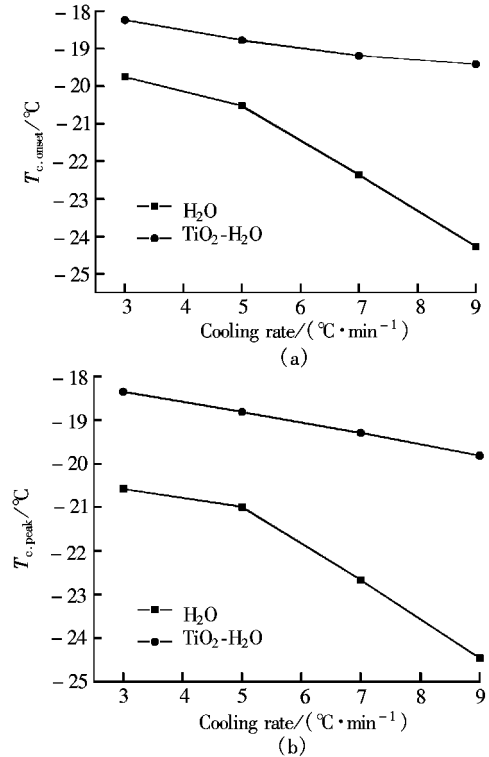


Fig. 2 Onset and peak crystallization temperatures vs. cooling rate. (a) Onset crystallization temperature; (b) Peak crystallization temperature

The relative degree of crystallinity (X_t) and temperature at various cooling rates are shown in Fig. 3. The plots for the deionized water and the water-TiO₂ nanofluid are similar and only a lag effect of the cooling rate on crystallization is observed. Because of the shorter crystallization time at a higher cooling rate, the values of X_t are lower than those at a lower

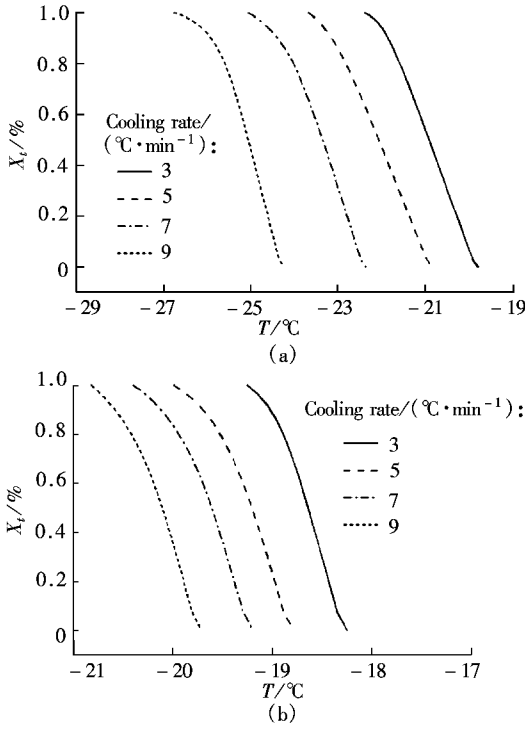


Fig. 3 Relative degree of crystallinity and temperature at different cooling rates. (a) Deionized water; (b) Water-TiO₂ nanofluid

cooling rate at the same crystallization temperature. According to Eq. (4), the dependence of X_t on the crystallization time t is shown in Fig. 4. As can be seen, the time needed for the deionized water and the water-TiO₂ nanofluid to finish crystallization decreases with the increase in the cooling rate.

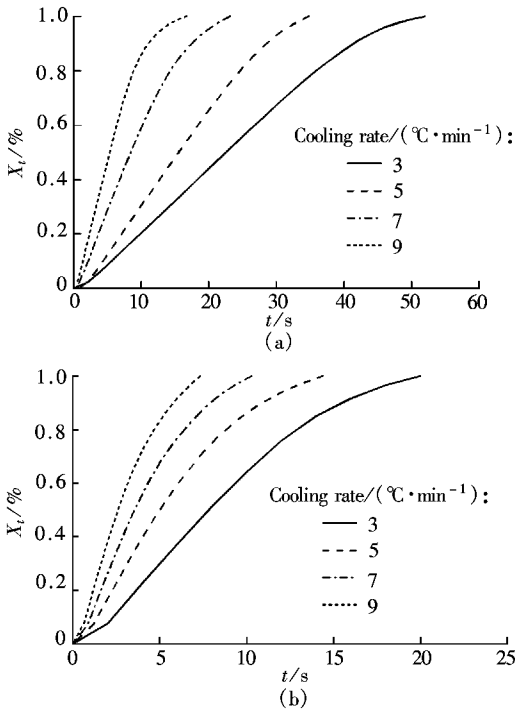


Fig. 4 Relative degree of crystallinity and time at different cooling rates. (a) Deionized water; (b) Water-TiO₂ nanofluid

The variation of $t_{1/2}$ with the cooling rate is shown in Fig. 5. Obviously, the value of $t_{1/2}$ of the water-TiO₂ nanofluid is

smaller than that of the deionized water at all cooling rates. This result indicates that the TiO₂ nanoparticles act as heterogeneous nucleating agents to facilitate the overall crystallization process of the deionized water. Moreover, with the increase in the cooling rate, the values of $t_{1/2}$ of both the water-TiO₂ nanofluid and the deionized water decrease and the difference between them is reduced. The addition of the TiO₂ nanoparticles makes $t_{1/2}$ decrease 65.26% at a cooling rate of 3 °C/min, and 51.22% at a cooling rate of 9 °C/min. It is suggested that the TiO₂ nanoparticles can reduce the crystallization rate with the increase in the cooling rate.

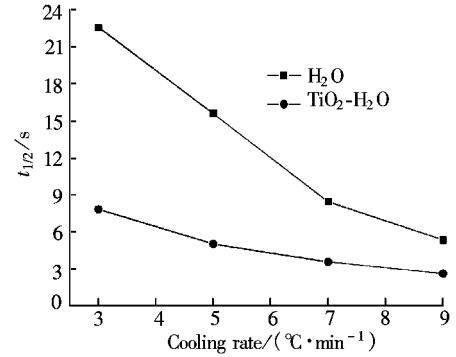


Fig. 5 Relationship of half crystallization time and cooling rate

The influence of the cooling rate on the crystallization heat is shown in Fig. 6. It can be seen that the values of ΔH_c of both fluids decrease with the increase in the cooling rate. In addition, the value of ΔH_c of the deionized water is smaller than that of the water-TiO₂ nanofluid at any cooling rate. It is possibly because the molecules become less active and have not enough time to diffuse into the crystallite lattice to adjust and reorganize better configurations when the cooling rate increases. As a result, the storage energy becomes less during the crystallization process with the increase in the cooling rate.

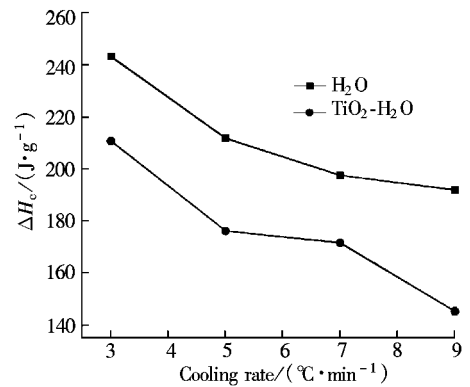


Fig. 6 Relationship of crystallization heat and cooling rate

2.2 Melting behaviors

Fig. 7 shows a series of DSC endothermic curves at three cooling rates (5, 7, 9 °C/min). With the increase in the cooling rate, the endothermic peaks of both fluids become sharper, which means that the melting processes become faster.

The values of $T_{m, onset}$ and $T_{m, peak}$ changing with the cooling

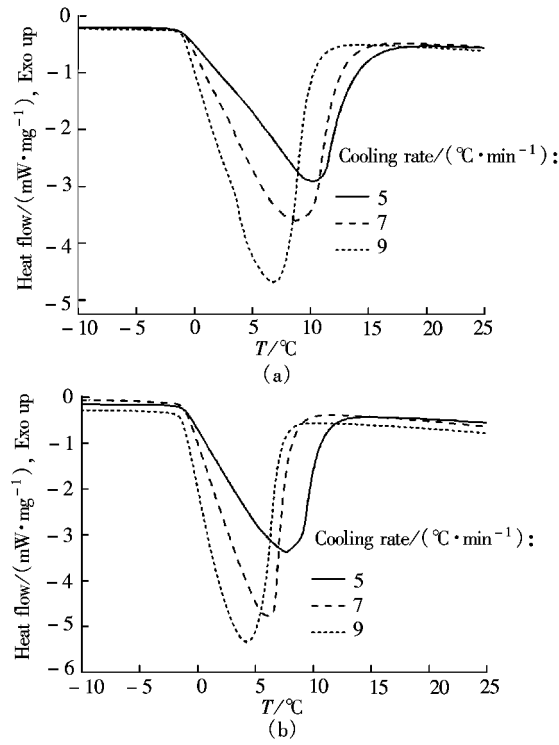


Fig. 7 DSC thermograms of melting after fluids cooled at different cooling rates. (a) Deionized water; (b) Water-TiO₂ nanofluid

rate are shown in Fig. 8. It can be seen that the values of $T_{m, peak}$ of both fluids change greatly with the cooling rate while the values of $T_{m, onset}$ keep constant. The value of $T_{m, peak}$ decreases from 10.26 to 6.7 °C for the deionized water as the cooling rate increases from 5 to 9 °C/min, while the value of $T_{m, onset}$ only changes from -1.13 to -1.03 °C. Obviously, the cooling rate has little impact on the onset melting temperature. It is suggested that it might be not the cooling rate but the heating rate which determines the onset melting temperature. The melting behaviors of the samples at the same heating rate are mainly influenced by the quality of the ice crystals during the crystallization process. The solid form of the tested material with better crystal quality needs more time and a higher temperature to melt. As discussed in section 2.1, the crystal quality deteriorates with the increase in the cooling rate. So the peak melting temperature decreases with the increase in the cooling rate. In addition, under the same cooling rate, the values of $T_{m, onset}$ and $T_{m, peak}$ of the water-TiO₂ nanofluid are lower than those of the deionized water. This

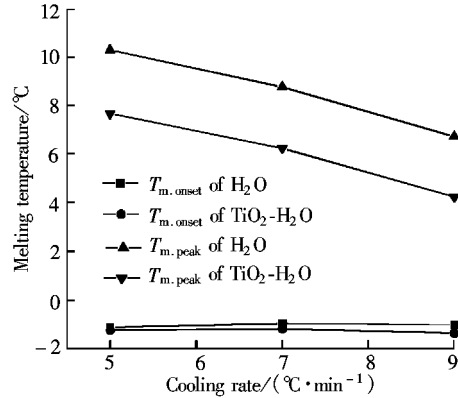


Fig. 8 Influence of cooling rate on $T_{m, onset}$ and $T_{m, peak}$

means that the crystal quality of the water-TiO₂ nanofluid is not as good as that of the deionized water at the same cooling rate. The influence of the cooling rate on $T_{m, index}$ is shown in Fig. 9. It can be seen that the values of $T_{m, index}$ of both fluids decrease with the increase in the cooling rate. That is, the melting time becomes less with the increase in the cooling rate. The value of $T_{m, index}$ of the deionized water is higher than that of the water-TiO₂ nanofluid at any given cooling rate, which means that the melting rate of the deionized water is slower than that of the water-TiO₂ nanofluid.

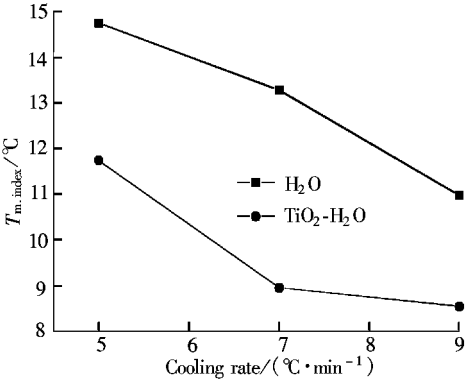


Fig. 9 Influence of cooling rate on $T_{m, index}$

The influence of the cooling rate on the heat of melting ΔH_m is shown in Fig. 10. Obviously, the values of ΔH_m of both the water-TiO₂ nanofluid and the deionized water decrease with the increase in the cooling rate. Moreover, the melting heat of the water-TiO₂ nanofluid is less than that of the deionized water. The degrees of supercooling, ΔT , of the

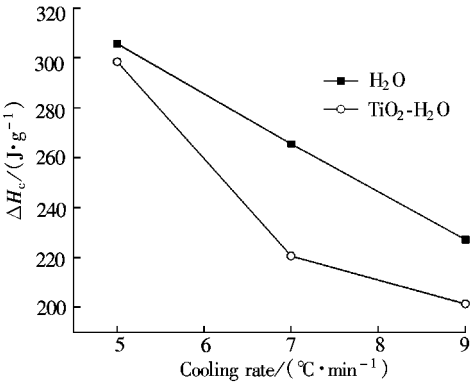


Fig. 10 Influence of cooling rate on heat of melting

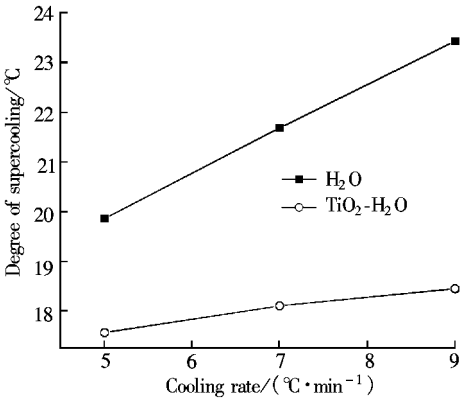


Fig. 11 Influence of cooling rate on degree of supercooling

deionized water and the water-TiO₂ nanofluid at different cooling rates are illustrated in Fig. 11. It can be seen that the values of ΔT of both fluids and the temperature difference between them increase with the increase in the cooling rate. In other words, the effect of the TiO₂ nanoparticles on the supercooling degree becomes greater with the increase of the cooling rate.

3 Conclusions

The nonisothermal crystallization and melting behaviors of the deionized water and the water-TiO₂ nanofluid are investigated by DSC. Some conclusions are drawn as follows:

1) For the deionized water and the water-TiO₂ nanofluid, the onset and peak crystallization temperatures and the peak melting temperatures decrease with the increase in the cooling rate while the onset melting temperature almost keeps constant.

2) With the increase in the cooling rate, the crystallization and melting rates increase while the heat of crystallization and melting decrease.

3) At any given cooling rate, the water-TiO₂ nanofluid has a higher onset crystallization temperature, higher crystallization and melting rates, and a smaller supercooling degree than the deionized water. The TiO₂ nanoparticles might act as nucleating agents to promote heterogeneous nucleation during the crystallization process.

4) The TiO₂ nanoparticles increase the crystallization rate and decrease the degree of the supercooling of the deionized water. However, due to the reduction in the latent heat caused by the addition of nanoparticles into the deionized water, it is very important to find suitable nanomaterials as additives to reduce the decline of the latent heat of nanoflu-

ids.

5) DSC is an effective technique to reveal the crystallization and melting properties of nanofluids.

References

- [1] Arnold D. Laboratory performance of an encapsulated ice store [J]. *ASHRAE Transactions*, 1991, **97**(2): 1170 – 1178.
- [2] Lee T S, Huang C L, Chen S L. Supercooling phenomenon of water inside horizontal cylinders [J]. *Journal of the Chinese Society of Mechanical Engineers*, 1996, **17**(4): 353 – 364.
- [3] Bigg E K. The supercooling of water [J]. *Proceedings of the Physical Society B*, 1953, **66**(8): 688 – 694.
- [4] Vail G, Stansbury E J. Time-dependent characteristics of the heterogeneous nucleation of ice [J]. *Canadian Journal of Physics*, 1966, **44**(3): 477 – 502.
- [5] Vonnegut B. Nucleation of ice formation by silver iodide [J]. *Journal of Applied Physics*, 1947, **18**(7): 593 – 595.
- [6] Afoakwa E O, Paterson A, Fowler M, et al. Characterization of melting properties in dark chocolates from varying particle size distribution and composition using differential scanning calorimetry [J]. *Food Research International*, 2008, **41**(7): 751 – 757.
- [7] Wen L W, Feng X, Yong D E, et al. Accurate determination of latent heat via differential scanning calorimetry [J]. *Journal of Instrumental Analysis*, 2006, **25**(2): 16 – 19.
- [8] Louis G, Sophie D, Serge B, et al. Non-isothermal crystallization kinetics of iPP/sPP blends [J]. *Thermochimica Acta*, 2009, **481**(1): 32 – 45.
- [9] Zhang T Z, Li T, Erik N, et al. Isothermal crystallization study on aqueous solution of poly(vinyl methyl ether) by DSC method [J]. *Polymer*, 2009, **50**(5): 1206 – 1213.
- [10] Li Q G, Yang W, Liu F. DSC research for the non-equilibrium solidification of Fe-B alloy [J]. *Materials Review*, 2009, **23**(9): 65 – 70. (in Chinese)

纳米流体结晶过程的 DSC 法实验研究

陈 颖 贾莉斯 莫松平

(广东工业大学材料与能源学院, 广州 510006)

摘要:以质量分数 5%、平均粒径 75 nm 的水基二氧化钛(TiO₂)纳米流体为材料,利用差示扫描量热仪,分别在 3, 5, 7, 9 °C/min 4 个冷却速率下研究了 TiO₂ 纳米粒子对去离子水结晶和熔化行为的影响。实验结果表明,与去离子水相比,水基 TiO₂ 纳米流体具有更低的过冷度和更快的结晶速率。随着冷却速率的增大, TiO₂ 纳米粒子对去离子水过冷度的影响增强,对其结晶速率的影响则减弱。在熔化过程中,与去离子水相比,水基 TiO₂ 纳米流体具有更低的熔化温度、更小的熔化潜热和更大的熔化速率。

关键词:水基二氧化钛纳米流体;成核;过冷度;差示扫描量热仪

中图分类号:TB61⁺1