An experimental investigation of nucleation probability of supercooled water inside cylindrical capsules

Sih-Li Chen ^{a,*}, Pong-Ping Wang ^a, Tzong-Shing Lee ^{b,1}

^a Department of Mechanical Engineering, National Taiwan University, Taipei 10764 Taiwan, ROC

^b R&D Department, King Machinery Co., Ltd., 20 Ting-hu 1st Street, Ta-Kang Tsun, Kuei-shan Hsing, Taoyuan County, Taiwan, ROC

Received 20 August 1997; received in revised form 10 March 1998; accepted 4 November 1998

Abstract

This article experimentally investigates the nucleation probability of supercooled water inside cylindrical capsules with or without nucleators during a cold storage process. The nucleation probability curves of initial appearance of dendritic ice as a function of coolant temperature, size of capsule, and mass of different heterogeneous nucleators are characterized, respectively, by performing a number of experiments. The results show that the lower the coolant temperature, the greater the nucleation probability. The larger the volume of water contained, the higher the nucleation temperature. The addition of nucleating agents, such as iron ore, iron chips and silver iodide, into the water container can effectively improve the nucleation probability, and thus increase the coefficient of performance (COP) of a thermal storage air-conditioning system. Since the crystal structure of silver iodide is very similar to that of ice, the comparison among three types of agents indicates that it has the best effect in facilitating nucleation. © 1999 Elsevier Science Inc. All rights reserved.

Keywords: Supercooling phenomenon; Ice nucleation; Nucleation probability

1. Introduction

Thermal storage air-conditioning system is an important concept of many energy conservation programs in industry and in commercial applications. Water is widely used as the phase-change material (PCM) for thermal storage because of the advantages such as: high value in latent heat, stable chemical property, low cost and easy acquisition, no environmental pollution concern, and compatibility with the material of air-conditioning equipment. However, there are a few disadvantages with the use of water as PCM. One of the most serious problems is the supercooling phenomenon occurring in the solidification of water during the cooling process of thermal storage.

As a quantity of water is cooled inside an enclosed container, freezing does not occur at its freezing point (0°C). Instead it is normally cooled below 0°C, before ice nucleation happens. Supercooled water refers to a state of metastable liquid even though the temperature of water is below its freezing temperature. The meta-

stable state will end when ice nucleation occurs and the thin plate-like crystal of dendritic ice grows into the supercooled region of water. During the dendritic ice growth process, latent heat released from the dendritic ice will be consumed by supercooled water. At the end of the growth process, the temperature of water will return to its freezing point (0°C). If the metastable state exists and remains during the thermal storage process, thermal energy can only be stored in the form of sensible energy. In order to let solidification occur, the evaporation temperature of the chiller must be lower than the nucleation temperature of ice. Thus, the coefficient of performance (COP) of the chiller will be reduced due to the supercooling phenomenon. Therefore, it is very important to prevent the occurrence of the supercooling state and to acquire precise knowledge related to the supercooling phenomenon of water during a thermal storage process.

There are a number of studies on the subject of nucleation behavior of water droplets. Bigg [1] studied the freezing process of supercooled water droplets with different diameters suspended by two insoluble liquid layers. His results indicated that the larger the droplet volume or the lower the cooling rate, the higher the mean nucleation temperature. Vail and Stansbury [2]

* Corresponding author. Tel.: 886-2-363-1808; fax: 886-2-363-1755.

¹ Tel.: 886-3-328 1226; fax: 886-3-328-4024.

investigated the nucleation behavior of water droplets under a constant cooling rate process. The experimental results are similar to those reported by Bigg. The release of supercooling can be improved by the addition of nucleating agents. Vonnegut [3] used the X-ray exposure method to inspect the crystal structure of several types of nucleating agents. He found that the hexagonal crystal structure of silver iodide (AgI) and lead iodide (PbI_2) are the closest to the structure of ice crystals. Therefore, Vonnegut was the first to use AgI and PbI_2 as the nucleating agents for supercooled water droplets in the atmosphere, and found that these agents greatly improved the supercooling phenomenon of small water droplets.

Many researchers have also published studies on the supercooling phenomenon inside enclosed containers. Gilpin [4,5] studied the extent of dendritic ice growth into supercooled water and determined the conditions under which blockage by dendritic ice was likely to occur in a pipe with no main flow. The effect of convective flow on the degree of supercooling has been studied by Kashiwagi et al. [6]. Saito et al. [7] conducted experiments on the supercooling phenomenon of pure water inside an enclosed cylinder by using round plates of five different characteristics of surface roughness as the heat transfer interface. Arnold [8] investigated the nucleation phenomenon of pure water contained inside spherical capsules and indicated that the nucleation temperature of water inside the container is affected by both the cooling rate and the addition of nucleating agent. Kurosaki and Satoh [9] experimentally studied the freezing characteristics of supercooled water on an oscillating cold surface. Recently, Lee et al. [10] studied the supercooling phenomenon of pure water inside horizontal cylinders and developed a correlation of supercooling period as a function of cooling rate and nucleation temperature.

The main purpose of this work is to investigate experimentally the nucleation probability of supercooled water inside cylindrical capsules, examine the effect of different macrofactors on the nucleation behavior of cylindrical capsules, and thus increase the COP of a thermal storage air-conditioning system. These factors include the coolant temperature, the size of capsules, and the mass of nucleators added. The probability curves of initial appearance of dendritic ice as a function of the inner diameter of capsules and mass of different nucleators are characterized and discussed.

2. Experimental apparatus and procedure

A schematic diagram of the experimental apparatus is shown in Fig. 1. All the experiments were conducted inside constant-temperature tanks, where the temperature is controlled at a precision of $\pm 0.1^\circ\text{C}$. The temperature is measured by three T-type thermocouples. Two are installed at the top and center point of the center cross-section of the cylindrical capsule. Another one is installed inside the constant-temperature tank to measure the coolant temperature. A YOKOGAWA HR-2300 hybrid recorder and a 486-DX66 PC complete the recording and data storage equipment. During the experimental process, the temperature data measured are shown on a screen to allow monitoring of the experiment. In this study, there are four different types of cylindrical capsules; photographs of these are shown in Fig. 2. The phase-change material is filled into screw-type impermeable capsules made of high-density polyethylene. Table 1 lists the dimensions of each encapsulated cylinder. The phase-change medium filled inside the cylindrical capsule includes pure water or water with different percentages of nucleating agents. The nucleating agents used in the study were iron ore, iron chips,

Fig. 1. Schematic diagram of experimental apparatus.

Fig. 2. Photograph of L, M1, M2, and M3 type capsules (from top to bottom).

Table 1
Detailed information of cylindrical capsules

Type	D (cm)	l (cm)	m (g)	D_{eq} (cm)
L	7.3	24	1000	12.4
M1	2.2	24	88	5.6
M2	2.2	15	54	4.8
M3	2.2	5	18	3.3

Table 3
Summary of estimated uncertainties of primary measurements

Parameter	Uncertainty
Length	0.068%
Inner diameter	0.263%
Temperature	1.92%
Time	0.42%

and silver iodide (AgI) (see Table 2). Uncertainties of the primary measurements, following the uncertainty analysis proposed by Moffat [11], are tabulated in Table 3.

Before the experiment begins, the capsule is placed inside the constant-temperature tank, and the temperature of the tank is set at 10°C, to get it ready. When the temperature inside the capsule reaches thermal equilibrium with the temperature of the constant-temperature tank, the temperature of the tank is reset to the testing temperature (−1, −2, −3, ..., −12°C) and the experiment is started. Also, the temperature data are begun to be recorded. When the water inside the capsule experiences nucleation, recording is terminated, and the experiment is considered completed. If nucleation does not occur 5 h after the experiment starts, the experiment is terminated. However, the occurrence of ice nucleation is not exactly reproducible. Even with the same experimental specimen, and strict control of all experimental conditions

and procedures, the temperature and the time when nucleation occurs rarely repeat themselves. Thus, there is a distribution of probability. The results from one experiment do not represent all the nucleation characteristics obtained under the experimental conditions involved. Therefore, it is necessary to repeat the experiment a number of times under the same operating conditions to obtain enough data. In this study, all the experiments under the same testing conditions were repeated at least 24 times to ensure the reliability of experimental results.

3. Results and discussion

From our visual observation, the typical curve of temperature changes with time during the cooling process of water inside a capsule is shown in Fig. 3. A coolant fluid with constant temperature T_f flows across

Table 2
Types of nucleating agents and experimental conditions for an L-type capsule

Type of nucleating agent	Testing temperature	Mass percentage (%)
A. Iron ore	−1, −2, −3, −4, −5, −6, −7, −8	0.05, 0.1, 1, 5, 10
B. Iron chips	−2, −3, −4, −5, −6, −7, −8	0.1, 0.5, 1, 2
C. Silver iodide (AgI)	0, −1, −1.5, −2, −3	0.005, 0.05

Fig. 3. Phase change during the cooling process of water inside a capsule.

the outside surface of the capsule. The cooling process experienced by pure water inside the capsule from the initial temperature, T_i , till the completion of freezing can be divided into four stages. The first stage involves the process from the beginning of cooling from initial temperature till the metastable state before nucleation occurs, which is called the sensible heat thermal storage process. As shown in Fig. 3(a), water remains in the liquid phase when the temperature drops below the freezing point. Let T_m and T_N represent the freezing

temperature and the nucleation temperature of water, respectively; then the degree of supercooling T_s is defined as $(T_m - T_N)$.

The second stage is the process from the occurrence of nucleation to the completion of dendritic ice formation, called the dendritic ice formation process. This process begins at the occurrence of nucleation, when the water temperature is T_N . Once nucleation occurs, a thin slice of dendritic ice, as shown in Fig. 3(b), spreads rapidly from the nucleation site down toward the center

region of the cylinder and, in the meanwhile, it also grows down along the cold boundary layer region adjacent to the inner cylinder surface. Latent heat released by dendritic ice enables the supercooled water temperature to rise to the temperature T_m , where ice and water can coexist inside the capsule. Once this equilibrium temperature is reached, the formation of dendritic ice ends. The time experienced by this process is very short, lasting only 1–3 s, depending on the degree of supercooling. Hence, the occurrence of the nucleation of ice can be easily detected by thermocouple reading, irrespective of the location of the nucleation site.

The third stage involves the phase-change process from the completion of ice crystal formation till the water inside the capsule is completely frozen, called the latent heat thermal storage process. This process begins after the dendritic ice formation is finished. As indicated in Fig. 3(d), a thick ice layer starts to form from the inner surface of the capsule toward the cell center till the water is completely frozen. The last stage involves the process of the cooling of ice till it reaches the same temperature as that of the coolant temperature. This process is similar to the water sensible heat thermal storage process.

3.1. Effect of coolant temperature on nucleation probability

Fig. 4 shows the probability distribution curves under the conditions of different coolant temperatures from -3°C to -10°C for pure water contained in the L-type capsule. The definition of nucleation probability is $P = (\text{the number of freezings})/(\text{the number of total tests})$. Every dot marked in the figure represents the result of the experiment; the experiment was repeated 24 times, each of which lasted 5 h at most. The results indicate that the lower the coolant temperature, the greater the nucleation probability. The coolant temperature ranges

Fig. 4. Nucleation probability of water inside an L-type capsule under different coolant temperatures.

from -4°C with the probability of zero to -9°C with the probability of unity, showing a temperature range of about 5°C . In relation to the encapsulated thermal-storage air-conditioning system with self-stacking water containers, if the inlet coolant temperature is higher than -4°C , then the thermal energy can only be stored in the form of sensible heat. If the coolant temperature falls within the range of nucleation probability (i.e., between -4°C and -9°C), water inside some of the containers will continue to exist in the metastable state without freezing. Therefore, if one wants to store the thermal energy all in the form of latent heat, the coolant temperature must be lower than -9°C . However, this process will compromise the efficiency of the refrigerating system, and increase the operating cost of the system. If the nucleation temperature of pure water can be raised, the coolant temperature would be set at a higher value to let the thermal energy store in the form of latent energy. The increase of coolant temperature raises the evaporator temperature of the refrigerating system and thus increases the COP of the system. The addition of nucleating agents is one of the approaches to effectively improve the nucleation behavior of water inside capsules, which will be discussed later.

3.2. Effect of capsule size on nucleation probability

Capsule size is also an important factor on the nucleation probability of water inside a cylindrical capsule. The experimental results are shown in Fig. 5, which indicates that under the same coolant temperature the larger the volume of water contained, the greater the probability of nucleation. Ice nucleation is the initial appearance of the formation of stable crystal nucleus due to the fluctuation of free energy. Embryos with larger size have a greater chance to become stable nucleus. The testing capsule with a larger volume of water contains a greater number of water molecules. The

Fig. 5. Nucleation probability of water inside different sizes of capsules.

Fig. 6. Relationship of coolant temperature and equivalent diameter of cylindrical capsules under different nucleation probabilities.

number of large-size embryos is thus relatively increased. As a result, the probability of forming a stable nucleus is greater, and the nucleation temperature also rises.

Fig. 6 shows changes of coolant temperature along with different types of cylindrical capsules under the nucleation probabilities of 0%, 50% and 100%. The results indicate that the greater the volume or the larger the diameter, the higher the freezing coolant temperature. It can be observed that the figure shows the linear behavior between the equivalent diameter, D_{eq} , of cylindrical capsules and the coolant temperature under different freezing probabilities. Then, an equation related to the coolant temperature and the equivalent diameter of capsules can be obtained as follows:

$$T = A_1 \cdot \ln D_{eq} + B_1, \quad (1)$$

where

$$D_{eq} = \left(\frac{3}{2} D^2 l \right)^{1/3}. \quad (2)$$

A_1 and B_1 are the curve-fitting constants, D the inside diameter of cylindrical capsule and l the length of the cylindrical capsule.

3.3. Effect of nucleating agents on nucleation probability

As far as a thermal storage air-conditioning system using latent heat is concerned, it is necessary to lower the coolant temperature below the nucleation temperature. If the water nucleation temperature can be raised, the release of supercooling can be accelerated to enter the latent heat thermal storage process earlier. Among the many improvement methods, the addition of nucleating agent is one of the approaches to effectively improve the release of supercooling. In this study, three types of nucleating agents are added into water

Fig. 7. Nucleation probability of water added with different percentages of nucleators: (a) iron ore, (b) iron chips, (c) AgI.

containers with different mass ratios, as indicated in Table 2.

Fig. 7 shows the probability curves of the addition of different mass percentages of iron ore, iron chips, and silver iodide (AgI) with the same type of cylindrical capsules. Regardless of the type of nucleating agent, the probability curve shifts to the left with an increase of the

mass ratio of nucleating agent. The comparison among the nucleation probability of various mass ratios indicates that after the addition of nucleating agent, the coolant temperature is higher than that of pure water. Fig. 7(a) shows the probability curves for iron ore with the mass ratios of 0.05%, 0.1%, 1%, 5% and 10%. As the quantity of nucleating agent increases, the coolant temperature also rises as a result till a certain ultimate value (about 1%). At this time, even additional increase of the nucleating agent (1–10%) cannot raise the nucleation temperature of water anymore. Although the addition of nucleating agent in the water container does facilitate nucleation, not all added agents have the same effects. In terms of the effect of nucleation facilitation, the comparison between three types of agent indicates that AgI has the best effect.

It is defined that the coolant temperature corresponding to the 50%-of-nucleation probability be the characteristic coolant temperature. Then, the characteristic coolant temperatures corresponding to different quantities of iron ore added for container water are illustrated in Fig. 8. For the same capsule diameter, the characteristic coolant temperature rises as the quantity of iron ore increases. On the other hand, with the same amount of iron ore, the characteristic coolant temperature declines as the diameter decreases. The correlation between the characteristic coolant temperature and the quantity of iron ore can be expressed as

$$T_c = A_2 \cdot X^{B_2}, \quad (3)$$

where T_c represents the characteristic coolant temperature corresponding to the nucleation probability with 50%, X the percentage of nucleating agent added; A_2 and B_2 are the curve fitting constants.

Fig. 9 shows the characteristic coolant temperature of L-type capsule after the addition of different mass percentages of iron ore, iron chips, and AgI. Regardless of the type of nucleating agents, the characteristic

Fig. 9. Correlation between the amount of various nucleators and the characteristic coolant temperature for L-type capsules.

coolant temperature increases as the amount of nucleating agents increases. This is due to the fact that the water contained not only comes in contact with the inner surface of cylindrical capsule, but also with the surface of nucleating agent in the bottom, which forms a new interface. Before any nucleation agent is added, water nucleation is affected by the inner surface properties of cylinder. After an agent is added, water nucleation is affected by both the inner surface properties of the cylinder and the properties of the contact interface with the nucleation agent. The properties with the nucleation agent have a greater impact on facilitating water nucleation than the inner surface of the cylinder.

4. Conclusions

A series of experiments related to the nucleation phenomenon of water inside cylindrical capsules was conducted in this study. Such macroperspective variables as capsule size, coolant temperature, amount of nucleating agent added, and type of nucleating agent are investigated on the nucleation behavior of water inside capsules. The following conclusions can be drawn from the present results: (1) The lower the coolant temperature, the greater the nucleation probability. (2) The larger the size of capsule (i.e., the larger the volume of water contained), the higher the nucleation temperature. (3) Effective nucleating agents can prevent supercooling inside the water capsule. Among the three types of nucleators, silver iodide has the best effect. (4) The nucleation probability for the encapsulated cylinder with nucleating agents added is greater than that containing only pure water. The probability distribution range of the former case is also narrower than that in the latter case.

Fig. 8. Correlation between the amount of iron and the characteristic coolant temperature for various types of capsules.

Nomenclature

A_1, A_2	constant coefficients
B_1, B_2	constant coefficients
D	inside diameter (cm)
D_{eq}	equivalent diameter, defined in Eq. (2) (cm)
l	length (cm)
P	nucleation probability
T	temperature (°C)
T_c	characteristic coolant temperature (°C)
t	time (s)
X	mass percentage of nucleating agent

Acknowledgements

The project is funded by the National Science Council, ROC under project no. NSC 86-2221-E-002-065.

References

- [1] E.K. Bigg, The supercooling of water, *Proc. Phys. Soc. B* 66 (1953) 688–694.
- [2] G. Vail, E.J. Stansbury, Time dependent characteristics of the heterogeneous nucleation of ice, *Can. J. Phys.* 44 (1966) 477–502.
- [3] B. Vonnegut, Nucleation of ice formation by silver iodide, *J. Appl. Phys.* 18 (1947) 593–595.
- [4] R.R. Gilpin, Cooling of a horizontal cylinder of water through its maximum density point at 4°C, *Int. J. Heat Mass Transfer* 18 (1975) 1307–1315.
- [5] R.R. Gilpin, The effect of cooling rate on the formation of dendritic ice in a pipe with no main flow, *J. Heat Transfer* 99 (1977) 419–424.
- [6] T. Kashiwagi, S. Itoh, Y. Kurosaki, S. Hirose, Effects of the natural convection in a partially supercooled water cell on the release of supercooling, *ASHRAE Trans.* 93 (1987) 49–61.
- [7] A. Saito, Y. Utaka, S. Okawa, K. Matsuzawa, A. Tamaki, Fundamental research on the supercooling phenomenon on heat transfer surfaces – Investigation of an effect of characteristics of surface and cooling rate on a freezing temperature of supercooled water, *Int. J. Heat Mass Transfer* 33 (8) (1990) 1697–1709.
- [8] D. Arnold, Laboratory performance of an encapsulated-ice store, *ASHRAE Transactions* 97 (2) (1991) 1170–1178.
- [9] Y. Kurosaki, I. Satoh, Freezing of supercooled water on an oscillating surface, *Proceedings of the 10th International Heat Transfer Conference*, Brighton, UK, 1994, pp. 61–66.
- [10] T.S. Lee, C.L. Hung, S.L. Chen, Supercooling phenomenon of water inside horizontal cylinders, *J. Chinese Soc. Mech. Engrg.* 17 (4) (1996) 353–364.
- [11] R.J. Moffat, Using uncertainty analysis in the planning of an experiment, *J. Fluids Engrg.* 107 (1985) 173–182.