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SOLID-LIQUID PHASE TRANSITION PROCESS OF WATER-BASED FERROFLUID

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Cold thermal energy storage (CTES) technology uses advanced materials like magnetic nanoparticles in combination with phase change materials (PCMs) to improve thermal performance. This offers a promising solution for making cooling systems more efficient and supporting the cold chain in food preservation and medical storage. Ferrofluids are ferromagnetic particles coated with surfactants to prevent aggregation, forming stable colloidal suspensions in carrier fluids like water or oil. Recent attention has been focused on modifying the thermophysical properties of ferrofluids using magnetic field applications to enhance heat transfer and thermal management. However, the underlying mechanisms during the phase-transition process of ferrofluids are not well understood. In this study, we synthesized a water-based magnetic fluid via the co-precipitation method and performed a differential scanning calorimetry (DSC) analysis to investigate the effect of an applied magnetic field on the solidification and melting of a water-based ferrofluid. The results demonstrate that applying a magnetic field reduces the heat flow during phase transitions, suggesting potential applications in energy-efficient thermal management systems.

Key words: DSC, ferrofluid, magnetic field, melting, solidification

Introduction.

Inefficient utilization of energy poses a significant challenge that intensifies the global energy crisis. As of 2015, refrigeration, air-conditioning, and heat pump equipment already accounted for about 30% of global electricity consumption, and this number is predicted to increase dramatically by the year 2100 [1]. Thus, there is an urgent need to shift towards more sustainable energy sources. This requires an increased focus on improving energy efficiency in transportation, industry, and in the building sector, as these areas are characterized by high energy consumption and emissions [2].

Refrigeration systems play a critical role in processing and preserving food through the cold chain ensuring food safety and reducing waste [3, 4]. In the field of medicine, these systems are essential for storing vaccines and medications, thereby protecting public health [5]. Additionally, they are responsible for maintaining comfortable temperatures in our houses and workplaces through air conditioning [6]. As a result, cold energy is in high demand for various applications, such as air conditioning, refrigeration, cold chain transportation, and medical uses. To address this demand, a thermal energy storage technology can be applied to cooling systems, where it can be utilized at low temperatures, known as CTES [7]. The latter improves overall energy efficiency and generates an enormous amount of thermal energy and electricity at considerably reduced cost [7, 8]. For many years, the use of phase PCM, a group of latent heat materials that take

advantage of the solid-liquid phase transition for energy storage, in CTES has attracted scientific and commercial attention [7]. However, most PCMs commonly used have low thermal conductivity and supercooling properties, which limits their applicability in fields requiring high transfer efficiency [9, 10]. To date, substantial efforts have been made to address this issue. A suggested approach is the use of magnetic nanofluids, commonly known as ferrofluids.

Ferrofluids are stable colloidal suspensions containing nano-sized particles of ferromagnetic materials or their oxides, dispersed in base fluids, such as water or oil [11]. These particles are coated with surfactants to prevent them from aggregating, and they remain stably dispersed within the fluids. The magnetic moment of these particles can undergo random changes in the presence of thermal energy [12, 13]. On the other hand, when a magnetic field is applied, the particles align and form chain-like clusters, potentially influencing the thermal conductivity and affecting the solid-liquid phase transition process [13, 14].

Thermal analysis includes studying how substances properties alter when subjected to heating or cooling. Differential scanning calorimetry (DSC) is one of the widely used methods for this purpose [15]. DSC is a technique used to analyze the heat changes that occur when a material is heated or cooled, primarily to examine phase transitions, melting, crystallization, and reactions of a material. In this technique, the temperature of a sample and a reference material are systematically controlled while the energy difference is measured as the temperature changes [16]. Despite numerous studies that have been conducted to investigate the properties of ferrofluids and their promising applications, the use of DSC analysis, the ferrofluid solidification and melting behavior, as well as the effects of applying magnetic field during the phase transition process remain inadequately understood.

In this paper, a water-based ferrofluid was synthesized via the co-precipitation method. This method ensures the uniform formation of magnetic nanoparticles within the water-based medium, providing a stable ferrofluid for analysis. A homemade DSC device was employed to precisely monitor the effects of an applied uniform magnetic field on the solid-liquid phase change of the synthesized ferrofluid. This allowed us to measure the heat flow associated with the phase transitions as well as the identification of any parameter changes when a magnetic field was applied. These observations are important for understanding how magnetic fields influence the thermophysical properties of ferrofluids, which are significant for their applications in various fields, such as in cooling systems.

1. Experimental details.

1.1. Materials. Iron (III) chloride solution ($FeCl_3$, 36–40% m/m), iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 99–102% m/m), ammonia solution (NH_3, 28–30% m/m), oleic acid (65% m/m) and sodium dodecylbenzene sulfonate (SDBS) were all purchased from FUJIFILM Wako Pure Chemical Corporation, Japan and were used without additional purification. Deionized water was consistently used throughout the experiments.

1.2. Synthesis of water-based ferrofluid. The co-precipitation method was applied to prepare the magnetite (Fe_3O_4) nanoparticles. Initially, ferric chloride was dissolved in water and ferrous sulfate heptahydrate was added to the solution for magnetite formation. The mixture was stirred at ∼320 rpm until homogenous. Subsequently, an ammonia solution diluted with water was added to the solution under vigorous stirring at 80°C for 1 hour. In a separate procedure, oleic acid was mixed with ammonia while being continuously stirred. This was used as a primary surfactant to coat the surface of the

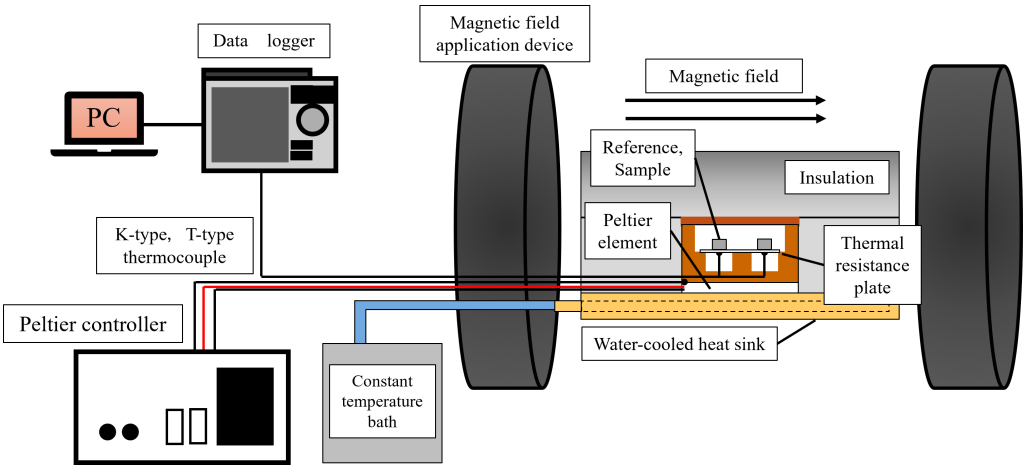

Fig. 1. Schematic diagram of the experimental setup.

magnetite nanoparticles. This oleic acid-ammonia mixture was gradually introduced into the magnetite solution and stirred for about 10 minutes. To facilitate the separation of components, the resulting mixture was left to settle and precipitate. Over time, this led to the formation of a black precipitate, primarily consisting of magnetite nanoparticles. The precipitated particles were then washed with deionized water and subjected to a filtration process, which was repeated until impurities and reactants were eliminated. Subsequently, SDBS is an additional surfactant to render the coated nanoparticles dispersible in water hence it was added to the filtered magnetite nanoparticles until a stable suspension was formed.

1.3. Differential scanning calorimetry. A DSC device is used to detect changes in heat flow during melting and solidification processes. In this study, a homemade DSC device was utilized to measure the thermal properties of the synthesized water-based ferrofluid under the influence of a magnetic field. An experimental setup, illustrated schematically in Fig. 1, was developed for this purpose. It comprises a magnetic field application type DSC, a magnetic field application device, a temperature measurement section (consists of thermocouples, a Peltier element, a thermal resistance plate, insulation, reference/sample holders), a low-temperature constant temperature bath, a Peltier controller, a data logger, and a computer. A Peltier element is utilized to harness the Peltier effect for controlling temperature in the measurement section. The Peltier effect occurs when an electric current passes through a junction of two different materials, causing a transfer of heat either to or from the intersection [17]. The magnetic field application device is installed outside the temperature measurement section. Power is supplied to the magnetic field application device via a DC-stabilized power supply. The magnetic field's strength and application's timing can be adjusted according to the experimental requirements. Additionally, measurements were made, assuming a uniform magnetic field near the center.

To verify the accuracy of the homemade DSC device, measurements were compared with those obtained from a commercialized DSC (DSC8230, RIGAKU Corporation) for analyzing the heat capacity and supercooling temperature in purified water. An empty aluminum-sealed container served as a reference substance, while another was filled with

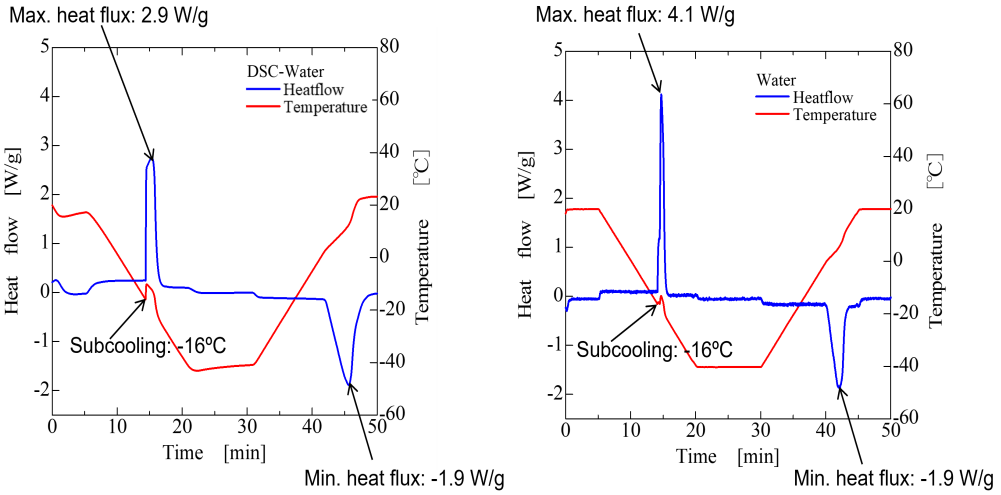

Fig. 2. Heat flow curve of pure water using commercialized DSC (left) and homemade DSC (right).

purified water for measurement. The temperature program consisted of holding the temperature at 20°C for 5 minutes, cooling to –40°C at a rate of 4°C/min, maintaining a 10-minute hold at –40°C, heating to 20°C at a rate of 4°C/min and, finally, holding the temperature at 20°C for 5 minutes. Peltier elements were employed for both sample heating and cooling, while a thermocouple measured the temperature of the pan. An insulation material was applied to mitigate any external heat influence. Fig. 2 shows that both systems consistently identify subcooling at –16°C, with a minimum heat flux at –1.9 W/g, indicating comparable accuracy. However, the homemade DSC showed a higher maximum heat flux of 4.0 W/g compared to 2.9 W/g in the commercialized one, suggesting a greater sensitivity to heat the flow during phase transitions. This increased responsiveness makes the homemade DSC a promising alternative for detecting subtle thermal events, though further investigation is necessary to verify its reliability and consistency. Overall, the homemade DSC demonstrates reliability and cost-effectiveness, making it a viable substitute for commercial DSC.

In this experiment, we utilized aluminum-sealed containers of the same mass to ensure consistency and minimize mass-related effects. An empty aluminum-sealed container was used as a reference substance, while the other container was filled with the synthesized ferrofluid sample. The temperature program was as follows: hold at 30°C for 5 minutes, then cool to –40°C at a rate of 5°C/min, hold at –40°C for 10 minutes, heating at 30°C at a rate of 5°C/min, and finally hold at 30°C for 5 minutes. Peltier elements were used for both sample heating and cooling, and a thermocouple measured the container's temperature. Insulation materials were used to prevent external heat influence, and the measurements were conducted assuming a uniform magnetic field inside the DSC.

The temperature of the pan containing a sample was altered while the applied magnetic field was present. The temperature difference between a reference sample and a measurement sample was recorded to detect heat transfer. This method also measures changes in heat flow and specific heat that occurs due to the influence of the magnetic

field. Changes in heat flow resulting from the application of a magnetic field are measured by controlling the Peltier element to adjust the temperature of the sample and recording the resulting temperature change. Since the only data obtained from a magnetic field-applied DSC is the temperature of each sample, this temperature is converted into heat flow by calculating the temperature difference ΔT between the measurement sample and the reference sample, as expressed in Eq. (1). Additionally, it is essential to calculate the device-specific thermal resistance R, which is necessary for determining the heat flow Q. In this study, we made DSC measurements of purified water three times to calculate the value of R. The average value was determined to be 56.294, which was used for the measurements in this study:

$$\int_t^\infty (\Delta T)\,\mathrm{d}t = RQ. \tag{1.1}$$

To investigate the impact of the applied magnetic field on the phase transition processes of the synthesized ferrofluid, a uniform magnetic field strength of 30 mT was applied horizontally. The data collection process was repeated three times to ensure accuracy and consistency.

2. Results and discussion.

The results of the DSC measurements made for the solidification process without a magnetic field and with the applied magnetic field of 30 mT are shown in Fig. 3. The temperature of the magnetic fluid at 0 mT was used as the reference value for the temperature change. As observed, the maximum heat flow is approximately 3.16 W/g at 0 mT and 2.71 W/g at 30 mT. This indicates that the heat flow decreases as the magnetic field strength is applied during solidification. Furthermore, at –13.5°C, there is a significant increase in heat flow as supercooling occurs, indicating heat generation.

For solidification to occur, energy is required to lower the liquid's temperature and halt its molecular motion. A substantial amount of energy is necessary to stop this motion resulting in supercooling. At 0 mT, ferromagnetic nanoparticles in the magnetic fluid exhibit Brownian motion without aligned magnetic moments. When a magnetic

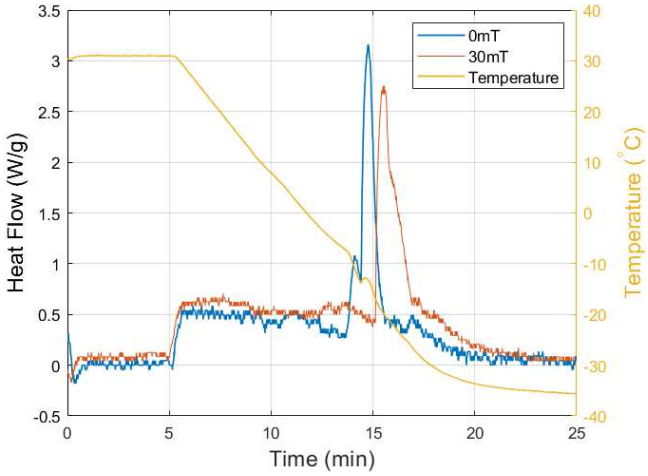

Fig. 3. DSC curve for the solidification process.

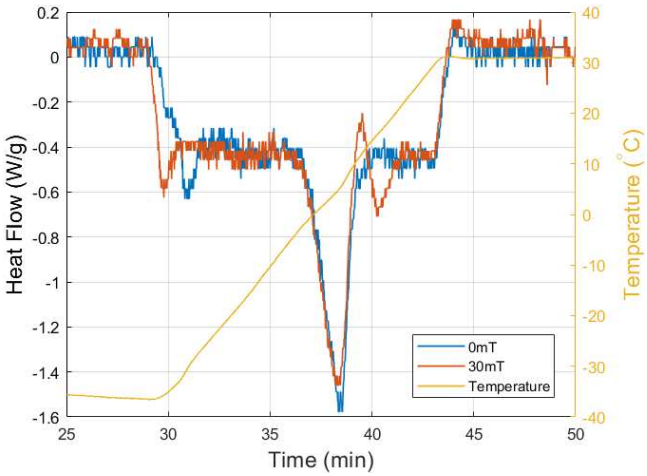

Fig. 4. DSC curve for the melting process.

field is applied, these moments align, causing the particles to arrange themselves neatly and decreasing the amount of energy needed [14]. This alignment strengthens bonds between the particles, suppressing the fluid movement and facilitating the transition to a solid state, thereby decreasing supercooling [10]. Additionally, a magnetic field decreases the system entropy, further aiding solidification. The increased magnetic field strength enhances these effects, reducing the heat required and the heat flow during the solidification process.

Fig. 4 shows the DSC measurements for the melting process without an applied magnetic field and with the applied magnetic field of 30 mT. It can be observed that there is a significant decrease in heat flow starting from around 0°C, indicating heat adsorption. During this process, the maximum heat flow is approximately –1.58 W/g at 0 mT and –1.46 W/g at 30 mT. Although the difference is not as significant as the solidification, the heat flow decreases as the magnetic field strength is applied during melting. When a magnetic field is applied during the melting process, it aligns magnetic moments, reducing so the movement of ferromagnetic nanoparticles. The alignment of magnetic moments may introduce additional energy to melting, leading to the belief that the application of a magnetic field reduces the amount of heat required for melting. However, the impact of the strength of the applied magnetic field on the heat of melting is less significant than that on the heat of solidification.

Conclusions.

In this study, we investigated the effect of applying a magnetic field to the solid-liquid phase transition of a synthesized water-based ferrofluid. We used a DSC device specialized for heat flow measuring while applying a magnetic field. Our findings showed that the heat flow decreased during the solidification process when the magnetic field was applied. Similarly, the magnetic field decreased the heat flow during the melting process, but not as significantly as during solidification. The synthesized water-based ferrofluid required less heat to solidify and melt when a magnetic field was applied compared to when no magnetic field was used. This suggests that the application of magnetic fields could improve energy efficiency in advanced applications.

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