International Journal of Thermophysics, Vol. 20, No. 1, 1999

Measuring the Specific Heat Capacity of Magnetic Fluids Using a Differential Scanning Calorimeter[1]

M. Higano,[2,3] A. Miyagawa,[2] K. Saigou,[4] H. Masuda,[2] and H. Miyashita[5]

The specific heat capacity of magnetic fluids was measured using a heat-flux-type differential scanning calorimeter (DSC). Magnetic fluids which contain 10 to 43 wt% ultrafine magnetite (Fe_3O_4) particles dispersed with surfactants in water or kerosene were used. The DSC was operated with the optimum heating rate ($10\,K \cdot min^{-1}$) and with equal heat capacities of sample and standard materials in the temperature range, 295 to 345 K. Synthetic sapphire (α-Al_2O_3) was used as the standard reference material, and the sample pan was made from aluminum. The differences between the measured specific heat capacity values of pure water and pure copper and the recommended values were within ±3 and ±1%, respectively. The specific heat capacity data of magnetic fluids showed weak temperature dependence, but strong concentration dependence. The measured values of specific heat capacity of magnetic fluids were compared with calculated values using a mixing rule.

KEY WORDS: concentration dependence; differential scanning calorimeter; magnetic fluids; magnetite; mixing rule; mixtures; specific heat capacity; temperature dependence.

1. INTRODUCTION

A magnetic fluid typically consists of a stable colloidal suspension of mono-domain ferromagnetic particles such as magnetite (Fe_3O_4; size smaller

---

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.

[2] Institute of Fluid Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan.

[3] To whom correspondence should be addressed.

[4] Plant Engineering Division, Ishikawajima-Harima Heavy Industries Co., Ltd., 3-2-16 Toyosu, Koto-ku, Tokyo 135, Japan.

[5] Mechanical Engineering Department, Tohoku Gakuin University, 1-13-1 Chuo, Tagajo, Miyagi 985-8537, Japan.

0195-928X/99/0100-0207$16.00/0 © 1999 Plenum Publishing Corporation

than 100 Å $= 10^{-8}$ m) in a nonmagnetic carrier fluid. A surfactant covering the particles prevents particle-to-particle agglomeration, and Brownian motion prevents particle sedimentation in gravitational or magnetic fields [1–4]. Magnetic fluids are used extensively in devices such as high-speed rotating shaft seals, inertial dampers, and as a coolant in heat exchangers [5]. Recently, these heat exchangers have been used in severe thermal environments. Hence, data for the thermophysical properties of magnetic fluids are required for the thermal design of devices. While many books and papers have been published [1–6] which include information on the structure and properties of magnetic fluids, the thermophysical properties of magnetic fluids for evaluating heat transfer are scarce.

The specific heat capacity of magnetic fluids is one of the important thermophysical properties for evaluating heat transfer. Its dependence on both temperature and ferromagnetic particle concentration is needed. Venger et al. [7] reported the temperature dependence of the specific heat capacity of magnetic fluids in the range 320 to 373 K without magnetic fields and presented the equation for calculating the specific heat capacity of magnetic fluids by the mixing rule [5, 6].

The purposes of this work are to measure the specific heat capacity of water-based and kerosene-based magnetic fluids with a differential scanning calorimeter (DSC) and to study its dependence on both temperature and magnetite concentration. Specific heat capacities of standard reference materials—copper, distilled water, and synthetic sapphire—were also measured to determine the optimum procedure and to check the reliability of the DSC.

2. MEASUREMENTS

2.1. Magnetic Fluids

Two magnetic fluids that contain magnetite (Fe_3O_4) as ferromagnetic particles are Marpo Magna FW-40 (magnetite, 42.0 wt%; surfactant, 14.7 wt%; water as a base liquid, 43.3 wt%) and Marpo Magna FN-40 (magnetite, 43.0 wt%; surfactant, 11.7 wt%; kerosene as a base liquid, 45.3 wt%) as reported in the technical bulletin of Matsumoto Yushi-Seiyaku Co., Ltd.. Both magnetic fluids are diluted by adding only a base liquid. Since the surfactant used is not shown in the technical bulletin, the oleic acid used here as a surfactant is assumed to have the same properties as those in the literature [6, 7].

2.2. Apparatus

A heat-flux-type differential scanning calorimeter (Rigaku-Dennki Co., Ltd.; Thermal Analysis System 200 with Model 8230-D module) is used for measuring the specific heat capacity of magnetic fluids. Maximum heating rate of this DSC is 20 $K \cdot min^{-1}$ (0.33 $K \cdot s^{-1}$). Synthetic sapphire (α-Al_2O_3) supplied by the manufacturer is used as a standard reference material. Sample pans are made from aluminum. Crimped pans for a reference material and solid samples, and sealed pans for liquid samples are used for measurements. A Mettler AE163 submicrobalance (resolution, ± 0.01 mg) is used to weigh all the pans. The mass differences of a set of any types of pans used for measurements are within ± 0.02 mg.

2.3. Procedure

Detailed procedures for using the DSC are described in the literature [8, 9]. The DSC for the heat capacity measurement was initially calibrated for temperature and calorimetric sensitivity. Temperature calibration was accomplished using the melting points of indium, tin, and lead, and the calorimetric sensitivity was determined using the enthalpy of fusion of these materials. Results of the temperature calibration at a heating rate of 10 $K \cdot min^{-1}$ were better than that at 1 $K \cdot min^{-1}$. Heat-flux-type DSCs have reverse behavior compared to power-compensated type DSCs [10]. The DSC temperatures were scanned with the optimum heating rate for a span of 70 K. The specific heat capacity of pure copper was measured with various heating rates, and the optimum heating rate for accurate measurement was determined. Distilled water and synthetic sapphire were used as standard reference materials to check the reliability of the DSC. The DSC temperatures were scanned under the condition that the total heat capacity (specific heat times mass) of the sample is equal to that of the standard reference material—synthetic sapphire. For accurate measurements, the sample mass was carefully determined. The output signals of the DSC were processed with consideration of the time lag of sample temperature to gain the isothermal baseline in the DSC curves.

3. RESULTS AND DISCUSSION

3.1. Specific Heat Capacity of Copper

In order to determine the optimum heating rate of the DSC, the specific heat capacity of copper with 99.99% purity was measured with heating rates ranging from 1 to 20 $K \cdot min^{-1}$ in the temperature range of 290 to 360 K. The results at 350 K were plotted as a function of heating rate

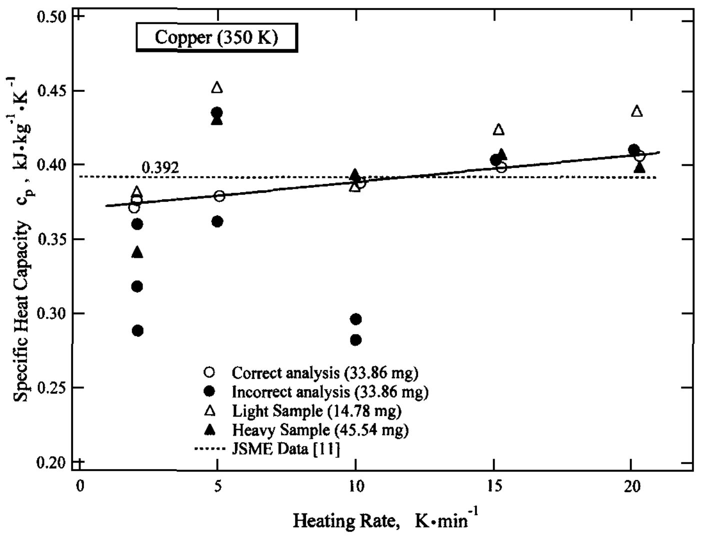

Fig. 1. Specific heat capacity of copper as a function of heating rate.

in Fig. 1. The total heat capacity of the sample with mass 33.86 mg was nearly equal to that of the standard reference material—synthetic sapphire, and the symbol ○ in Fig. 1 shows the processed data with the correct analysis. The solid line was determined by least squares. These data depend linearly on the heating rate, and agree with the recommended value [11] at a heating rate of $12\ \mathrm{K \cdot min^{-1}}$. The symbol ● represents the same output signals as for the symbol ○ except that the data were processed without consideration of the time lag of the sample temperature. Deviations of these values are very large at lower heating rates than at $12\ \mathrm{K \cdot min^{-1}}$, and are very small at higher heating rates. Figure 1 also shows that results obtained with a heavy sample (symbol ▲) are in good agreement with recommended values, but with a light sample (△), data were more scattered. After taking into consideration our results obtained at other temperatures, the optimum heating rate was determined to be $10\ \mathrm{K \cdot min^{-1}}$ ($0.167\ \mathrm{K \cdot s^{-1}}$), which is also the design value given by manufacturer. The specific heat capacity of copper measured at a heating rate of $10\ \mathrm{K \cdot min^{-1}}$ agreed with recommended values within ±1.02%, and the data of two different operators agreed within ±1%.

3.2. Specific Heat Capacities of Water and Synthetic Sapphire

In order to check the reliability of the DSC, specific heat capacities of water and synthetic sapphire were measured at a heating rate of

10 K · min^{-1} under the condition of equal total heat capacities ($m \cdot c_p$) of the sample and standard reference material—synthetic sapphire.

Measured values of the specific heat capacity of distilled water agreed with recommended values [12] within 3% in the temperature range of 300 to 340 K, and the data of two different operators agreed within 3%. The uncertainty for the specific heat capacity measurement of liquid is estimated to be ±3%.

Agreement of measured values of the specific heat capacity of synthetic sapphire with the recommended values used in the analysis was within 0.5% in the temperature range of 310 to 393 K.

3.3. Specific Heat Capacities of Water-Based Magnetic Fluids

Many experiments with different sample masses were carried out. Figure 2 shows the variation of specific heat capacity of water-based magnetic fluids as a function of sample mass. The measured specific heat capacity values ranged from 1.94 to 3.12 kJ · kg^{-1} · K^{-1}. The heat capacity experiment operates under optimal conditions when the total heat capacity ($m \cdot c_p$) of sample is equal to that of the standard reference material—synthetic sapphire. The heat capacity ratio was calculated and replotted in Fig. 3. The specific heat capacity of the magnetic fluid was adopted whose heat capacity ratio is nearly equal to unity. The additional uncertainties which arise in carrying out mixture experiments using a differential scanning

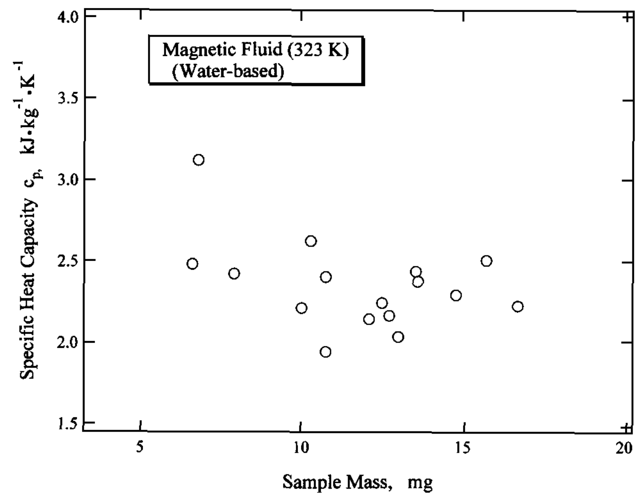

Fig. 2. Specific heat capacity of water-based magnetic fluids as a function of sample mass.

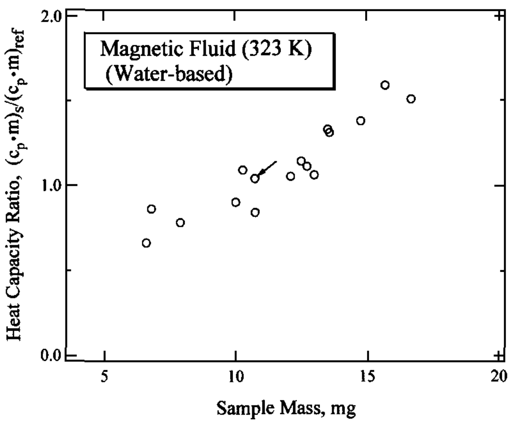

Fig. 3. Heat capacity ratio of water-based magnetic fluids as a function of sample mass.

calorimeter are attributed mainly to the time lag of the temperature response to particles in a carrier fluid. As the thermal diffusivity of magnetite [6] is one order of magnitude larger than that of a carrier fluid, the time lag of the temperature response to particles is negligible. In this way the uncertainties for the specific heat capacity measurement of the magnetic fluids

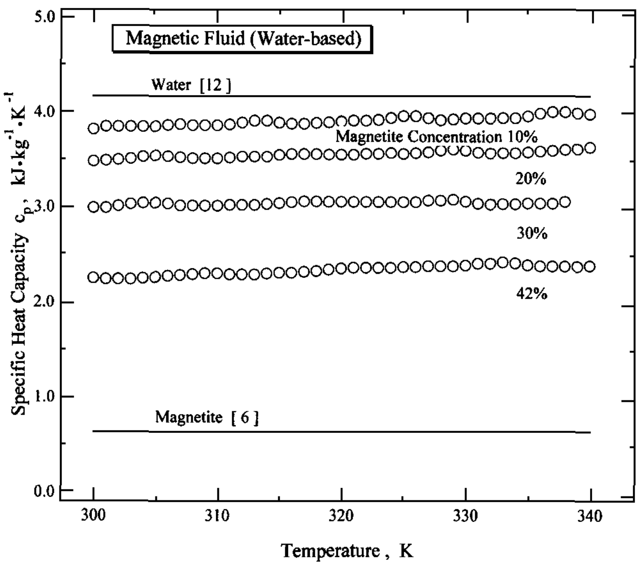

Fig. 4. Specific heat capacity of water-based magnetic fluids as a function of temperature.

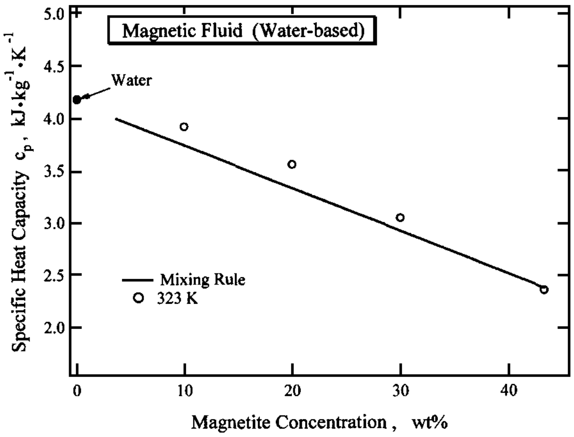

Fig. 5. Specific heat capacity of water-based magnetic fluids as a function of magnetite concentration.

are assumed to be comparable to those obtained with carrier fluids. The spread of the correct data adopted in Fig. 2, whose heat capacity ratio is nearly equal to unity, is estimated to be $\pm 12\%$. Magnetic fluids at different magnetite concentrations were measured. Figure 4 shows the variation of specific heat capacity of waster-based magnetic fluids with temperature. In this figure, the specific heat capacity shows a weak temperature dependence but a strong concentration dependence. Figure 5 shows the variation of the specific heat capacity of the magnetic fluid as a function of magnetite concentration. The solid line in Fig. 5 is the value calculated with a mixing rule which gives the wt% concentration average of the pure component heat capacities. Specific heat capacity data of water [12], magnetite [6], and oleic acid [6, 7] were used. Measured and calculated values agreed within 6.7%. This mixing rule for specific heat capacity is useful for water-based magnetic fluids even when uncertainties of measurement, unknown surfactant, unknown specific heat capacity of ultrafine magnetite particle, etc., are involved. Venger et al. [7] demonstrated the validity of this mixing rule for transformer oil-based magnetic fluids.

3.4. Specific Heat Capacities of Kerosene-Based Magnetic Fluids

Figure 6 also shows the variation of specific heat capacity of kerosene-based magnetic fluids as a function of temperature. The broken line in Fig. 6 shows the data for the magnetic fluid measured by Venger et al. [7], and the symbol ▲ represents the kerosene data obtained in this work. In Fig. 7, the variation of the specific heat capacity of kerosene-based

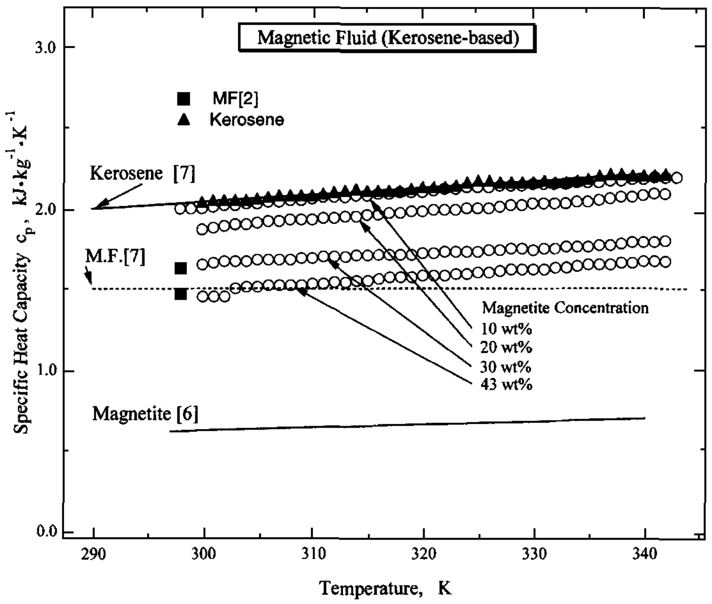

Fig. 6. Specific heat capacity of kerosene-based magnetic fluids as a function of temperature.

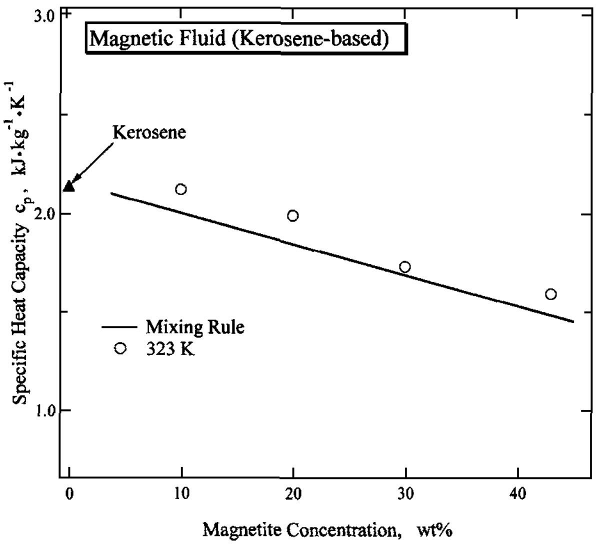

Fig. 7. Specific heat capacity of kerosene-based magnetic fluids as a function of magnetite concentration.

magnetic fluids as a function of magnetite concentration shows the same tendency as in Fig. 5. The solid line in Fig. 7 is the value calculated with a mixing rule of specific heat capacities [6, 7] employing the measured data of kerosene. Measured and calculated values agreed within 6.5 %. This shows that the mixing rule of specific heat capacities is also useful for kerosene-based magnetic fluids.

ACKNOWLEDGMENTS

The authors express their thanks to Mr. M. Ibe, former graduate student, for his valuable assistance in the measurements and the data analysis, and to Mr. N. Hishinuma for his technical assistance in this experiment. We also wish to acknowledge sincere gratitude to an anonymous reviewer for valuable comments. This research was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Calture, Japan under Contract No. 08455101.

REFERENCES

1. B. Berkovsky, *Thermomechanics of Magnetic Fluids: Theory and Applications* (Hemisphere, Washington, DC, 1978), p. 1.
2. R. E. Rosensweig, *Ferrohydrodynamics* (Cambridge University Press, Cambridge, 1985), p. 38.
3. R. E. Rosensweig, in *Annual Review of Fluid Mechanics, Vol. 19*, J. L. Lumley and M. Van Dyke, eds. (Annual Reviews, Palo Alto, CA, 1987), p. 437.
4. V. G. Bashtovoy, B. Berkovsky, and A. N. Vislovich, *Introduction to Thermomechanics of Magnetic Fluids* (Hemisphere, Washington, DC, 1998), p. 1.
5. V. E. Fertman, *Magnetic Fluids Guidebook: Properties and Applications* (Hemisphere, New York, 1990), p. 75.
6. N. P. Matusevich, L. P. Orlov, V. B. Samoilov, and V. E. Fertman, *Heat Transfer-Soviet Res.* **19**:25 (1987).
7. A. Ye. Venger, A. S. Larin, V. Ye. Fertman, and Yu. Te. Frayman, *Fluid Mechanics-Soviet Res.* **18**:82 (1989).
8. M. J. Richardson, in *Compendium of Thermophysical Property Measurement Methods, Vol. 1*, K. D. Maglic, A. Cezairliyan, and V. E. Peletsky, eds. (Plenum Press, New York, 1984), p. 669.
9. S. C. Mraw, in *Specific Heat of Solids, Vol. I-2*, C. Y. Ho, ed. (Hemisphere, Washington, DC, 1988), p. 395.
10. G. W. H. Hoehne, H. K. Cammenga, W. Eysel, E. Gmelin, and W. Hemminger, *Thermochim. Acta* **160**:1 (1990).
11. *JSME Data Book: Heat Transfer*, 4th ed. (JSME, Tokyo, 1986), p. 314.
12. *JSME Data Book: Heat Transfer*, 4th ed. (JSME, Tokyo, 1986), p. 331.