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THERMAL PERFORMANCE OF SELF-REWETTING FLUID HEAT PIPE CONTAINING DILUTE SOLUTIONS OF POLYMER-CAPPED SILVER NANOPARTICLES SYNTHESIZED BY MICROWAVE-POLYOL PROCESS.

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ABSTRACT

Dilute aqueous solutions of higher carbon number (≥ 4) alkyl alcohols have particular properties that the surface tension increases with temperature. In the case of boiling phenomena, increasing surface tension at a higher temperature of such kinds of fluids causes supply of cooling liquid at dry patch on the heated surface. Therefore, using these kinds of fluid, named "self-rewetting fluid" as heat pipe working fluid has led to improvement of heat transfer performance comparing conventional heat pipe working fluid such as water. In this study, thermal performance of a new type of self-rewetting fluid heat pipe containing aqueous 1-butanolic solution with microwave-assisted synthesized very dilute (2.5×10^{-4} mol/dm³) polyvinylpyrrolidone (PVP) -capped silver nanoparticles (nano-self-rewetting fluid) has been investigated experimentally. Dryout limits of some PVP-capped silver nano-self-rewetting fluid heat pipe were almost twice as high as that of base working fluid heat pipe. Also, the positive surface tension gradients with temperature of same kinds of PVP-capped silver nano-self-rewetting fluids were

increased. On the other hand, other thermophysical properties such as thermal conductivity and viscosity were almost same as those of base fluid. Thus, the thermal performance enhancement of heat pipes with PVP-caped silver nano-self-rewetting working fluids was mainly caused by the surface tension temperature dependencies changes of silver nano-self-rewetting fluids.

NOMENCLATURE

g	gravitational constant
m	weight of the liquid drop
r	capillary radius
R	thermal resistance
Q	input power
T	temperature
V	volume of the drop
σ	surface tension
ψ	correlation factor

1. INTRODUCTION

It is well known that the surface tension of common liquids decreases with the increase in temperature. Some exceptional liquids, however, show the opposite behavior, i.e. the surface tension increases with increasing temperature. For example, dilute aqueous solutions of alcohols with carbon chain length longer than four [1, 2], dilute aqueous 1, 5-pentanediol [3] and aqueous solutions of long-chain alkylammonium chloride [4, 5] have positive surface tension dependency with temperature in higher temperature (20 to 60 °C) region. The Marangoni force induced by this anomaly surface tension dependency results in a flow opposite to the ordinary thermocapillary convection. Using these kinds of fluids, named “self-wetting fluids”, as new working fluids have led to great improvement of heat transfer performance for heat management devices including heat pipe [6-8].

Nanofluid, engineered by dispersing nanometer-sized solid particles in conventional liquids is another attractive heat transfer fluid because of their potential of exhibiting higher thermal properties compared to their base fluids for over the past decade [9,10]. The significant improvement of thermal conductivity for a variety of nanofluid system has been reported by many researchers [10-15]. Also, several researches in convective heat transfer [16-18], boiling heat transfer [19, 20] using nanofluids were investigated. More recently, some researchers reported the thermal performance of heat pipes with gold [21] and silver [22-24] nanoparticles dispersed nanofluids, and their results showed that the thermal resistance of heat pipe with both types of nanofluids was lower than that of pipes containing pure water.

Recently, we investigated the positive temperature dependency for surface tension of chemically synthesized gold and platinum nanofluid containing some higher (C4-C7) alcohols or DAC [25]. It was found that several times larger positive surface-tension gradient with temperature can be developed by adding small amount of higher alcohols or DAC into suspensions of gold (Au) or platinum (Pt) nanoparticles prepared by sodium borohydride reduction method. However, the thermal performances of heat pipe with Au nanofluid containing 1-butanol were poor in spite of the superior positive surface tension tendency with temperature [7]. The most probably reason is that existence of excess amount of noncondensable reductant gaseous H₂ remaining in the Au nanofluid.

In the present study, therefore, we adopt the microwave-assisted polyol process [26] for metallic silver (Ag) nanofluid preparation from aqueous media. The major advantage of this method is easily control

of several nanoparticle physical properties such as diameter and shape within very short reaction time (≤ 3 min.) without generating of noncondensable gases. We measured the positive temperature dependency for surface tension of obtained Ag nanofluid containing 1-butanol. Also, we measured the thermal performances of series of heat pipes with different working fluids including aqueous 1-butanolic solution and Ag nanofluid containing 1-butanol.

2. EXPERIMENTS

2.1. Synthesis and characterization of silver nanofluids

Aqueous dispersions containing Ag nanoparticles were prepared by using a microwave-polyol method [26], as follows: H₂PtCl₆ · 6H₂O (2.3×10^{-5} mol), acts as a precursor Pt seed for nucleation of Ag nanoparticles, was first dissolved in 30 cm³ of ethylene glycol (EG). Consequently, silver source AgNO₃ (92×10^{-3} mol/dm³) and 0.524 mol of four different average molecular weight (10,000, 40,000, 360,000 and 1,300,000) of polyvinylpyrrolidone stabilizer (PVP10k, 40k, 360k and 1300k) was added in EG. Then, the reagent solution was irradiated by microwave (MW) under continuous wave (CW) heating condition for 3 min. up to 198 °C by using MW reactor (Shikoku Keisoku μ Reactor, SMW-087, 2.45 GHz, maximum power 700 W). 0.272 cm³ of the obtained Ag nanoparticle/EG solution was added into 100 cm³ of pure water for adjusting 2.5×10^{-4} mol/dm³ Ag nanoparticle concentration.

Product Ag nanoparticles were characterized by field emission scanning electron microscopy (FE-SEM: Hitachi S-4500) and dynamic light scattering method using a ZetaPALS particle size and zeta potential analyzer (Brookhaven Instruments). The UV-vis absorption of the nanoparticle solutions was measured by a Jasco V550 UV-vis spectrometer with an ETC-505 Peltier thermostatted single cell holder. The viscosities of silver nanofluids were measured by using glass made Cannon Fenske type capillary viscometer immersed into thermostat water bath with 30°C to 80°C, $\pm 0.1^\circ\text{C}$.

Surface tension temperature dependency on the silver nanofluids was measured by using laboratory made drop-weight method apparatus that relies on forming drops quasistatically from a small glass capillary into thermostat glass jacket and measuring the weight of the liquid that falls off. The weight of the liquid drop and the radius of the tip of the capillary glass tube are employed to calculate the surface tension, using the following equation [27]:

$$\sigma = \frac{mg}{2\pi r\psi(r/V^{1/3})} \quad (1)$$

where σ is the surface tension, m is the weight of the drop, g is the gravitational acceleration, V is the volume of the drop, $\psi(r/V^{1/3})$ is the correction factor, and r is the radius of the tip of the glass tube. The correction factor $\psi(r/V^{1/3})$ is determined by calculating the following equation [27]:

$$\psi(r/V^{1/3}) = 0.4512(r/V^{1/3})^2 - 0.7694(r/V^{1/3}) + 0.9267 \quad (2)$$

The densities of measurement liquids were measured by using glass made pycnometer. Both of surface tension and density measurement apparatuses were connected to external thermostat water bath/ circulator with 30°C to 80°C, $\pm 0.1^\circ\text{C}$.

2.2. Heat pipe thermal performance tests

Tubular and thin flat heat pipes were used in the present study. The former was same as described in the previous paper [7], copper made 250 mm in length, and 4 mm in diameter and its container with composite wick and groove structure. The latter also made of copper with 1.5mm in thickness, 8.7mm in width and 150 mm in length. The compositions of heat pipe working fluids are summarized in Table 1. The temperature distribution on heat pipe wall was monitored by sheathed K-type thermocouples of 0.25mm in diameter, and in total ten thermocouples were attached on the heat pipe wall, i.e. four at both the evaporation region and the condensation region, and two at the adiabatic region. Heat pipe to be tested was placed in a vacuum chamber for thermal insulation. All the tests so far conducted have been performed at the horizontal configuration. One end of heat pipe was heated up by a 30 mm long copper block in which four cartridge heaters were embedded. The other end of heat pipe was cooled down by a 70 mm long copper water jacket in which cooling water was circulated. The temperature and the flow rate of the cooling water were kept constant by a thermostatic bath and a gear pump, respectively. The inlet and outlet temperatures of the cooling water jacket were also measured. Thermal output was calculated from the flow rate and the temperature difference between the outlet and the inlet. Voltage was applied to copper block heater and the experiment was started. The heat pipe reached steady state, and after checking that it is stable for a while, same operation was performed, and this operation was performed until the heat pipe reached dry out. The details of experimental

procedures and apparatus were also described in our previous paper [7].

Table 1 Working fluid compositions.

Water	Water
BuOH	5 wt.% 1-butanol aq. soln.
BuOH/ Ag-PVPnk (n=10, 40, 360, 1300)	Ag nanoparticle concentration 2.5×10^{-4} mol/dm ³ 5 wt.% 1-butanol aq. soln.

3. RESULTS AND DISCUSSIONS

3.1. SYNTHESIS AND CHARACTERIZATION OF SILVER NANOFLUIDS

Fig. 1 shows FE-SEM photographs and outlooks of four different PVP capped silver nanofluids prepared by MW assisted polyol method. Solution color of each silver nanofluids was half-transparent, bright yellow (PVP10k-capped silver nanofluids), white-yellow (PVP40k-capped) and pale white (PVP360k and 1300k capped), respectively. The PVP-10k, 40k and 360k-capped Ag nanoparticles average particle diameter obtained from DLS measurements is around 40, 100 and 300 nm, respectively, which is corresponding to SEM image shown in Fig. 1. When PVP 360k or 1300k was used as a protective polymer, on the other hand, discrete silver nanoparticles of different shapes including nanoflake (Fig. 1c-1) and nanowire (Fig. 1c-2, 1d-1 and 1d-2) resulted.

Fig. 2 shows the UV-vis absorption spectra of Ag nanofluids under various heat pipe operating temperatures. In all cases, the local absorption peak at ~ 410 nm, which could be attributed to the surface plasmon resonance (SPR) band of silver nanoparticles [28-29] was observed. In addition, in the case of PVP 360k and 1300k capped Ag nanofluids, shoulder peak at 350 nm can be ascribed to SPR band of longitudinal mode of Ag nanoflakes or nanowires similar to that of bulk Ag [28-29]. Gao et al. represented a long tail band above 450 nm was appeared when long Ag nanowire produced [30] and almost same broad peak of PVP 1300k capped Ag nanofluid was observed, as shown in Fig. 2-d. These results are corresponding to SEM pictures shown in Fig. 2. The SPR spectra of Ag nanofluids were not dramatically changed with temperature. Therefore, the PVP capped Ag nanofluids have the long-term dispersion stability even at higher temperature region.

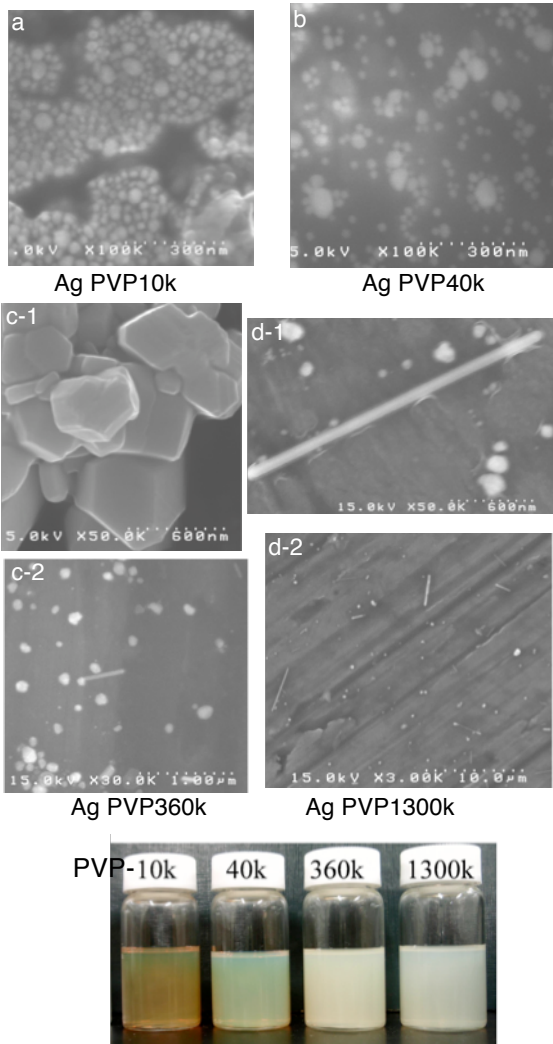


Fig. 1 SEM photographs and solution colors of four different PVP capped silver nanofluids.

Fig. 3 shows surface tension temperature dependency of Ag nanofluids containing 5 wt. % of 1-butanol by using drop-weight method. In the case of 1-butanol-containing PVP-10k, 360k and 1300k capped Ag nanofluids, it was found that both positive surface-tension gradient with temperature and temperature region of positive surface tension dependency increased. In contrast, surface tension tendency of PVP 40k capped Ag nanofluid was almost same as that of base fluid, 5 wt. % aqueous 1-butanol solution.

Temperature dependencies of viscosities of 1-butanol-containing Ag nanofluid are shown in Fig. 4. Prasher et al. reported on viscosities of alumina-based nanofluids and their experimental results suggest that the increase in the nanofluid viscosity is higher than the enhancement in the thermal conductivity to make the nanofluid thermal performance worse than

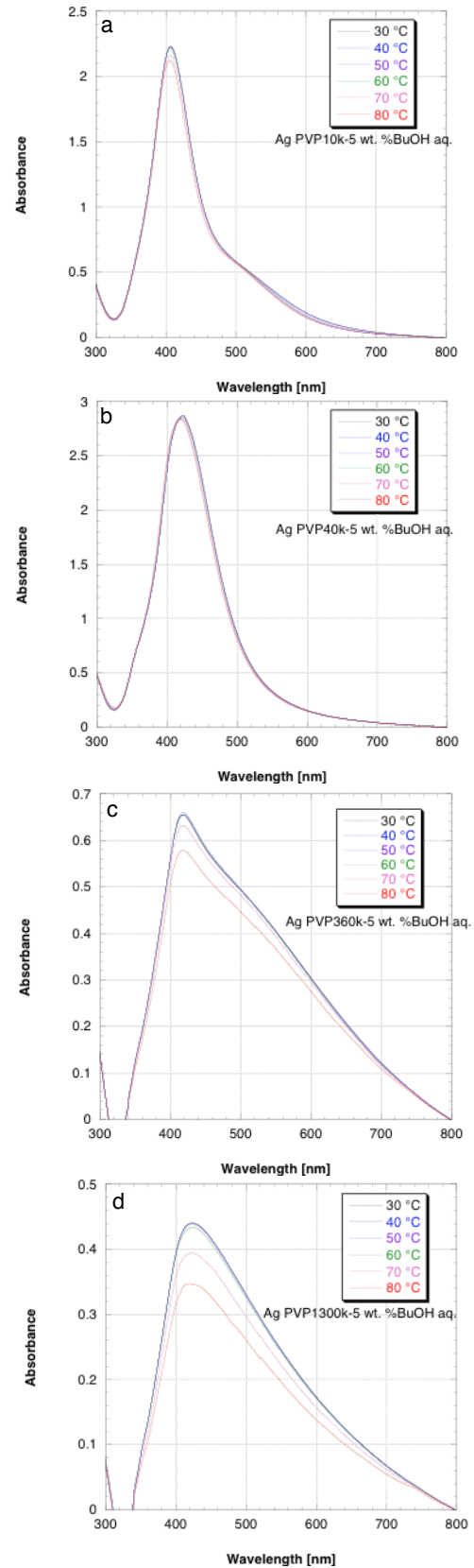


Fig. 2 The surface plasmon resonance spectra of four different Ag nanofluid with 5 wt. % 1-butanol

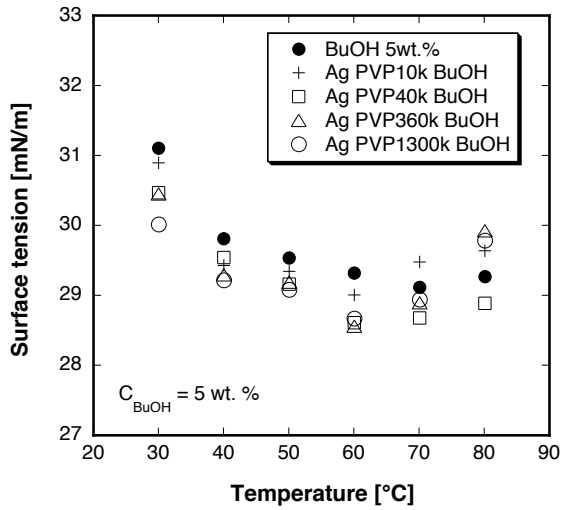


Fig. 3 surface tension temperature dependency of four different PVP capped silver nanofluid containing 5 wt. % 1-butanol.

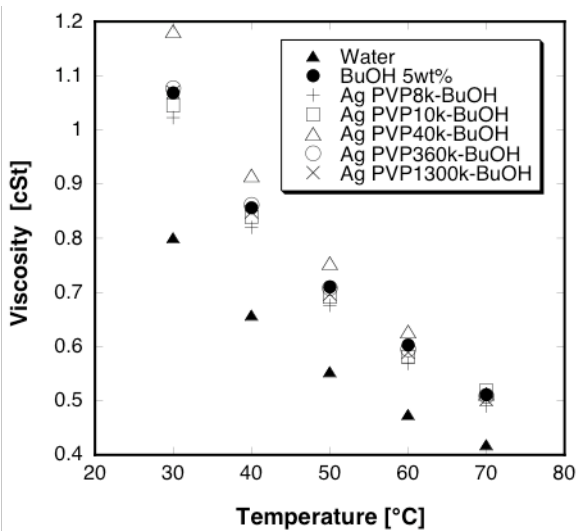


Fig. 4. Effect of temperature on viscosities of several self-wetting fluids.

that of base fluid [31], whereas viscosities of Ag nanofluids in the present case were almost same as base fluid 5wt.% 1-butanol aqueous solution because of dilute Ag nanoparticle concentration. These tendencies of the dilute PVP-capped Ag nanofluids are favorable for thermal application.

3.2. HEAT PIPE THERMAL PERFORMANCE TESTS

Figs. 5 and 6 show the typical thermal performance of tubular and thin plate heat pipes with different working fluids listed in Table 1. Comparing with the water heat pipe, remarkable increases of dryout limit were observed in both cases of tubular

and thin plate heat pipes with 5wt.% 1-butanol-containing Ag-PVP nanofluids. Note that remarkable improvement of thermal resistances R of nanofluid heat pipe has been reported by many investigators [21-24], whereas almost unchanged R values and significant increase of maximum applied heater power Q was observed in the present study. This difference can be attributed to differences between surface tension temperature dependencies of some Ag-PVP/1-butanol nanofluids and base 1-butanol aqueous solution, as shown in Fig. 3.

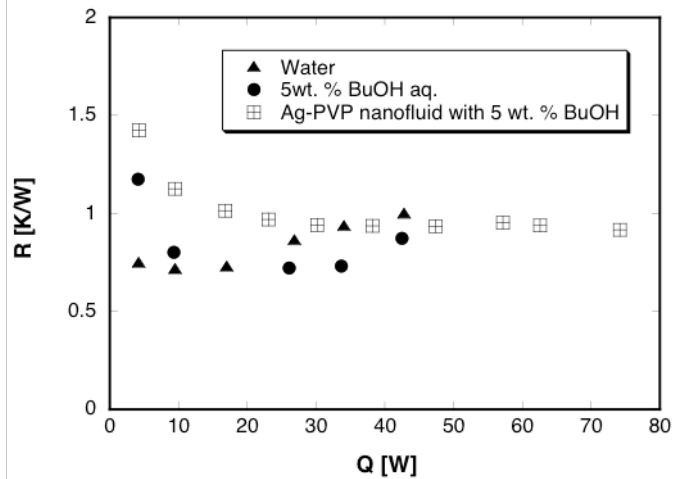


Fig. 5. Thermal performances of water, 1-butanol (5wt. %) and 1-butanol contained Ag-PVP nanofluid tubular heat pipes.

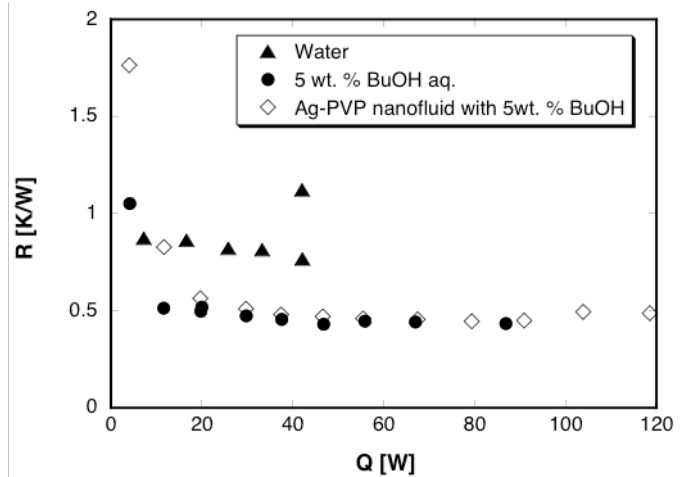


Fig. 6. Thermal performances of 1-butanol (5wt. %) and 1-butanol contained Ag-PVP nanofluid thin plate heat pipes.

4. CONCLUSION

We have investigated temperature dependencies of surface tension and viscosities of 1-butanol-containing chemically synthesized PVP capped Ag nanofluids. Accelerated positive surface tension temperature dependencies of some 1-butanol-containing PVP-capped Ag nanofluids were observed. Viscosities of 1-butanol-containing various PVP capped dilute Ag nanofluids were almost same as base 1-butanol aqueous solution. These results show 1-butanol-containing PVP-capped Ag nanofluids seem to be suitable for heat pipe working fluids.

Thermal performances of 4mm tubular and 1.5 mm thin plate heat pipe with the PVP-capped Ag nanofluid containing dilute 1-butanol were examined. From the result of the thermal performance test, the dryout limit of heat pipes containing PVP-capped Ag nanofluid with dilute 1-butanol were significantly larger than the other working fluid, water and 5wt. % 1-butanol aqueous solution. The reason for improvement of thermal performance of 1-butanol containing PVP-capped Ag nanofluid heat pipe can be explained that the accelerated positive surface tension dependencies of the nanofluid. These results indicate the 1-butanol-containing PVP-capped Ag nanofluid has the remarkable potential for working fluid of high thermal performance heat pipe.

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REFERENCES

[1] R. Vochten & G. Petre, "Study of the heat of reversible adsorption at the air-solution interface. II. Experimental determination of the heat of reversible adsorption of some alcohols," *J. Colloid Interface Sci.* **42**: 320-327 (1973).

[2] D. Villers & J. K. Platten, "Temperature dependence of the interfacial tension between water and long-chain alcohols." *J. Phys. Chem.* **92**: 4023-4024 (1988).

[3] J. Glin'ski, G. Chavepeyer, & J-K. Platten, "Untypical surface properties of aqueous solutions of 1,2 pentandiol." *Colloid Surf. A* **162**: 233-238 (1999).

[4] K. Motomura, S. Iwanaga, Y. Hayami, S. Uryu, & R. Matsuura, "Thermodynamic studies on adsorption at interfaces. IV. Dodecylammonium chloride at water/air interface." *J. Colloid Interface Sci.* **80**: 32-39 (1981).

[5] J. C. Legros, "Problems related to non-linear variations of surface tension," *Acta Astronautica* **13**: 697-703 (1986).

[6] Y. Abe, "About self-wetting fluids-possibility as a new working fluid." *Therm. Sci. Eng.* **12**: 9-18 (2004).

[7] Y. Abe, K. Tanaka, M. Mochizuki, M. Sato, N. Francescantonio, & R. Savino, "Heat pipe with self-wetting fluids." *Proc. 8th International Heat Pipe Symp. (8IHPS)*, Kumamoto, Japan, Sep. 24-27, 76-81 (2006).

[8] N. Francescantonio, R. Savino, & Y. Abe, "New alcohol solutions for heat pipes: Marangoni effect and heat transfer enhancement." *Int. J. Heat Mass Trans.* **51**: 6199-6207 (2008).

[9] S.U.S.Choi, "Enhancing thermal conductivity of fluids with nanoparticles." *ASME-FED* **231**: 99-105 (1995).

[10] X. Q. Wang & A. S. Mujumdar, "Heat transfer characteristics of nanofluids: a review." *Int. J. Therm. Sci.* **46**: 1-19 (2007).

[11] H. Masuda, A. Ebata, K. Teramae, & N. Hishinuma, "Alteration of thermal conductivity and viscosity of liquid by dispersing ultra-fine particles, dispersion of Al₂O₃, SiO₂ and TiO₂ ultra-fine particles." *Netsu Bussei* **7**: 227-233(1993).

[12] Y. Xuan & Q. Li, "Heat transfer enhancement of nanofluids." *Int. J. Heat Fluid Flow* **21**: 58-64 (2000).

[13] J. A. Eastman, S. U. S. Choi, S. Li, W. Yu, & L. J. Thompson, "Anomalously increased thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles." *Appl. Phys. Lett.* **78**: 718-720 (2001).

[14] H. E. Patel, S. K. Das, T. Sudararajan, A. S. Nair, B. George & T. Pradeep, "Thermal conductivities of naked and monolayer protected metal nanoparticle based nanofluids: Manifestation of anomalous enhancement and chemical effects." *Appl. Phys. Lett.* **83**: 2931-2933 (2003).

- [15] S. A. Putnam, D. G. Cahill, & P. V. Braun, "Thermal conductivity of nanoparticle suspensions." *J. Appl. Phys.* **99**: 084308-1-6 (2006).
- [16] B.C. Pak & Y.I. Cho, "Hydrodynamic and heat transfer study of dispersed fluids with submicron metallic oxide particles." *Exp. Heat Trans.* **11**: 151-170 (1999).
- [17] Y.M. Xuan & W. Roetzel, "Conceptions for heat transfer correlation of nanofluids." *Int. J. Heat Mass Trans.* **43**: 3701-3707 (2000).
- [18] Y. Xuan & Q. Li, "Investigation on convective heat transfer and flow features of nanofluids." *ASME J. Heat Trans.* **125**: 151-155 (2003).
- [19] S. K. Das, N. Putta, & W. Roetzel, "Pool boiling characteristics of nano-fluids." *Int. J. Heat Mass Trans.* **46**: 851-862 (2003).
- [20] S. J. Kim, I. C. Bang, J. Buongiorno, & L. W. Hu, "Effects of nanoparticle deposition on surface wettability influencing boiling heat transfer in nanofluids." *Appl. Phys. Lett.* **89**: 153107-1-3 (2007).
- [21] C. Y. Tsai, H. T. Chien, P. P. Ding, B. Chan, T. Y. Luh, & P. H. Chen, "Effect of structural character of gold nanoparticles in nanofluid on heat pipe thermal performance." *Mater. Lett.* **58**: 461-465 (2004).
- [22] S-W Kang, W-C Wei, S-H Tsai, & S-Y Yang, "Experimental investigation of silver nano-fluid on heat pipe thermal performance." *Appl. Therm. Eng.* **26**: 2377-2382 (2006).
- [23] Y-H. Lin, S-W. Kang, & H-L. Chen, "Effect of silver nano-fluid on pulsating heat pipe thermal performance." *Appl. Therm. Eng.* **28**: 1312-1317 (2008).
- [24] H. B. Ma, C. W. B. Borgmeyer, K. Park, Q. Yu, S. U. S. Choi, & M. Tirumala, "Effect of nanofluid on heat transport capability in an oscillating heat pipe." *Appl. Phys. Lett.* **88**: 143116 (2006)
- [25] M. Sato, W. Matsuyama, M. Takahashi, S. Mashiyama, Y. Kobayashi, K. Iimura, T. Furusawa, N. Suzuki, & Y. Abe, "Suspensions of metallic nanoparticles (nanofluids) with positive Surface tension temperature dependency for new heat pipe working fluids." *Proc. 8th International Heat Pipe Symp. (8IHPS)*, Kumamoto, Japan, Sep. 24-27, 380-384 (2006).
- [26] M. Tsuji, Y. Nishizawa, M. Hashimoto, & T. Tsuji, "Syntheses of Silver Nanofilms, Nanorod, and Nanowires by a Microwave-polyol Method in the Presence of Pt Seeds and Polyvinylpyrrolidone." *Chem. Lett.* **33**: 370-371 (2004).
- [27] W. D. Harkins & F. E. Brown, "The determination of surface tension (free surface energy), and the weight of falling drops: the surface tension of water and benzene by the capillary height method." *J. Am. Chem. Soc.* **41**: 499-524 (1919).
- [28] Y. Sun, B. Gate, B. Mayers, & Y. Xia, "Crystalline silver nanowires by soft solution processing." *Nano Lett.* **2**: 165-168 (2002)
- [29] Y. Sun, Y. Yin, B. Mayers, T. Herricks, & Y. Xia, "Uniform silver nanowires synthesis by reducing AgNO₃ with ethylene glycol in the presence of seeds and poly(vinyl pyrrolidone)." *Chem. Matter.* **14**: 4736-4745 (2002)
- [30] Y. Gao, L. Song, P. Jiang, L.F. Liu, X. Q. Yan, Z. P. Zhou, D. F. Liu, J. X. Wang, H. J. Yuan, Z. X. Zgang, X. W. Zhao, X. Y. Dou, W. Y. Zhou, G. Wang, S. S. Xie, H. Y. Chen, & J. Q. Li, "Studies on silver nanodecahedrons synthesized by PVP-assisted N,N-dimethylformamide (DMF) reduction." *J. Cryst. Growth* **289**: 376-380 (2006)
- [31] R. Prasher, D. Song, & J. Wang, "Measurements of nanofluid viscosity and its implications for thermal applications." *Appl. Phys. Lett.* **89**: 133108-1-3 (2006).