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Yuhiro Iwamoto, Atsushi Yoshioka, Takuya Naito, Jhon Cuya, Yasushi Ido, Ryo Okawa, Balachandran Jeyadevan, Hiroshi Yamaguchi

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AUTHORS LIST

Yuhiro Iwamoto*1, Atsushi Yoshioka*2, Takuya Naito*3, Jhon Cuya*3, Yasushi Ido*1, Ryo Okawa*1, Balachandran Jeyadevan*3, Hiroshi Yamaguchi*2

AUTHOR AFFILIATIONS

*1 Department of Electrical and Mechanical Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi, 466-8555, Japan

*2 Department of Mechanical Engineering, Doshisha University, Kyotanabe, Kyoto, 610-0321, Japan

*3 Department of Engineering, The University of Shiga Prefecture, 2500, Hassaka-cho, Hikone, Shiga, 522-8533, Japan

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Corresponding Author

Yuhiro Iwamoto, Ph.D.

Department of Electrical and Mechanical Engineering, Nagoya Institute of Technology

Postal Address: Room 904, Building 3, Nagoya Institute of Technology, Gokiso-cho, Nagoya, Aichi, 466-8555, Japan

E-mail address: iwamoto.yuhiro@nitech.ac.jp

Tel.: +81-52-735-7542
ABSTRACT

Nanoparticles (NPs) or nanowires (NWs) dispersed suspensions with high thermal conductivity have gained much attention as thermal interface materials in developing thermal engineering applications. Here, a novel silver (Ag) NW - dispersed magnetic functional fluid (NWD-MFF), whose thermal conductivity is actively tunable with an external magnetic field, has been proposed. The NWD-MFFs were prepared by dispersing either Ag NWs with an average diameter of 70 nm and aspect ratios ranging between 29-162 or Ag NPs with an average diameter of 70 nm in water-based magnetic suspension composed of 5.0 vol.% of magnetic NPs. The influence on thermal conductivity enhancement in the above fluids due to the orientation of non-magnetic Ag NWs and magnetic NPs under external magnetic field was measured using the transient hot-wire method. The Ag NWs performed better than Ag NPs, when their thermal conductivities were measured under an external magnetic field. Furthermore, the thermal conductivities exhibited a linear increase for higher Ag NW concentrations and higher aspect ratios ranging between 0.029 ~ 0.110 vol.% and 29-162, respectively for the external magnetic field applied parallel to the direction of thermal gradient. The maximum thermal enhancement of 7% was recorded for the NWD-MFF dispersing a mere 0.110 vol.% of Ag NWs with an aspect ratio of 162. On the other hand, a 7% decrease in thermal conductivity was recorded when the external magnetic field was applied perpendicular to the thermal gradient direction. The reason for the enhancement and decrease in thermal conductivity was considered due to the orientation of NWs in the magnetic field direction, which was experimentally confirmed using the dark field microscopy. The above results suggested that the novel NWD-MFF could be used as an efficient thermal interface material for effective heat dissipation as well as heat accumulation that can be easily manipulated using external magnetic field.
1. Introduction

In recent years, with development of MEMS and NEMS technologies, high-density heat generation has become a critical issue [1]. For further advances of MEMS and NEMS systems, the development of thermal interface materials with high heat transfer characteristics is absolutely imperative. As a consequence, fluids dispersing metal nanoparticles (NPs) such as Cu, Ag, Au, etc., are being considered as potential candidates for thermal interface materials with high heat transfer properties. And their thermal conductivity enhancement potential have been evaluated theoretically and experimentally [2-6]. For example, thermal conductivity enhancement of about 14 % for n-tetradecane-based suspension dispersing 20 vol.% Cu NPs[2] and 20% for a suspension dispersing 2.0 vol.% of Ag NPs in ethylene glycol[3] have been reported.

On the other hand, thermal conductivity enhancement through the formation of nano- and micro- magnetic structures induced by external magnetic field has also been attempted. In general, the inherent thermal conductivity of the magnetic NPs is higher than that of the carrier liquids. In addition, the magnetic particles in a magnetic fluid align along the magnetic field direction and form anisotropic chain-like structures. And these chain-like structures contribute to the heat conduction and large amount of heat is anisotropically transferred in the magnetic field direction [7,8]. Several research groups have examined the anisotropic and tunable thermal conductivity of the magnetic fluids in the presence of the magnetic field [9-18]. The thermal conductivity of aqueous magnetic fluids dispersing 0 vol.% to 5.0 vol.% of 26 nm diameter Fe NPs has been measured by the transient hot-wire method and a tunable enhancement has been observed by varying the strength of external magnetic field applied parallel to the direction of temperature gradient [11]. Numerical simulation studies by Fang et al. [12] predicted that the
anisotropic feature of the thermal conductivity was a consequence of the chain-like structure formed along the direction of external magnetic field and this was subsequently confirmed experimentally.

In the case of suspensions dispersing metal NPs, the thermal conductivity enhancement is not large enough to be used for thermal engineering systems. Aiming for higher thermal conductivity, suspensions dispersing metal nanowires (NWs) have been attempted and 1350% enhancement has been reported for a polymer composite composed of 0.9 vol.% of copper NWs [19]. The degree of enhancement has been quite high compared to suspensions dispersing metal NPs. Since the inherent thermal conductivity of silver is ~429 W/mK, an ethylene glycol-based suspensions dispersing a mere 0.1 vol.% of Ag NWs has been considered and a dramatic thermal conductivity enhancement of about 15.6% [20] has been reported. Furthermore, the influence of aspect ratio on the thermal conductivity was also confirmed.

Although many attempts have been made to enhance the thermal conductivity, the increment was insufficient. Furthermore, the thermal conductivity has been isotropic and considered inadequate for thermal engineering applications. Thus in this study, we propose “Ag nanowire dispersed-magnetic functional fluid” that could exhibit considerable anisotropic thermal conductivity enhancement in the presence of an external magnetic field. As for the design principle of the proposed functional fluid exposed to an external magnetic field, the magnetic surface charge generated on non-magnetic Ag NW [21], and their subsequent alignment in the magnetic field direction is the key. Consequently, the thermal conductivity of the proposed functional fluid is expected to be highly tunable due to anisotropic feature of the Ag NWs in the magnetic field direction.
In this manuscript, we discuss about the preparation of the water-based magnetic suspension dispersing Ag NWs and their thermal conductivity measurements in the presence and absence of external magnetic field using hot-wire method. Consequently, a preliminary investigation was carried out to determine the thermal conductivity of this fluid dispersing varying concentrations and aspect ratios of Ag NWs. Furthermore, thermal conductivity enhancement mechanism was confirmed by visual observation of the dynamic behavior of Ag NWs in the presence of the external magnetic fluid using a dark field microscopy.

2. Experimental Section

2.1 Preparation and characterization of Ag NWs

In the present work, a mixture of Ag NWs and water-based magnetic suspension was used as test fluids for thermal conductivity measurements. The preparation of Ag NWs with different dimensional properties was achieved using the polyol process with appropriate modifications. In a typical synthesis of Ag NWs, first, 2.5 g of polyvinylpyrrolidone (PVP) and 60 g of ethylene glycol (EG) were heated at 135°C. Then 0.006 g of sodium chloride and 0.85 g of silver nitrate were added to the above solution one after another. The mixture was kept at this temperature for 3 h. After the reaction, the resulting grey colour products were washed with methanol thoroughly to remove the residual organics and the resulting cotton-like products were stored in methanol at room temperature. Ag NPs with an average size of 70 nm are also synthesized using similar experimental procedure, but in the absence of sodium chloride in the reaction system.
Morphology of Ag NWs was characterized by field-emission scanning electron microscope (FE-SEM, Hitachi 4500). And the structural analysis of the Ag NWs was carried out using X-ray diffractometer with Cu-Kα irradiation.

2.2 Preparation of Ag NW-dispersed Magnetic Functional Fluid (NWD-MFF)

The Ag NWs synthesized using polyol process are suspended in water-based magnetic suspension (Ferri1003S, Taihokozai Co., Ltd.) dispersing 5 vol.% of magnetite particles having an average diameter of about 10 nm. The thermal conductivity, density and saturated magnetization of Ferri1003S are 0.52W/m·K, 1210kg/m³ and 20.0mT, respectively. In the present study, NWD-MFF suspensions dispersing 0.029, 0.057, 0.085 and 0.110 vol.% of Ag NWs were used.

2.3 Experimental Observation of the Dynamic Behaviour of Ag NWs in NWD-MFF in the Presence and Absence of Magnetic Field

The thermal conductivity enhancement under external magnetic field may depend on the orientation of the Ag NWs in the test fluid. Thus, understanding of the dynamic behaviour of Ag NWs and the morphology in the presence and absence of external magnetic field is essential. In the present work, dark field microscopy technique was utilized to visualize the dynamic behaviour of Ag NWs in NWD-MFF. The experimental setup was equipped with an electromagnet to apply a uniform magnetic field of 31 mT. The schematic diagram of the
2.4 Thermal Conductivity Measurement of NWD-MFF in the Presence and Absence of Magnetic Field

The thermal conductivity of the test fluids is measured by the transient hot-wire method using the device TPSY02 produced by CLIMA-TEC. The sensor probe (TP08, CLIMA-TEC) is embedded into the test fluid filled in a cylindrical container whose longitudinal axis is in parallel to the direction of gravity. The heat generated by the probe is dissipated in the radial direction (perpendicular to the direction of gravity) and the heat flux and the temperature of the test fluid
are monitored. The thermal conductivity is calculated by using the following linear relationship between $\ln(t)$ and $4\pi\theta/q$:

$$\lambda = \frac{q/4\pi}{d\theta/d(\ln(t))}$$  \hspace{1cm} (1)$$

where, $\lambda$ is the thermal conductivity, $q$ the heat flux, $\theta$ the temperature difference between initial and after an elapsed time, $t$. In order to investigate the effect of magnetic field on the thermal conductivity enhancement, uniform magnetic field strengths of 79 mT (Nd-Fe-B permanent magnet) and 20 mT (Helmholtz coil) were applied parallel and perpendicular to the temperature gradient $\nabla T$ (in perpendicular with the gravity direction), respectively. In order to prevent the effect of the heat convection on thermal conductivity, the test fluid was exposed to an external magnetic field at 25 °C for 15 min prior to any measurements. Thermal conductivity of glycerin in the presence and absence of the external magnetic field was measured to determine influence of the magnetic field on the experimental observations. Since glycerin is non-magnetic, the thermal conductivity values should be the same irrespective of the presence or absence of magnetic field. The thermal conductivity of glycerin in the presence as well as in the absence of the magnetic field was 0.29 W/m · K, and was in good agreement with the reference value [22].

The above results imply that the external magnetic field imposed on the fluid does not influence the thermal conductivity measurement using transient hot-wire method. The resolution of the thermal conductivity measurement device used in this study is 0.01 W/m · K. Several
experimental measurements were conducted at the same condition. The maximum standard deviation of 0.007 W/m·K was obtained.

3. Results and Discussion

3.1 Synthesis of Ag NPs and Ag NWs with Varying Aspect Ratios and Preparation of Ag NWs Dispersed Magnetic Functional Fluid (NWD-MFF)

Figure 2(a) SEM images of Ag NWs, whose average diameter and aspect ratio are 70 nm and 162, respectively. Inset is the magnified image of Ag NWs, (b) XRD pattern of Ag NWs.

The Ag NWs were synthesized using the procedure described in 2.1 and typical results of the structural and morphological analysis of the product are shown in Figure 2. The synthesis of Ag
NWs with varying aspect ratios was synthesized by sonicating the suspension dispersing Ag NWs with an average diameter of 70 nm and average length of 11 μm obtained using the process described in sec. 2.1. Consequently, the length of the NWs was reduced to almost half (5 μm) when the suspension was sonicated for 30 minutes and is shown in Figure 3(a). Then, for further reduction in size, the NWs with length of about 5 μm were subjected to further 30 minutes of sonication. Here again, the length of the sonicated wires became almost half (2 μm) as shown in Figure 3(b). Thus, NWD-MFF samples suspending Ag NWs with an average diameter of 70 nm and lengths 11, 5 and 2 μm were prepared for thermal conductivity measurements. The NW-dispersed magnetic functional fluids were prepared by suspending the Ag NWs synthesized using polyol process in water-based magnetic suspension.

Figure 3 The SEM micrographs of Ag NWs with average lengths (a) 5 and (b) 2 μm prepared by sonication.
3. 2. Dark-field Microscopic Observation of Ag NWs in MFF in the Presence and Absence of External Magnetic Field

Theoretical Consideration for dynamic behavior of non-magnetic materials dispersed in magnetic fluid under an external magnetic field should be considered to understand the experimental behavior of NWs in magnetic suspension. Figure 4 illustrates the dynamic behavior of non-magnetic bodies dispersed in magnetic suspension under an external magnetic field. When an external magnetic field is imposed on the magnetic suspension with a magnetization of \( M \), the magnetic moments of the magnetic NPs dispersed in the suspension align themselves in the magnetic field. On the other hand, the surfaces of the non-magnetic of bodies dispersed in the magnetic suspension and exposed to the external magnetic field become magnetically charged as a result of the magnetization of the surroundings \[21\] and apparently behave as magnetic materials. Coulomb’s law describes the interaction force acting between infinitely small surface of two non-magnetic bodies and is given as follows:

\[
F = \frac{M \Delta S_1 M \Delta S_2}{4 \pi \mu r^2} \frac{r}{r}
\]

Where, \( \mu \) is the permeability of the magnetic fluid, \( r \) is the distance between the small surface of \( \Delta S_1 \) and \( \Delta S_2 \). When considering the interaction forces between non-magnetic bodies 1 and 2, the intensities of the interaction forces between non-magnetic body 1 and two small surfaces, i.e. \( \Delta S_2 \) and \( \Delta S_2' \) in non-magnetic body 2, could be represented as \( F \) and \( F' \), and their values differ
due to the differences in inter-particle distances. This is because the interaction force is inversely proportional to the square of the distance. As a consequence, a torque is generated on non-magnetic body and tend to orient itself in the magnetic field direction. Additionally, attraction force also acts between non-magnetic bodies, and chain-like structures are formed [21]. If the non-magnetic bodies are highly thermally conductive metallic NWs, the thermal conductivity becomes enhanced, anisotropic and highly tunable by varying the magnetic field strength and direction.

Figure 4 Schematic of non-magnetic bodies dispersed in magnetic suspension and exposed to an external magnetic field.

The preparation of the Figure 5(a) and (b) show the images of Ag NWs dispersed in magnetic suspension before and after imposing the magnetic field, respectively. Here, it must be noted that the diameter and the length of the Ag NWs are 348 nm and 26.2 μm, respectively for easy
visualization. As shown in Figure 5(a), the Ag NWs are randomly oriented prior to the application of the external magnetic field. However under an external magnetic field, Ag NWs oriented along the magnetic field direction within a few seconds as shown in Figure 5(b). The above dynamic behavior of the Ag NWs could be due to the magnetic interaction between the non-magnetic Ag NWs and the magnetic NPs as described above. Resultantly, in the case of the proposed Ag NW dispersed water-based functional fluid, it is speculated that the Ag NWs orient in the magnetic field direction. Furthermore, Ag NWs were observed to vibrate in the absence of the magnetic field due to the Brownian motion of the water molecules and magnetic particles in the vicinity. This is considered as the driving force for homogeneous dispersion of the Ag NWs in magnetic suspension and also for the maintenance of constant properties during the experiments.

![Figure 5 Dark-field micrographs of Ag NWs dispersed in MFF in the (a) absence and (b) presence of external magnetic Field.](image)
3.3 Thermal Conductivity Measurements of Ag NWD-MFF in the Presence and Absence of Magnetic field

From the previous studies, it could be expected that the dispersion of Ag NWs in magnetic suspension should give an enhancement in the thermal conductivity. However, it is important to understand the feature of the thermal conductivity of the test fluids in the absence of the magnetic field to evaluate the influence of external magnetic field. Thus, the thermal conductivity measurement of the test fluids in the absence of external magnetic fields was carried out.

Figure 6 shows the measured thermal conductivity of the test fluids with various volume concentrations and aspect ratios of Ag NWs in the absence of external magnetic field. Ag NWs with an average diameter of about 70 nm and aspect ratios of Ag NWs 29, 70 and 162 were considered in this study. In addition, NPs (aspect ratio 1) whose size is similar to the diameter of NW was also considered. Furthermore, the volume concentrations of Ag NWs were varied between 0 and 0.11%. As shown in Figure 6, adding Ag NWs to the magnetic suspension enhances the thermal conductivity. A 9.6 % enhancement was observed in a test fluid that had 0.11 vol.% of Ag NWs with an aspect ratio of 162. These results also indicated that the increase in volume concentration and the aspect ratio of the Ag NWs enhanced the thermal conductivity. It should be noted that for similar volume concentrations, the thermal conductivity of Ag NWs is higher than that of Ag NPs (the aspect ratio of 1). The reason may be that the formation of Ag NWs network structure facilitates the heat conductivity. Similar trend have been observed by Fang et. al. [20] while examining the effect of NPs shapes on thermal conductivity enhancement using nanofluids of ethylene glycol dispersing Ag NPs or NWs. Wang et al. [19] also revealed that the thermal conductivity enhancement become larger with the increase of the aspect ratio of
the NWs. This is because the morphology of the NW fluid, namely the network structure of the NWs, contributes much effectively on the heat conductivity with the increase in the aspect ratio.

Figure 6 Thermal conductivities of Ag NW dispersed in water-based magnetic suspension at various volume concentrations and aspect ratios, under magnetic field–free conditions [20].

The most interesting results in the present study are the thermal conductivity enhancement of the test fluids in the presence of magnetic field. The measured thermal conductivity enhancement in the presence of magnetic field imposed parallel (\( H // \nabla T \)) and perpendicular to the temperature gradient (\( H \perp \nabla T \)) are shown in Figure 7(a) and (b), respectively. Though the thermal conductivity of the test fluids dispersing Ag NWs varies with concentration under external magnetic field, the Ag NW-free magnetic suspension (Ferri1003S) did not exhibit any change under magnetic fields parallel and perpendicular to the temperature gradient. The results obtained in this study for magnetic suspension (Ferri1003S) are different from the ones reported
by other research groups [9-18]. This discrepancy in thermal conductivity measurements could be due to the presence of excess amount of surfactant in the magnetic suspension (Ferri1003S).

Furthermore, there was no enhancement in the thermal conductivity in case of the Ag NPs dispersed in the magnetic suspension (aspect ratio of 1). This may be due to the inter Ag NP resistance caused by low particle volume concentration. Parekh and Lee [16] have found that the critical concentration magnetic NP to be 1.0 vol.%. In the present work, it is clearly known that the Ag NPs dispersed in magnetic suspension behave as diamagnetic body under external magnetic field. The concentration of the Ag NPs is 0.11 vol.%, which is very low and the Ag NPs do not influence the thermal conductivity in the presence of the magnetic field. On the other hand, in the case of Ag NWs, the thermal conductivity of the test fluids dramatically changes when exposed to external magnetic field. Namely, the thermal conductivity enhances when the magnetic field is imposed parallel to the temperature gradient (Figure 7(a)). However, the thermal conductivity exhibited a decrease when the external magnetic field is applied perpendicular with the temperature gradient (Figure 7(b)). The above behavior is due to the magnetic field induced morphology of the Ag NWs dispersed in the magnetic suspension. Therefore, the thermal conductivity enhancement observed in external magnetic suspension is mainly due to the alignment of Ag NW in the magnetic field direction.

It should be noted that in the case of Ag NWs, thermal conductivity enhancement is observed even in the case of low volume concentration of 0.11 vol. % as shown in Figure 7. Furthermore, the thermal conductivity is further enhanced when the aspect ratio as well as the volume concentration Ag NWs was increased. This is due the easiness with which the network-structures of the Ag NWs are formed when the aspect ratio and the volume concentration are increased and subsequent facilitation of effective heat conduction.
By taking the visual observation results (Figure 5) into account, the difference in the thermal conductivity of the Ag NW dispersed magnetic suspension could be assumed due to the field-induced morphology. Figure 8 shows schematics of the field induced morphology of Ag NWs in magnetic suspension in the absence and the presence of the external magnetic fields. As to the morphology of Ag NWs in the test suspension in the absence of the magnetic field (Figure 8 (a)), it is speculated that the Ag NWs randomly distribute and orient. Consequently, the thermal conductivity becomes isotropic.

On the other hand, when magnetic field is imposed parallel to the temperature gradient (Figure 8(b)), the Ag NWs are believed to align along the magnetic field direction (in parallel with the temperature gradient). Since the Ag NWs has inherent high thermal conductivity, the
heat is conducted through the Ag NWs and leads to the enhancement in thermal conductivity. When the external magnetic field is imposed in the direction perpendicular to the temperature gradient, the reduction in thermal conductivity was considered due to the heat conduction along the Ag NWs as shown in Figure 8(c). As a consequence, heat transfer is damped in the temperature gradient direction.

The present work reveals that the thermal conductivity of the proposed water-based magnetic suspension dispersing Ag NWs are tunable by imposing external magnetic fields. The thermal conductivity was enhanced by about 7 % for a Ag NW concentration of 0.11 vol.% under magnetic field applied parallel to the temperature gradient. On the other hand, thermal conductivity was reduced by about -7 % when the magnetic field was applied perpendicular to the temperature gradient.

Figure 8 Schematic illustration of (a) Ag NW dispersed water-based magnetic suspension in the absence of external magnetic field and in the presence of magnetic field applied (b) parallel and (c) perpendicular to the temperature gradient.
Table 1 lists the thermal conductivity enhancement obtained using different materials and Ag NW dispersed water-based magnetic suspensions under magnetic field. As already stated, the thermal conductivity enhancement is solely influenced by the Ag NWs dispersed in the magnetic suspension. Thus the water-based magnetic suspension of Ferri1003S could be regarded as the carrier liquid.

As shown in Table 1, several research groups have investigated the thermal conductivity of the magnetic suspensions using magnetic particle volume concentration of about 5.0 ~ 10.0 vol.% and observed an enhancement of up to 45 %. On the other hand, the thermal conductivity values of the proposed water-based magnetic suspension dispersing a mere 0.11 vol.% of Ag NWs were tunable in a range of -7 % to 7 %. This is due to the higher inherent thermal conductivity of the Ag NWs compared to the magnetic particles (i.e. magnetite, Mn-Zn ferrite...
and so on and magnetic field induced non-magnetic structures. This suggests that NWs has great potential for the thermal conductivity enhancement, and the thermal conductivity can be dramatically enhanced up to $10^3$ % order. Taking account of the results shown in Table 1, we propose that by increasing the concentration of Ag NW to be dispersed in water-based magnetic suspension, functional suspension with highly tunable thermal conductivity could be achieved.

4. Conclusions

A novel Ag nanowire dispersed-magnetic functional fluid was proposed and their potential as heat transfer material has been successfully demonstrated. The thermal conductivity measurements using the above fluid dispersing Ag NWs with the diameter of approximately 70 nm, the aspect ratio of 29, 70 and 162 and a volume concentrations between 0 and 0.11% suggested that a maximum enhancement of 7 % could be obtained by dispersing a mere 0.11 vol. % of Ag NWs with a diameter of 70 nm and an aspect ratio of 162. The reason for the above behavior was confirmed due to the orientation of the long axis of the Ag NWs in the external magnetic field direction using the dark field microscopy measurements. Furthermore, -7 % decrease in thermal conductivity under an external magnetic field applied perpendicular to the temperature gradient direction suggested that such fluids could also be used in thermal storage applications. Further enhancement in thermal conductivity is speculated by using Ag NWs with higher aspect ratio and volume concentration. Studies are in progress to determine the optimal composition of the fluid from thermal property and economic considerations.
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