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Mark Horton,<sup>1</sup> Haiping Hong,<sup>1,a)</sup> Chen Li,<sup>2</sup> Bo Shi,<sup>3</sup> G. P. Peterson,<sup>4,a)</sup> and Sungho Jin<sup>5</sup>

<sup>1</sup>*Department of Material and Metallurgical Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota 57701, USA*

<sup>2</sup>*Department of Mechanical Engineering, University of South Carolina, Columbia, South Carolina 29208, USA*

<sup>3</sup>*Department of Mechanical Engineering, University of Colorado, Boulder, Colorado 80309, USA*

<sup>4</sup>*Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA*

<sup>5</sup>*Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, California 92093, USA*

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Thermal conductivity (TC) of heat transfer nanofluids containing magnetic-metal-coated carbon nanotubes can be significantly enhanced ( $>60\%$ ) by applied magnetic field. In this paper, we report the observed real images of Ni-coated single wall carbon nanotubes in water and oils (polyalphaolefin, polyol ester) under magnetic field by high speed microscopy, and correlate them with TC measurements. Initially, the nanotubes are randomly dispersed in the fluid, however, on longer holding in magnetic field the nanotubes gradually stretch and are finally aligned. The chain length in the images is found to be around  $30\sim 150\ \mu\text{m}$ , which is much longer than the real length of individual nanotubes ( $5\sim 40\ \mu\text{m}$ ), indicating that nanotubes are aligned and form some chains and clusters. Because of the semicontinuous nature of Ni magnetic nanoparticles, as well as the viscosity resistance of the fluid itself, it takes some time for the Ni-coated nanotubes to respond to the applied magnetic field and align. Time dependent TC experiments indicate that alignment process dominates the TC enhancement rather than microconvection. Finally, scanning electron microscopy images also show that the Ni coated nanotubes are aligned well under the influence of a magnetic field. Transmission electron microscopy images indicate that nickel remains stable and attached onto the nanotubes after the magnetic field exposure and movements. © 2010 American Institute of Physics. [doi:10.1063/1.3428450]

### I. INTRODUCTION

The discovery of carbon nanotubes (CNTs) has instigated tremendous research efforts in recent years. It has been reported that single wall CNTs (SWNTs) exhibit a thermal conductivity (TC) value as high as 2000–6000 W/m K (Ref. 1) under ideal circumstances. By contrast, typical heat transfer fluids like water and oil have TC values of only 0.6 W/m K and 0.2 W/m K, respectively.

We prepared a composite fluid containing high-TC materials of CNTs and magnetic-field-responsive magnetic nanoparticles which increased the TC of the fluid. Such fluids with enhanced TC are useful for a variety of applications such as heat transfer coolants and lubricants.<sup>2,3</sup> The fluids containing CNTs (called “nanofluids” hereafter) should exhibit substantially improved TC values.<sup>4–6</sup> However, a simple nanotube-containing composite fluid structure turned out to be not so effective in enhancing the TC of nanofluids. At low nanotube percentage loading, no significant improvements in TC were reported. At the loading of 1 vol % CNTs ( $\sim 1.4\ \text{wt}\%$ ), there is about 10%–20% TC increase reported by different groups.<sup>7,8</sup> However, at such high filler concen-

trations, the fluid became very viscous and mudlike, losing most of its fluidity, thus making the fluid much less useful for coolant and lubricant applications.

A possible explanation for this lack of sufficient TC increase in such nanotube-containing fluids may be attributed to a lack of alignment and orientation in the fluids when the CNTs are irregularly positioned in the fluids with only a random and infrequent chance for them to contact each other for percolations. Therefore, only very high concentrations of CNTs produce noticeable TC improvements.

We introduced a new concept of incorporating “magnetically guided CNTs” in a fluid. Magnetic particles in a liquid medium can have a variety of configurations depending on the nature of magnetic particles and the field strength.<sup>9,10</sup> Under a relatively strong magnetic field, small magnetized particles form connected networks and also tend to get somewhat oriented toward the field direction, which also moves the CNTs nearby and induces more physical contacts. Thus, improved TC is anticipated. We incorporated CNTs and magnetic-field-sensitive nanoparticles of  $\text{Fe}_2\text{O}_3$  into water and the results confirmed this assumption.<sup>11</sup> Also, enhanced TC is observed in the magnetically polarizable nanofluid that consists of a colloidal suspension of magnetite nanoparticles with average diameter of 6.7 nm.<sup>12</sup>

Based on the above results, we also estimated that the

<sup>a)</sup>Electronic mail: haiping.hong@sdsmt.edu, bud.peterson@gatech.edu.

metal encapsulated CNTs (Ref. 13) dispersed in water, water/ethylene glycol or oil with the help of appropriate chemical surfactant, could also significantly increase the TC value under a magnetic field if the coating metal is magnetic. The coated layer configuration of the magnetic material could be more beneficial than the presence of isolated magnetic nanoparticles as small magnetic particles tend to be superparamagnetic with a weak response to applied magnetic field. We investigated nanofluids containing 0.05 wt % of Ni-coated CNTs in water under different magnetic field strengths and the results strongly supported this assumption that TC of nanofluids containing magnetically sensitive metal coated CNTs can be significantly enhanced (>60%) by applied magnetic field.<sup>14</sup>

In this paper, we tried to observe the real images of Ni-coated SWNTs in water and oils (polyalphaolefin, polyol ester) under magnetic field by high speed microscopy. Understanding of nanotube alignment in magnetic field would be valuable in analysis and design of better performance nanofluids.

## II. EXPERIMENTAL

Single wall CNTs (SWNTs) were purchased from Helix Material Solutions Inc. (Helix, Richardson, Texas). Chemical surfactant sodium dodecylbenzene sulfonate was purchased from Sigma Aldrich. DURASYN<sup>®</sup> 166 is a commercial polyalphaolefin (PAO) oil product from Chemcentral (Chicago, IL). ROYCO<sup>®</sup> 500, 808 are the commercial polyol ester oil products from Royal Lubricants Inc. (East Hanover, New Jersey).

Ni coated SWNTs were prepared using the methodology as reported previously.<sup>13,14</sup>

Sonication was performed using a Branson Digital Sonifier, model 450. Magnetic field was provided by a pair of spaced apart Ba-ferrite magnet plates ( $4 \times 6 \times 1$  in. dimension) and placing the sample in the middle of the gap between the magnets.

Microscope image was recorded by Motion Scope (Redlake MASD Inc., San Diego, CA), Model PCI 2000S. Parameters set as: record rate 250, shutter 1/250, and trigger 70%. The lens is WHB 10 $\times$ /20 and MPlan 10 $\times$ /0.25. The TC data was obtained by the Hot Disk<sup>™</sup> thermal constants analyzer.<sup>15</sup> The magnetic field intensity was recorded by Bell Gaussmeter Model 5060.

Scanning electron microscopy (SEM) images were acquired using the backscattered electron detector on a Zeiss Supra40VP variable pressure system. Transmission electron microscopy (TEM) images were acquired with a Hitachi H-7000 FA.

## III. RESULTS AND DISCUSSION

Microscope images of 0.05 wt % Ni coated SWNT in de-ionized (DI) water [(A): before magnetic field. (B): after magnetic field for 30 min] are shown in Fig. 1. It is clearly seen in the high speed microscope video that before magnetic field, Ni coated nanotubes are randomly dispersed in water. Like pristine nanotubes, Ni coated nanotubes also entangle and look like scattered dots (most of these dots is

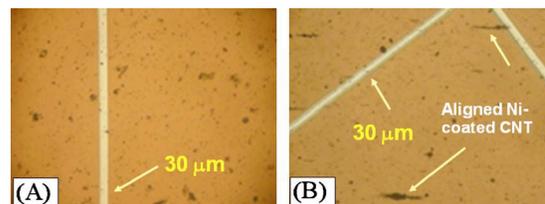


FIG. 1. (Color online) Microscope image of 0.05 wt % Ni coated SWNT in DI water. (A) Before magnetic field and (B) after magnetic field ( $H = 0.62$  kG) is applied.

much less than  $30 \mu\text{m}$  in the diameter) in the microscope image. With the addition of external magnetic field, the Ni coated nanotubes start to stretch, vibrate, and enlarge, eventually these randomly dispersed dots form short lines, indicating aggregated and entangled nanotubes form aligned chains and clusters. It is intuitive that the particles would move toward the direction of magnetic field. However, the Ni coated nanotubes do not show significant movement under the magnetic field. Instead, they start to precipitate after some time. The lines of black particles along the magnetic field at bottom of vessel are clearly observed.

This observed phenomenon coincides very well with our previous reported time dependent TC results of Ni coated nanotubes in water.<sup>14</sup> Without a magnetic field, the TC value of Ni coated SWNT loaded nanofluids is around  $0.63\text{--}0.64$  W/m K, which is essentially the value for the DI water itself. The reasonable explanation could come from the microscope image, too few contacts among these randomly dispersed Ni coated CNTs particles.

Under the magnetic field, TC shows very interesting behavior. TC initially increases with time but eventually reaches a peak ( $1.10$  W/m K) after two-four minutes of magnetic field exposure as shown in Table I. It could be explained by the nanotube alignment process. Microscope video shows that it takes some time for nanotubes from initially stretching to be oriented completely. As time in the magnetic field increases, TC decreases. It is because nanotubes get excessively agglomerated into larger particles and start to precipitate or sediment, which was confirmed by microscopic examinations.

Microscope images of 0.05 wt % Ni coated SWNT in PAO oil (A: Before magnetic field. B: After magnetic field for 30 min) are shown in Fig. 2. Similar Ni coated SWNT images before and after external magnetic field have been observed in DI water (Fig. 3). The alignment of Ni-coated CNTs in PAO oil appears to be less pronounced or slower as compared with that in less viscous water. To better under-

TABLE I. TC maximum values and increase ratios for 0.02 wt % Ni coated SWNT in water and oils under magnetic field of 0.38 kG after 2–6 min.

Fluids brand names	Component	Viscosity (cP)	TC maximum	
			value (W/m K)	TC increase ratio
DI water	H <sub>2</sub> O	1	1.10	0.80
Durasyn 166	PAO	40	0.21	0.11
Royco 500	Polyol ester	39	0.22	0.16
Royco 800	Polyol ester	16	0.24	0.26

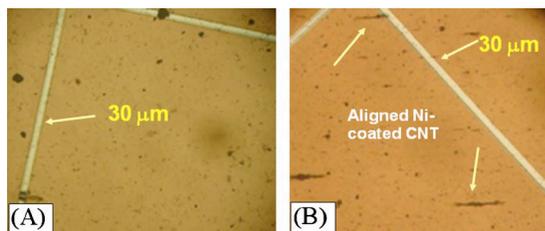


FIG. 2. (Color online) Microscope image of 0.05 wt % Ni coated SWNT in PAO oil. (A) Before magnetic field and (B) after magnetic field ( $H = 0.62$  kG) is applied.

stand how the viscosity would influence the TC and alignment process, time dependent thermal conductivities of Ni coated nanotubes in various oils with different viscosities are measured after 2–6 min exposure to the magnetic field and the data are listed in Table I. It is clearly seen that in all samples, TC values increase under the magnetic field. However, viscosities of fluids (water, oils) do influence the increase ratio of TC. The more viscous fluid, the less enhanced TC ratio. Water has the lowest viscosity (1 cP), therefore the TC increase ratio is highest ( $\sim 80\%$ ), while the PAO oil with the highest viscosity (40 cP) exhibits smaller TC increase ratio ( $\sim 11\%$ ). The reasonable explanation is that highly viscous fluid would make it difficult for the Ni nanotube particle to stretch and move for alignment.

It is pointed out that good dispersion and stability of fluids containing Ni-coated SWNT are critical for obtaining the reliable TC data. Nickel is a metal with molecular weight and density much higher than those for carbon, and hence, an optimal amount of Ni coating is also important. Too much Ni coating of nanotubes may lead to gravity-induced sedimentation, which may not be desirable for long term operation of nanofluids, especially in the lower viscosity fluids such as water.

Macrogeometrical effect of 0.05 wt % Ni coated SWNT on applied magnetic field is evaluated by taking digital camera images as shown in Fig. 3, (a) in DI water and (b) in PAO. It is clearly observed that black particles form the lines along the magnetic field on the bottom of vessel as shown in

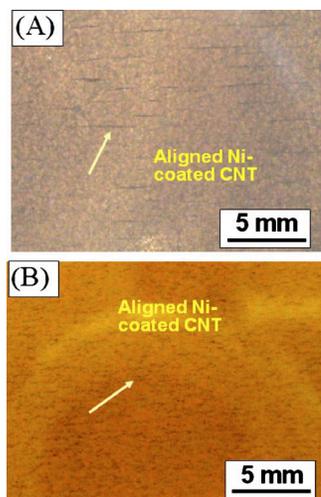


FIG. 3. (Color online) Macroeffect of magnetically aligned, 0.05 wt % Ni coated SWNT taken by digital camera. (a) in DI water and (b) in PAO.

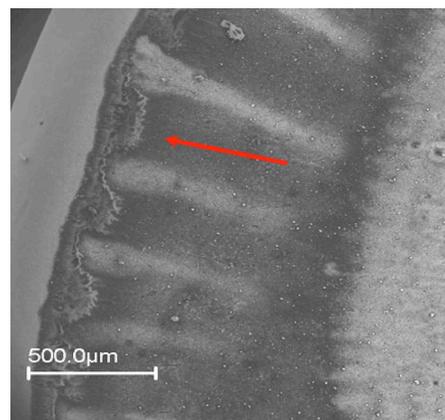


FIG. 4. (Color online) Backscattered electron SEM image of 0.01 wt % Ni coated SWCNTs aligned with magnetic field. Scale bar is 500  $\mu\text{m}$ . The red arrow is the applied magnetic field direction.

Fig. 3(a). While the trend of alignment is the same, due to relative high viscosity of PAO, it takes more time for Ni-coated nanotubes to align or move to precipitate to the bottom. Such a viscosity effect is also reflected in the relative TC improvements shown in Table I.

In order to make sure that alignment process dominates the TC enhancement rather than microconvection, we have tried to alter the magnet height and positions (and hence the magnetic field intensity and orientation) during the time dependent TC measurements to increase the turbulence in the fluids. However, no significant differences are observed for TC data. Magnetic field direction was also reversed manually by switching the magnets during the experimental period to see if enhanced tangling and contacts among the magnetically coated nanotubes could be obtained. Again, the TC data does not show significant differences. Further evidences include that TC enhancement could be observed along the applied magnetic field direction, but not along the perpendicular direction (data not shown). If microconvection assumption is true, then TC enhancement in all directions should be comparable. Normally, microconvection effect only lasts several minutes. The longer time scale TC enhanced phenomenon should also be the strong evidence that TC enhancement is not due to microconvection.<sup>16</sup>

The above microscope and TC results strongly demonstrate that a good alignment and orientation of nanotubes in a fluid are critical and essential to the enhancement of TC of the composite fluid. However, the increase ratio of TC is not as significant due to the thermal contact resistance in the nanofluids.<sup>17</sup>

From Fig. 4 it is clearly seen that under the magnetic field, the nanotubes align well along the magnetic field direction due to the magnetic moment of the Ni coating. The red arrow represents the magnetic field direction. The black material represents a layer of Ni coated CNTs. The white part may reflect the nature of sample holder (usually made by Al). Since Al is heavier than carbon, Al appears brighter in the backscattered electron image. The black bundled materials are aligned under the magnetic field. Energy-dispersive x-ray analysis showed that the black materials contain Ni which is consistent with our nanotube samples. To prepare the Fig. 4

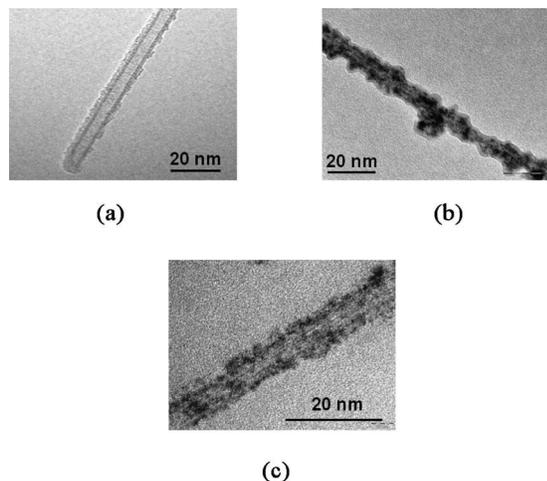


FIG. 5. TEM images of carbon nanotube. (A) As received, uncoated. (B) Ni-coated nanotube sample before the magnetic field experiment. (C) Ni-coated nanotube sample after the experiment. Scale bar is 20 nm.

SEM sample, drops of nanofluids containing Ni coated nanotubes were placed on the SEM sample holder and left to dry under the magnetic field.

In order to make sure that all these interesting results are solely due to the Ni-coated SWNT, and not by Ni particles detached from the nanotubes, several TEM pictures were taken. Figure 5 shows TEM images of carbon nanotube, (A) as received, uncoated, (B) Ni-coated before the experiment, and (C) Ni-coated after the experiment. It is clearly seen that Ni particles are still attached to the nanotube surface after the magnetic field experiment. This confirms that the results reflect the magnetically guidable nature of Ni coated SWNT.

#### IV. CONCLUSION

In summary, we have observed the real images of Ni coated SWNT in water and oils (polyalphaolefin, polyol ester) under magnetic field by high speed microscopy. Initially, the nanotubes are randomly dispersed (entangled) in the fluid. Upon longer holding in magnetic field, the nanotubes gradually stretch out linearly and finally aligned. The chain length in the images is found to be around 30–150 microns, which is much longer than the real length of individual nanotube (5–40 microns), indicating that nanotubes are aligned, but form chains and clusters. Because of the semicontinuous nature of Ni magnetic nanoparticles, as well as the viscosity resistance of the fluid itself, it takes some time for the Ni-coated nanotubes to respond to the applied magnetic field and align. Further research is underway to improve the morphology, configuration, and volume of magnetic nanoparticles so that the magnetic strength is enhanced and the response time to magnetic field is shortened.

Time dependent TC experiments indicate that alignment process dominates the TC enhancement rather than micro convection. SEM images also show that the Ni-coated nanotubes are aligned well under the influence of a magnetic field. TEM images indicate that nickel remains attached onto the nanotubes after the magnetic field exposure and nanotube movements.

Similar alignment phenomena have been observed in the water system incorporated CNTs and magnetic-field-sensitive nanoparticles of  $\text{Fe}_2\text{O}_3$ .<sup>18</sup> The use of magnetic guidance for enhanced carbon nanotube percolation in fluid is thus applicable to a variety of magnetic materials, either in the nanoparticle form or coated configuration. These advances may open up new routes for the research and applications of nanofluids.

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- <sup>1</sup>S. Berber, Y. K. Kwon, and D. Tománek, *Phys. Rev. Lett.* **84**, 4613 (2000).
- <sup>2</sup>H. Hong, J. Wensel, F. Liang, W. E. Billups, and W. Roy, *J. Thermophys. Heat Transfer* **21**, 234 (2007).
- <sup>3</sup>P. Keblinski, J. A. Eastman, and D. G. Cahill, *Mater. Today* **8**, 36 (2005).
- <sup>4</sup>X. Wang, X. Xu, and S. Choi, *J. Thermophys. Heat Transfer* **13**, 474 (1999).
- <sup>5</sup>S. Choi, Z. Zhang, W. Yu, F. E. Lockwood, and E. A. Grulke, *Appl. Phys. Lett.* **79**, 2252 (2001).
- <sup>6</sup>B. H. Kim and G. P. Peterson, *J. Thermophys. Heat Transfer* **21**, 451 (2007).
- <sup>7</sup>H. Xie, H. Lee, W. Youn, and M. Choi, *J. Appl. Phys.* **94**, 4967 (2003).
- <sup>8</sup>H. Hong, J. Wensel, S. Peterson, and W. Roy, *Polym. Mater. Sci. Eng.* **95**, 1076 (2006).
- <sup>9</sup>S. Jin and M. McCormack, *J. Electron. Mater.* **23**, 735 (1994).
- <sup>10</sup>X. R. Ye, C. Caraiio, C. Wang, J. B. Talbot, and S. Jin, *J. Nanosci. Nanotechnol.* **6**, 852 (2006).
- <sup>11</sup>H. Hong, B. Wright, J. Wensel, S. Jin, X. Ye, and W. Roy, *Synth. Met.* **157**, 437 (2007).
- <sup>12</sup>J. Philip, P. D. Shima, and B. Raj, *Appl. Phys. Lett.* **92**, 043108 (2008).
- <sup>13</sup>Y. Zhang, N. W. Franklin, R. J. Chen, and H. Dai, *Chem. Phys. Lett.* **331**, 35 (2000).
- <sup>14</sup>B. Wright, D. Thomas, H. Hong, L. Groven, J. Puszynski, D. Edward, X. Ye, and S. Jin, *Appl. Phys. Lett.* **91**, 173116 (2007).
- <sup>15</sup>Detail information see [www.hotdisk.se](http://www.hotdisk.se)
- <sup>16</sup>P. D. Shima, J. Philip, and B. Raj, *Appl. Phys. Lett.* **95**, 133112 (2009).
- <sup>17</sup>M. Bahrami, J. R. Culham, and M. M. Yovanovich, *J. Heat Transfer* **126**, 896 (2004).
- <sup>18</sup>J. Wensel, B. Wright, D. Thomas, W. Douglas, B. Mannhalter, W. Cross, H. Hong, J. Kellar, P. Smith, and W. Roy, *Appl. Phys. Lett.* **92**, 023110 (2008).