Experimental Study on Thermal Conductivity and Magnetization Behaviors of Kerosene-Based Ferrofluid Loaded with Multiwalled Carbon Nanotubes

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1. INTRODUCTION

Ferrofluid (FF), also called magnetic fluid, is a colloid suspension of ferrimagnetic or ferromagnetic nanoparticles dispersed in a nonmagnetic carrier fluid.  These nanoparticles are coated with a molecular of surfactants to ensure the stability of ferrofluid. As typical functional nanomaterials, ferrofluid exhibits both flowability of fluid and magnetization behaviors of the solid. Therefore, ferrofluid has been applied in the fields of sealing, energy transport, shock absorption, sensors, and so on. In the recent 30 years, ferrofluid seals, which are one of the mature applications of ferrofluid, have been widely used in many fields because of their advantages of zero leakage, long life, and zero wear, especially in the FF + p-MCNTs nano fluid. Moreover, few studies involve in the improvement of ferrofluid sealing devices, have been proposed to lower the temperature of ferrofluid in the sealing gap. Many studies concentrate on the structure designs improvement, such as the design of cooling channels, adjusting number of sealing stages, adjusting height of the sealing gap, and so on. However, the improvement of structure designs often leads to the complexity of the ferrofluid seals and the reduction of load-bearing capacity of shaft. Moreover, few studies involve in the improvement of ferrofluid’s thermophysical properties because minor changing of ferrofluid’s thermophysical properties might have a noticeable effect on the performances of ferrofluid seals. In this paper, the first method, which aims to accelerate heat conduction in ferrofluid seals by improving the thermal conductivity of ferrofluid, is proposed to lower the temperature in the sealing gap. The thermal conductivity of ferrofluid is a critically important parameter to accelerate heat conduction in ferrofluid

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seals. There are several available methods to increase the thermal conductivity of ferrofluid, for instance, changing the carrier, increasing volume fractions of magnetic nanoparticles, and adding heat conduction materials into ferrofluid.  

Numerous works have been conducted to investigate the thermal conductivity of ferrofluid. Sunder et al. studied the thermal conductivity and viscosity of water-based nanofluids containing Fe₃O₄ nanoparticles at 0.0–2.0% volume fraction in the temperature range of 20–60 °C. Karimi et al. considered the thermal conductivity of nanofluids containing Fe₂O₃ or CoFe₂O₄ nanoparticles dispersed in deionized water. The maximum enhancement of thermal conductivity was found to be 196% for Fe₂O₃ nanofluid and 148% for CoFe₂O₄ nanofluid at a volume fraction of 4.8%. The thermal conductivity of water-based magnetite and hematite ferrofluid was investigated experimentally in the presence and absence of a magnetic field. Experimental results showed that the magnetic field had a more significant effect on magnetite ferrofluid, compared with hematite ferrofluid. Gui et al. studied diluted commercial water-based ferrofluid for the viscosity and thermal conductivity and further measured heat transfer properties for single phase forced convective ferrofluidic flow in microchannels. Goharkhah et al. investigated experimentally the thermal conductivity of water-based ferrofluid flowing in a tube in the Reynolds numbers range of 400–800 and in the volume fractions range of 1.0–2.0% in the absence and presence of a magnetic field. Liu et al. conducted experiments to examine the thermal conductivity of water–Fe₃O₄ ferrofluid under a constant and an oscillating magnetic field. Results revealed that the thermal conductivity of ferrofluid increased and then decreased under a constant magnetic field, and the decrease was prevented under an oscillating magnetic field. Doganay et al. considered the thermal conductivity of water-based ferrofluid in the presence of a magnetic field. The maximum enhancements were 5.6 and 10% in perpendicular and parallel orientations of magnetic field, respectively, for ferrofluid with 4.8% volume concentration. Some thermal parameters of a Fe₃O₄/kerosene ferrofluid, such as the effective thermal conductivity, the effective thermal diffusivity, and the effective specific heat, were studied in the presence and absence of a static magnetic field. The results showed that the abovementioned thermal parameters can be controlled by manipulating an external magnetic field. These studies on the thermal conductivity of ferrofluid mostly consider the water-based ferrofluid.  

There are some studies considering the thermal conductivity of nanofluids containing magnetic nanoparticles and carbon nanotubes. Carbon nanotubes (CNTs) are concentric cylindrical structures composed of carbon atoms, which have drawn tremendous attention for outstanding thermal, electrical, and mechanical properties since they were first synthesized in 1991. The thermal conductivity of an isolated carbon nanotube was reported to be a high value of about 6600 W/m·K. Hong et al. prepared heat transfer nanofluids by dispersing carbon nanotubes and Fe₃O₄ nanoparticles in deionized water. It was reported that the thermal conductivity of nanofluids could increase in the presence of a magnetic field for the first time. This phenomenon was attributed to the chains formed by Fe₃O₄ particles, which contributed to the connection of nanotubes. The thermal conductivity of nanofluids with Ni-coated single wall carbon nanotubes was found to be enhanced by external magnetic field, owing to aligned chains formed by Ni-coated nanotubes. A surfactant-free magnetic nanofluid was presented by dispersing core–shell type nanoparticles (Fe₂O₃@SiO₂) decorated multiwall carbon nanotubes (MCNTs) in deionized water. Thermal conductivity enhancement of 24.5% was observed at a volume fraction of 0.03% under applied magnetic field. These studies mentioned above incorporated magnetically sensitive metal oxide or metal nanoparticles in a fluid containing CNTs to prepare heat transfer nanofluids. Shahsavari et al. prepared a hybrid nanofluid by incorporating CNTs in a water-based ferrofluid containing Fe₃O₄ nanoparticles. The effects of ultrasonication, magnetic nanoparticle weight fractions, CNT weight fractions, temperature, and magnetic field on the thermal conductivity of the hybrid nanofluids were comprehensively studied. To sum up, after the literature review about the thermal conductivity of ferrofluid, we find that most previous studies concentrate on the thermal conductivity of water-based ferrofluid with a low volume fraction of magnetic nanoparticles. However, there are few studies considering kerosene-based ferrofluid with a high volume fraction of magnetic nanoparticles. Meanwhile, many studies concentrating on the thermal conductivity of ferrofluid discount the magnetization behaviors of ferrofluid, which are significant parameters for ferrofluid. After the literature review about the nanofluids containing CNTs, we find that in order to improve the thermal conductivity of nanofluids, incorporating magnetic nanoparticles in a fluid containing CNTs attracts more attention than incorporating CNTs in ferrofluid, which is used to prepare samples in this study. In addition, there are few studies considering the effect of function groups of CNTs on the thermal conductivity of ferrofluid. Furthermore, previous studies mostly consider to enhance the thermal conductivity of ferrofluid and utilize ferrofluid as heat transfer medium in thermal engineering. However, few studies explore the potential application in high-speed ferrofluid seals. According to the literature review and our best knowledge, water-based ferrofluid usually has a lower stability than kerosene-based ferrofluid; moreover, a low volume fraction of magnetic nanoparticles in ferrofluid leads to a low magnetization and thus a low resistance to pressure, which is not suitable for ferrofluid seals. Therefore, in this paper, the kerosene-based ferrofluid containing MCNTs, with a high volume fraction of magnetic nanoparticles, is prepared to improve the performances of high-speed ferrofluid rotary seals, and the magnetization behaviors are investigated furthermore. In order to improve the performances of high-speed ferrofluid rotary seals, the kerosene-based ferrofluid containing MCNTs is prepared in this work. Kerosene-based ferrofluid is chosen for the reasons as follows. Kerosene-based ferrofluid is a type of cheap and stable commercial ferrofluid. The viscosity of kerosene-based ferrofluid is low; thus, less heat will be generated in the high-speed ferrofluid seals for short time occasions when kerosene-based ferrofluid instead of other types of stable commercial ferrofluid is used. The performances of high-speed ferrofluid seals are further ensured. Furthermore, the effects of MCNTs on the thermal conductivity and magnetization behaviors of the kerosene-based ferrofluid are investigated experimentally by changing temperature, weight fractions of MCNTs, and function groups of MCNTs.  

2. RESULTS AND DISCUSSION  

Experiments are conducted to investigate the influences of temperature, weight fractions of MCNTs, and function groups of MCNTs on the thermal conductivity and magnetization behaviors of the kerosene-based ferrofluid loaded with MCNTs. The thermal conductivity data in Figures 1–3 are measured next.
day since the nanofluids are prepared because it takes a long time to reach thermal equilibrium during measurements. The magnetization data in Figures 7 and 8 are measured as soon as the nano fluids are prepared. The results and detailed discussion are clarified in the following paragraphs.

2.1. Influence of Temperature on the Thermal Conductivity. In order to clarify the mechanism about the thermal conductivity enhancement more clearly, the comparative thermal conductivity is defined in eq 1

$$\frac{\Delta \lambda}{\lambda} = \left(\frac{\lambda_{\text{FF+MCNTs}}}{\lambda_{\text{FF}}} - 1\right) \times 100\%$$

(1)

where $\lambda_{\text{FF+MCNTs}}$ and $\lambda_{\text{FF}}$ are the thermal conductivity for FF + MCNTs nano fluids and ferro fluid, respectively. The variation of thermal conductivity and comparative thermal conductivity with temperature for FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nano fluids are shown in Figure 1. Besides, Figure 1 also demonstrates the temperature dependence of thermal conductivity of the ferro fluid. It can be seen that the addition of p-MCNTs, MCNTs-COOH, and MCNTs-OH obviously increases the thermal conductivity of the ferro fluid. Over the temperature range of 20–50 °C, the thermal conductivity of FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nano fluids and FF decreases with the increase of temperature. A similar trend for the temperature dependence of the thermal conductivity of nano fluids was reported in kerosene-based ferro fluid and kerosene-based silver nano fluids; however, those nano fluids do not contain MCNTs. The comparative thermal conductivity of FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nano fluids keeps almost constant and increases slightly with the increase of temperature from 20 to 50 °C in different cases. Some studies demonstrate that temperature has a significant influence on the comparative thermal conductivity of aqueous and nonaqueous nano fluids. The comparative thermal conductivity of nano fluids increases with temperature. In these cases, the viscosity of nano fluids decreases and the Brownian motion of nanoparticles is intensified when temperature rises. Hence, nanoparticle clustering and microconvection induced by the Brownian motion play a more

Figure 1. Variation of thermal conductivity and comparative thermal conductivity with temperature for (a,b) FF + p-MCNTs, (c,d) FF + MCNTs-COOH, and (e,f) FF + MCNTs-OH nano fluids.
important role in heat transport, which explains the temperature dependence of the comparative thermal conductivity. However, some other studies demonstrate another phenomenon about the temperature independence of the comparative thermal conductivity for water and oil-based nanofluids.\(^{35-38}\) In these studies, the comparative thermal conductivity of nanofluids keeps constant with a rise in temperature. In other words, the thermal conductivity of nanofluids simply tracks that of base fluids. Brownian motion of nanoparticles and microconvection mechanism have a negligible effect on the thermal conductivity enhancement. In the present work, the abovementioned phenomena take place for different cases. The disagreement in the comparative thermal conductivity is mainly attributed to types of nanoparticles, types of base fluids, addition of different surfactants, and different methods of measurement.

In this study, in the cases of FF + p-MCNTs, FF + MCNTs-COOH, and FF + 0.1 wt % MCNTs-COOH nanoﬂuids, the comparative thermal conductivity remains almost constant, which suggests that Brownian motion of carbon nanotubes and microconvection play a slight role in the thermal conductivity enhancement when p-MCNTs, MCNTs-COOH, and MCNTs-OH are added in kerosene-based ferroﬂuid. However, in cases of FF + 0.5 wt % MCNTs-COOH and FF + 0.1 wt % MCNTs-COOH nanoﬂuids, the comparative thermal conductivity slightly increases. The possible reason for the slight increase will be discussed in Section 2.3.

2.2. Influence of Weight Fractions on the Thermal Conductivity. Figure 2 shows the variation of thermal conductivity and comparative thermal conductivity with MCNT weight fractions for FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nanoﬂuids. It is obvious that the thermal conductivity and the comparative thermal conductivity increase monotonously with MCNT weight fractions. To describe the experimental results more concisely, the average comparative thermal conductivity is deﬁned as the average of the comparative thermal conductivity at different temperatures for a certain MCNT weight fraction. The average comparative thermal conductivity of 2.14–12.47, 1.93–7.87, and 0.46–10.21% is obtained for FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nanoﬂuids, with MCNT weight fractions

![Figure 2. Variation of thermal conductivity and comparative thermal conductivity with weight fractions for (a,b) FF + p-MCNTs, (c,d) FF + MCNTs-COOH, and (e,f) FF + MCNTs-OH nanoﬂuids.](https://dx.doi.org/10.1021/acsomega.0c00964)
ranging from 0.1 to 1 wt.%. Some other studies have revealed a
similar result that the thermal conductivity and the comparative
thermal conductivity increase with MCNT weight fractions or
volume fractions.\textsuperscript{39–41}

Based on a detailed analysis of the major mechanisms about
nano\textsuperscript{fluid heat transfer, Shahsavar et al.\textsuperscript{10} deduced that
nanoparticle clustering and microconvection caused by the
Brownian motion of the nanoparticles are the two more
reasonable mechanisms. In the present work, MCNT clustering
plays a more important role in enhancing the thermal
conductivity referring to a more detailed analysis in Sections
2.3 and 2.4. Clustering of MCNTs creates paths of lower thermal
resistance. With the increase of MCNT weight fractions in
nano\textsuperscript{fluids, there are more MCNTs in per unit volume and it is
much easier to form clusters, even networks of MCNTs.

\textbf{2.3. Influence of Function Groups on the Thermal
Conductivity.} Figure 3 presents variation of thermal
conductivity and comparative thermal conductivity with temperature for FF + p-MCNTs, FF + MCNTs-COOH, and
FF + MCNTs-OH nano\textsuperscript{fluids at 0.1 (a,b), 0.5 (c,d), and 1 wt % (e,f), respectively.}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Variation of thermal conductivity and comparative thermal conductivity with temperature for FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nano\textsuperscript{fluids at 0.1 (a,b), 0.5 (c,d), and 1 wt % (e,f), respectively.}}
\end{figure}
FF + MCNTs-COOH nanofluids because of its better dispersibility and fewer weight fractions in ferrofluid. At 1 wt % condition, the thermal conductivities of nanofluids increase in the sequence \( \lambda (FF + MCNTs-COOH) < \lambda (FF + MCNTs-OH) < \lambda (FF + p-MCNTs) \), and this may be attributed to the gradual decrease of the dispersibility of MCNTs in ferrofluid, which decreases in the sequence \( FF + MCNTs-COOH > FF + MCNTs-OH > FF + p-MCNTs \). In the meantime, the differences of the comparative thermal conductivity among \( FF + p-MCNTs, FF + MCNTs-COOH, \) and \( FF + MCNTs-OH \) nanofluids are more obvious at 1 wt % condition than at 0.1 and 0.5 wt % conditions. This may be explained as follows: the increase of MCNT weight fractions in nanofluids leads to more MCNTs in per unit volume, and thus, MCNTs are more likely to form clusters and networks, especially for \( p-MCNTs \) with low dispersibility in kerosene-based ferrofluid. According to the abovementioned analysis, it can be seen that the larger the weight fractions, the more significant the influence of MCNTs’ dispersibility on nanofluids’ thermal conductivity.

2.4. Influence of Time on the Thermal Conductivity. In this study, the stability of nanofluids is evaluated by thermal conductivity measurements during eleven weeks. Since the nanofluids are prepared, they remain still unless the thermal conductivity is measured (decanted, if necessary). No sedimentation is observed in \( FF + 1 \) wt % \( p-MCNTs, FF + 1 \) wt % MCNTs-COOH, and \( FF + 1 \) wt % MCNTs-OH nanofluids. From Figure 4, it can be seen that the thermal conductivity of \( FF + 1 \) wt % \( p-MCNTs \) nanofluid almost remains constant during the first three weeks and decreases very slowly during the latter days. The thermal conductivity of \( FF + 1 \) wt % MCNTs-COOH, and \( FF + 1 \) wt % MCNTs-OH nanofluids appears similar when newly prepared. However, the thermal conductivity of \( FF + 1 \) wt % MCNTs-OH nanofluid increases suddenly the next day and then remains almost constant for the latter days. The thermal conductivity in \( FF + 1 \) wt % MCNTs-COOH nanofluid increases slowly during the whole time. The above phenomenon could be called an aging effect or an evolution in thermal conductivity. An aging effect was also reported in alumina nanofluids by other researchers. Figure 5 illustrates microscopy images of the \( FF + 1 \) wt % \( p-MCNTs \) \((a, b)\), \( FF + 1 \) wt % MCNTs-COOH \((c, d)\), and \( FF + 1 \) wt % MCNTs-OH \((e, f)\) nanofluids at \( t = 0 \) (top row) and \( t = 77 \) (bottom row). The red background is ferrofluid and the black dots are MCNTs. As revealed in Figure 5, when the nanofluids are newly prepared, clusters of MCNTs in the \( FF + 1 \) wt % p-MCNTs nanofluid connect to each other and become networks. However, there are some gaps among the clusters in the \( FF + 1 \) wt % MCNTs-COOH and \( FF + 1 \) wt % MCNTs-OH nanofluids. After few weeks, there are also networks in the \( FF + 1 \) wt % MCNTs-COOH and \( FF + 1 \) wt % MCNTs-OH nanofluids. Figure 6 shows TEM images of the \( FF + 1 \) wt % \( p-MCNTs \) \((a, b)\), \( FF + 1 \) wt % MCNTs-COOH \((c, d)\), and \( FF + 1 \) wt % MCNTs-OH \((e, f)\) nanofluids at \( t = 0 \) (top row) and \( t = 77 \) (bottom row). It can be seen that there are only a small amount of magnetic nanoparticles attached to MCNTs in all cases when the nanofluids are newly prepared. After few weeks, a large number of magnetic nanoparticles are attached to the carbon nanotubes, which provide a promising potential to magnetically control the arrangement of carbon nanotubes and then further regulate the thermal conductivity of nanofluids. From the above analyses of microstructures among MCNTs and microstructures between MCNTs and MNPs in nanofluids, the aging effect may be mainly attributed to the dependence of thermal conductivity on the clusters and networks of MCNTs. MNPs attached to MCNTs may have little effect on improving the thermal conductivity of nanofluids because the thermal conductivity of \( FF + 1 \) wt % \( p-MCNTs \) nanofluid remains almost constant even though there are also more MNPs attached to MCNTs over eleven weeks. In the present work, the initial sizes of MCNT’s clusters can be ordered as \( p-MCNTs > MCNTs-OH \approx MCNTs-COOH \). Because networks of \( p-MCNTs \) occur in the ferrofluid and then \( p-MCNTs \) can support each other, the thermal conductivity of \( FF + p-MCNTs \) nanofluids is more stable. The thermal conductivity in \( FF + MCNTs-COOH \) nanofluids increases slowly rather than a sudden rise in \( FF + MCNTs-OH \) nanofluids, and this can be attributed to a better dispersibility of MCNTs-COOH than that of MCNTs-OH in kerosene-based ferrofluid. In conclusion, it can be said that clusters and networks of MCNTs play a more important role in improving thermal conductivity of ferrofluid in this study.

2.5. Magnetization Behaviors of FF and FF + MCNTs Nanofluids. Access to previous studies, the magnetization of ferrofluid can be described by Langevin theory when the interactions among particles are ignored. Ignoring particle size distribution, the Langevin magnetization formula is

\[
M(T) = \frac{\alpha M_s}{\coth \left( \frac{1}{\alpha} \right)}
\]

where

\[
\alpha = \frac{\pi \mu_0 M_s H d^3}{6 kT}
\]

\( \alpha \) is estimated from the relationship \( M \sim 1/H \) at the high field according to the experimental data, \( M(T) \) \((A \cdot m^{-1})\) is the magnetization of ferrofluid, \( M_s \) \((A \cdot m^{-1})\) is the bulk saturation magnetization, \( H \) \((A \cdot m^{-1})\) is the external magnetic field, and \( T \) \((K)\) is the absolute temperature. Figure 7a shows magnetization data from the experiment and Langevin theory curve for the ferrofluid at 20 °C. It can be seen that the magnetization of the Langevin theoretical curve is higher than that of the experimental curve in high field, and the deviation is small when the external magnetic field is extremely high. This is associated with the aggregation of particles that is caused by the field-induced interaction between the particles. In our experiment, the total energy of ferrofluid obtained during magnetization process can be separated into magnetized energy and
aggregate structure energy; however, Langevin theory ignores the aggregate structure energy.42

Figure 7b shows the magnetization curves and magnetization at $H = 20000$ Oe of the ferrofluid at 20, 30, 40, and 50 °C. The magnetic field strength is extremely large, even up to 20,000 Oe, under the pole shoes in the ferrofluid seal. Thus the magnetization at $H = 20,000$ Oe is chosen to measure the magnetization behaviors of nanofluids. From these curves, the difference between the magnetization at different temperatures can be measured at each magnetic field. It is obvious that the magnetization decreases when the temperature rises. When the external magnetic field grows larger, $\alpha \gg 1$, the asymptotic form of eq 2 is

$$M(T) = \sigma M_d = \frac{6}{\pi} \frac{\sigma k}{\mu_0 H_d^3} T$$

where $M_d$ is a function of temperature. Hence, $M_d$ and $\frac{6}{\pi} \frac{\sigma k}{\mu_0 H_d^3} T$ are both concerned with temperature. The inset of Figure 7b shows the magnetization of ferrofluid and its linear fit when $H$ equals to 20000 Oe. The slope of the linear fit is 0.074; however, $\frac{6}{\pi} \frac{\sigma k}{\mu_0 H_d^3}$, which represents a confrontation between Brownian motion and the applied magnetic field, is calculated to be 0.002. It can be inferred that the variation of the magnetization of ferrofluid with the temperature is mainly caused by the decrease of $M_d$. The variation of $M_d$ in high field can be described by the Bloch law

$$M_d(T) = M_d(0)(1 - BT^\beta)$$

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$$M_d(T) = M_d(0)(1 - BT^\beta)$$

when the temperature rises, the thermal fluctuations of the magnetic moments are more intense and $M_d$ decreases.44

Figure 5. Microscopy images of the FF + 1 wt % p-MCNTs (a,b), FF + 1 wt % MCNTs-COOH (c,d), and FF + 1 wt % MCNTs-OH (e,f) nanofluids at $t = 0$ (top row) and $t = 77$ (bottom row).

Figure 6. TEM images of the FF + 1 wt % MCNTs (a,b), FF + 1 wt % MCNTs-COOH (c,d), and FF + 1 wt % MCNTs-OH (e,f) nanofluids at $t = 0$ (top row) and $t = 77$ (bottom row).
As revealed in Figure 7c, the magnetization of FF + 1 wt % p-MCNTs nanofluid is lower than that of the original ferrofluid; this may be attributed to two factors, which will be clarified in next part. Besides, the magnetization of the FF + 1 wt % p-MCNTs nanofluid decreases with the increase of temperature, similar to ferrofluid.

The variation of magnetization and comparative magnetization at $H = 20,000$ Oe with temperature for FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nanofluids are shown in Figure 8. In order to clarify the mechanism about magnetization behaviors more clearly, the comparative magnetization is defined as

$$\frac{\Delta M}{M} = \left( \frac{M_{FF+MCNTs}}{M_{FF}} - 1 \right) \times 100\%$$  

(6)

where $M_{FF+MCNTs}$ and $M_{FF}$ are the magnetization for FF + MCNTs nanofluids and ferrofluid, respectively. As revealed in Figure 8, the addition of MCNTs decreases the magnetization of ferrofluid. The more the addition of carbon nanotubes, the greater the reduction in magnetization. This may be interpreted as follows. One reason is that the addition of carbon nanotubes makes per kilogram of FF + MCNTs nanofluids have less magnetic particles than that of the ferrofluid. The other reason is “viscomagnetic effect”. The addition of carbon nanotubes increases the viscosity of ferrofluid. The increased viscosity of nanofluids restrains the Brownian motion of magnetic nanoparticles, and the nanoparticles are more likely to aggregate as ring-like structures. The ring-like structures are stable even under high magnetic field for low movability resulting from the increased viscosity in nanofluids. However, these ring-like structures of closed magnetic flux do not make any contribution to the magnetization of nanofluids under external magnetic field. The greater the viscosity of nanofluids, the more the reduction of magnetization. As shown in Figure 8, the comparative magnetization almost keeps constant when temperature rises in FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nanofluids, which means that variation of the magnetization of FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nanofluids with temperature is similar to that in ferrofluid. To describe the experimental results more concisely, the average comparative magnetization is defined as the average of the comparative magnetization at different temperatures for a certain MCNT weight fraction. From Figure 8, when nanotube weight fractions range from 0.1 to 1 wt %, the average comparative magnetization obtained for FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nanofluids is 2.79–7.73, 2.43–5.41, and 3.50–4.60%, respectively. Besides, the comparative magnetization of FF + 1 wt % p-MCNTs nanofluid is higher than that of FF + 1 wt % MCNTs-COOH and FF + 1 wt % MCNTs-OH nanofluids, and the deviation is reduced at lower carbon nanotube weight fractions. The abovementioned two reasons may also be the explanations for the differences of the magnetization reduction among FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nanofluids. Considering the abovementioned microstructures among MCNTs and thermal conductivity data of nanofluids, it may be inferred that the viscosity of FF + p-MCNTs is greater than that of FF + MCNTs-COOH and FF + MCNTs-OH nanofluids, and this leads to the differences of the magnetization reduction.

3. CONCLUSIONS

In this study, two major properties, the thermal conductivity and magnetization behaviors, of FF + MCNTs nanofluids are...
investigated to further improve the performances of high-speed ferrofluid seals. Varying temperature, weight fractions of MCNTs, and function groups of MCNTs are concerned in the present work. For this purpose, the FF + MCNTs nanofluids are prepared ultrasonically by dispersing the MCNTs in kerosene-based ferrofluid.

The conclusions about thermal conductivity are as follows:

1. The addition of MCNTs in ferrofluid increases its thermal conductivity. The higher the weight fractions of MCNTs, the higher the thermal conductivity.

2. The variation of the thermal conductivity of FF + MCNTs nanofluids with temperature almost follows the trend of ferrofluid, which means that Brownian motion of MCNTs and microconvection have little effect on the thermal conductivity enhancement.

3. The thermal conductivity of FF + p-MCNTs nanofluids is higher than that of FF + MCNTs-COOH and FF + MCNTs-OH nanofluids. There is an aging effect especially in the FF + MCNTs-COOH and FF + MCNTs-OH nanofluids, the thermal conductivity of which increases over time. The differences of the thermal conductivity enhancement among the FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nanofluids mainly result from the sizes of clusters of MCNTs.

4. The average comparative thermal conductivity of FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nanofluids increases from 2.14 to 12.47%, 1.93 to 7.87%, and 0.46 to 10.21%, respectively, with nanotube weight fractions ranging from 0.1 to 1 wt %.

The conclusions about magnetization behaviors are as follows:

1. The addition of MCNTs in ferrofluid leads to the reduction of its magnetization. The higher the weight fractions of MCNTs, the greater reduction of magnetization.

2. The magnetization of ferrofluid decreases when temperature rises, resulting from the Brownian motion of magnetic nanoparticles and mainly the decrease of the
bulk saturation magnetization. The variation of the magnetization of FF + MCNTs nano fluids with temperature almost follows the trend of ferro fluid.

(3) The reduction of magnetization in FF + 1 wt % p-MCNTs nano fluid is greater than that of FF + 1 wt % MCNTs-COOH and FF + 1 wt % MCNTs-OH nano fluids, and the deviation decreases at lower carbon nanotube weight fractions, mainly resulting from the “viscomagnetic effect”.

(4) The average comparative magnetization for FF + p-MCNTs, FF + MCNTs-COOH, and FF + MCNTs-OH nano fluids increases from 2.79 to 7.73%, 2.43 to 5.41%, and 3.50 to 4.60%, respectively, with nanotube weight fractions ranging from 0.1 to 1 wt %.

In conclusion, the experimental results show that the addition of MCNTs in ferrofluid increases the thermal conductivity and decreases the magnetization of ferrofluid; however, the increase of thermal conductivity is greater than the decrease of magnetization, which might be beneficial to improve the performances of high-speed ferrofluid seals. The addition of 1 wt % p-MCNTs nano fluid can be stable for at least eleven weeks, which might be a good choice for high-speed ferrofluid seals.

4. EXPERIMENTAL SECTION

4.1. Materials. The ferrofluid, with a density of 1.35 g/cm³, used in the present work is prepared by chemical coprecipitation method in our lab. Fe₃O₄ nanoparticles are coated with oleic acid and dispersed in kerosene. Figure 9 shows a TEM image and a hysteresis loop of the ferrofluid. Fe₃O₄ nanoparticles with an average diameter of 9.43 nm (standard deviation, 0.24 nm) are well coated and have a good dispersion in the kerosene. The hysteresis loop is measured at 20°C, and it can be seen that the ferrofluid exhibits superparamagnetism, with no hysteresis and coercivity. The pristine MCNTs (p-MCNTs), MCNTs functionalized with carboxylic groups (MCNTs-COOH), and MCNTs functionalized with hydroxyl groups (MCNTs-OH) produced by chemical vapor deposition are purchased from Shanghai aladdin Biochemical Technology Co., Ltd. More details are shown in Table 1.

4.2. Sample Preparation. Desired amounts of different types of MCNTs are weighed using an electronic balance (ME104E, METTLER TOLEDO) and then added to the ferrofluid. Afterward, the mixtures are homogenized for an optimal time of 4 h using an ultrasonicator with a frequency of 40 kHz and a maximum power output of 600 W. More details of finished samples are shown in Table 2.

4.3. Measurement of Thermal Conductivity. In the present work, the thermal conductivity is measured by using the transient hot wire method, which is widely used in liquid samples. In the most designs, a thin wire with a large length-to-diameter generates a radial heat flux through the liquid sample when it is heated electrically. It is assumed that the heat is transferred completely from the thin wire to the liquid sample in the initial heating instant, and this results in the temperature distribution of both the liquid and the wire. Furthermore, the heat conduction equation under the initial heat equilibrium state is established to calculate the thermal conductivity. During the measurements, based on the temperature-dependent electrical resistance of the wire, the temperature can be obtained by measuring the variation of electrical resistance of the wire in a short time. Further, the thermal conductivity can be calculated according to the measured data. Figure 10 shows the schematic of the experimental apparatus for measuring the thermal conductivity.

Table 1. Details of p-MCNTs, MCNTs-COOH, and MCNTs-OH

| chemical name | function groups content | length (μm) | outer diameter (nm) | purity (%) |
|---------------|-------------------------|-------------|---------------------|-----------|
| p-MCNTs       | 0                       | 0.5−2       | <8                  | ≥95       |
| MCNTs-COOH    | 3.86%                   | 0.5−2       | <8                  | ≥95       |
| MCNTs-OH      | 5.58%                   | 0.5−2       | <8                  | ≥95       |

Table 2. Details of Finished Samples

| sample name     | MCNT type       | MCNT weight fraction (%) |
|-----------------|-----------------|--------------------------|
| FF + 0.1 wt % p-MCNTs | p-MCNTs        | 0.1                      |
| FF + 0.5 wt % p-MCNTs | p-MCNTs        | 0.5                      |
| FF + 1 wt % p-MCNTs      | p-MCNTs        | 1                        |
| FF + 0.1 wt % MCNTs-COOH | MCNTs-COOH    | 0.1                      |
| FF + 0.5 wt % MCNTs-COOH | MCNTs-COOH    | 0.5                      |
| FF + 1 wt % MCNTs-COOH      | MCNTs-COOH    | 1                        |
| FF + 0.1 wt % MCNTs-OH       | MCNTs-OH      | 0.1                      |
| FF + 0.5 wt % MCNTs-OH      | MCNTs-OH      | 0.5                      |
| FF + 1 wt % MCNTs-OH        | MCNTs-OH      | 1                        |
conductivity. The apparatus consists of a probe, a measurement control unit, a temperature control unit, and a computer. To suppress heat convection during the measurements, the probe has a platinum wire with a length of 130 mm and a diameter of 60 μm and guarantees a close approximation of the line heat source. Based on these, the apparatus can ensure an accuracy of 3% for measuring the thermal conductivity of liquid samples at different temperatures. The experimental apparatus is calibrated by glycerinum and deionized water at room temperature before measurements. During the measurements, the thermal conductivity is measured in the temperature range of 20–50 °C with intervals of 10 °C. At each temperature, the thermal conductivity of the sample is measured twice and the time interval between two measurements is set to 30 min, which will ensure the accuracy of measurement results.

4.4. Measurement of Magnetization Behaviors (Magnetic Hysteresis Curves). The magnetization behaviors of the samples are measured by using EZ8 vibrator sample magnetometers (VSM, MicroSense, LLC). This VSM instrument provides a maximum field of 20,500 Oe and an accuracy of 1% for the measurement of magnetic moments. Before the measurements, calibration is conducted using a nickel standard field. The magnetization of samples is measured at an external magnetic field of 20,500 Oe and an accuracy of 1%.

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**NOMENCLATURE**

Except the variables and their units emphasized in the main text, other variables and their units are as follows.

- $\lambda$ thermal conductivity of samples (W/m·K)
- $\omega$ weight fractions of MCNTs in ferrofluid
- $t$ number of days after ultrasonication
- $M$ the magnetization of samples (emu/g)
- $T$ test temperature (°C)
- $H$ the external magnetic field (Oe)
- $\varnothing$ the particle volume fraction of ferrofluid
- $\mu_a$ the permeability constant of the vacuum
- $d_0$ the average particle diameter (m)
- $k$ the Boltzmann constant
- $\beta$ the Bloch exponent

**Notes**

The authors declare no competing financial interest.
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