ENHANCED THERMAL CONDUCTIVITY THROUGH THE DEVELOPMENT OF NANOFULIDS*

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ABSTRACT

Low thermal conductivity is a primary limitation in the development of energy-efficient heat transfer fluids required in many industrial applications. To overcome this limitation, a new class of heat transfer fluids is being developed by suspending nanocrystalline particles in liquids such as water or oil. The resulting "nanofluids" possess extremely high thermal conductivities compared to the liquids without dispersed nanocrystalline particles. For example, 5 volume % of nanocrystalline copper oxide particles suspended in water results in an improvement in thermal conductivity of almost 60% compared to water without nanoparticles. Excellent suspension properties are also observed, with no significant settling of nanocrystalline oxide particles occurring in stationary fluids over time periods longer than several days. Direct evaporation of Cu nano-particles into pump oil results in similar improvements in thermal conductivity compared to oxide-in-water systems, but importantly, requires far smaller concentrations of dispersed nanocrystalline powder.

INTRODUCTION

Despite considerable previous research and development focusing on industrial heat transfer requirements, major improvements in cooling capabilities have been held back because of a fundamental limit in the heat transfer properties of conventional fluids. It is well known that metals in solid form have orders-of-magnitude larger thermal conductivities than those of fluids. For example, the thermal conductivity of copper at room temperature is about 700 times greater than that of water and about 3000 times greater than that of engine oil, as shown in Table 1. The thermal conductivities of metallic liquids are much larger than those of nonmetallic liquids. Therefore, fluids containing suspended solid metallic particles are expected to display significantly enhanced thermal conductivities relative to conventional heat transfer fluids.

Numerous theoretical and experimental studies of the effective thermal conductivity of dispersions containing particles have been conducted since Maxwell's theoretical work was published more than 100 years ago [1]. However, all previous studies of the thermal conductivity of suspensions have been confined to those containing mm- or micron-sized particles. Maxwell's model shows that the effective thermal conductivity of suspensions containing spherical particles increases with the volume fraction of the solid particles. It is also known that the thermal conductivity of suspensions increases with the ratio of the surface area to volume of the particle. Using Hamilton and Crosser's model [2], calculations [3] have been performed by one of us (USC) that predict, for constant particle size, the thermal conductivity of

Table 1. Thermal conductivities of various solids and liquids.

	Material	Thermal Conductivity (W/m-K)
Metallic Solids:	Silver	429
	Copper	401
	Aluminum	237
Nonmetallic Solids:	Silicon	148
	Alumina (Al_2O_3)	40
Metallic Liquids:	Sodium @644K	72.3
Nonmetallic Liquids:	Water	0.613
	Ethylene Glycol	0.253
	Engine Oil	0.145

a suspension containing large particles is more than doubled by decreasing the sphericity of the particles from a value of 1.0 to 0.3 (the sphericity is defined as the ratio of the surface area of a particle with a perfectly spherical shape to that of a non-spherical particle with the same volume). Since the surface area to volume ratio is 1000 times larger for particles with a 10 nm diameter than for particles with a 10 mm diameter, a much more dramatic improvement in effective thermal conductivity is expected as a result of decreasing the particle size in a solution than can obtained by altering the particle shapes of large particles.

Nanofluids are expected to have superior properties compared to conventional heat transfer fluids, as well as fluids containing micron-sized metallic particles. The much larger relative surface areas of nanophase powders, compared to those of conventional powders, should not only markedly improve heat transfer capabilities, but also should increase the stability of the suspensions. Conventional micron-sized particles cannot be used in practical heat-transfer equipment because of severe clogging problems. However, nanophase metals are believed ideally suited for applications in which fluids flow through small passages because the metallic nanoparticles are small enough to behave similarly to liquid molecules. Therefore, nanometer-sized particles will not clog flow passages, but will improve the thermal conductivity of the fluids. This will open up the possibility of using nanoparticles even in microchannels for many envisioned high-heat-load applications. This report describes the synthesis, suspension properties, and heat transfer behavior of fluids containing nanocrystalline alumina, copper oxide, and copper.

EXPERIMENTAL PROCEDURE

Two procedures were used in synthesizing nanofluids for this investigation. In the first, nanocrystalline powders were prepared by the gas condensation (IGC) process [4] and then were subsequently dispersed in deionized water. Nanocrystalline Cu and Al_2O_3 powders were produced at Argonne, while nanocrystalline CuO and additional Al_2O_3 powder were purchased [5]. No special procedures were required to form stable suspensions of commercial oxide powders in water. Difficulties in dispersing Cu and Al_2O_3 powders synthesized at Argonne will be described in the next section. Transmission electron microscopy was used to characterize particle sizes and agglomeration behavior.

To successfully produce a nanofluid with dispersed nanocrystalline Cu particles, a second preparation method was used based on the vacuum evaporation onto a running oil substrate (VEROS) technique of Yatsuya *et al.* [6]. With this technique, nanocrystalline particles are produced by direct evaporation into a low vapor pressure liquid. The system built at Argonne (Fig. 1) was based on a modification of the VEROS technique and is similar to an earlier design by Günther and co-workers at the Fraunhofer Institute for Applied Materials Research in Bremen [7]. With the system shown schematically in Fig. 1, nanocrystalline Cu was evaporated resistively into two types of pump oil [8]. These oils were chosen because they are designed for vacuum applications and thus have extremely low vapor pressures. Low vapor pressures are required with the VEROS technique to prevent vaporization of the liquid during the evaporation process.

Thermal conductivities were measured using a transient hot-wire apparatus shown schematically in Fig. 2. This system measures the electrical resistivity of the fluid systems and thermal conductivities are then calculated from the known relationship between electrical and thermal conductivities.

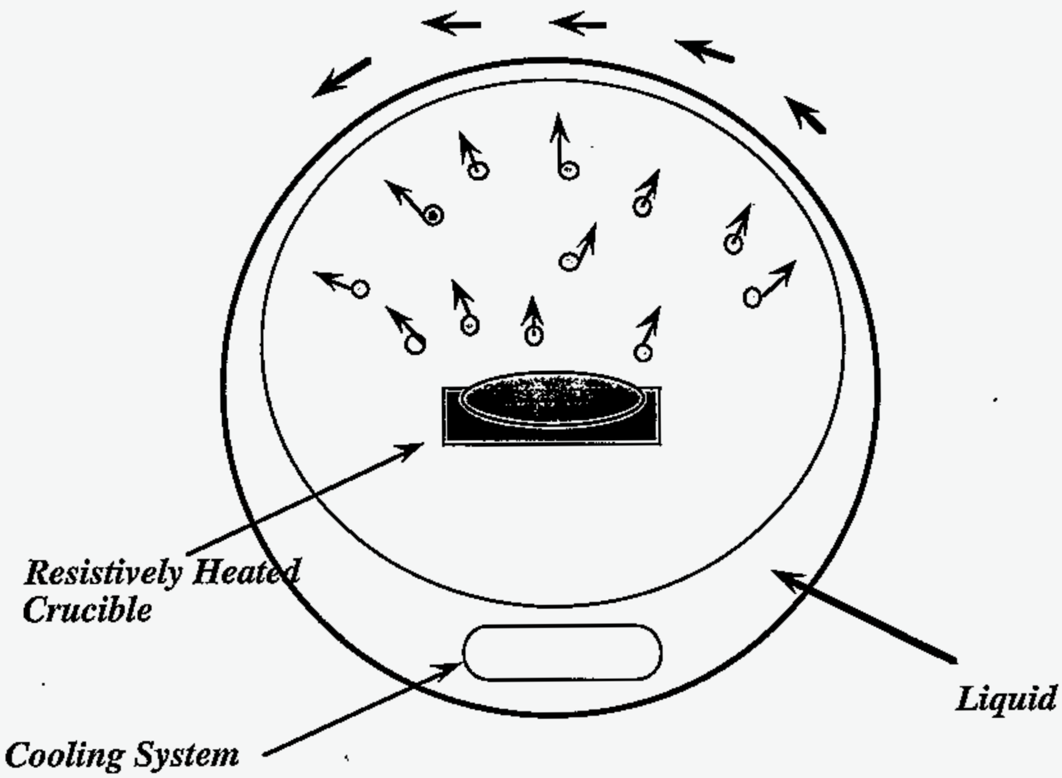


Figure 1. Schematic diagram of a VEROS-type evaporation system [6,7] designed for direct evaporation of nanocrystalline particles into low vapor pressure liquids. The liquid is located in a cylinder that is rotated to continually transport a thin layer of liquid above a resistively-heated evaporation source. The liquid is cooled to prevent an undesirable increase in vapor pressure due to radiant heating during the evaporation.

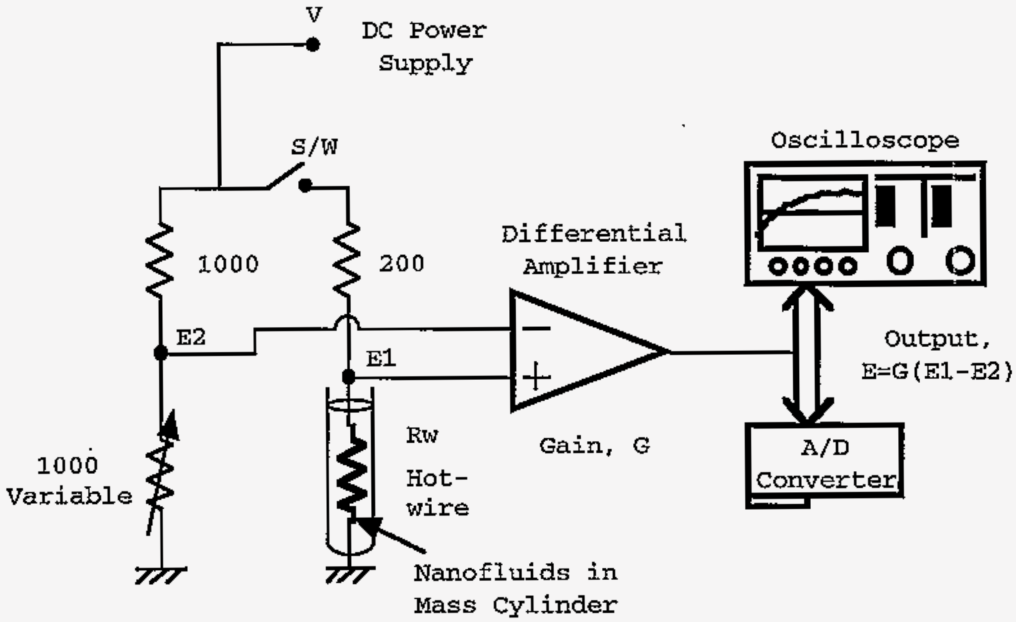


Figure 2. Schematic diagram of a transient hot-wire apparatus for measuring thermal conductivities of nanofluids.

RESULTS

Bright field TEM micrographs of nanocrystalline Cu and CuO produced by IGC are shown in Figure 3 (a) and (b). It can be seen that while the typical grain size of the Cu particles is smaller than that of the CuO particles by approximately a factor of two, it appears that a greater degree of agglomeration is present in Cu powders than in CuO. Fig. 3(c) shows beakers of deionized water after attempts to disperse both Cu and CuO. As indicated by the dark color of the CuO-containing beaker (left), a stable suspension is produced in this case. In fact, suspensions of CuO in water are stable under static conditions indefinitely with little apparent settling even after weeks of shelf life. CuO/H_2O nanofluids have been prepared with concentrations of CuO nanoparticles as high as 5 volume %. In contrast, the Cu produced by IGC did not form stable suspensions in water, but instead settled rapidly as seen Fig. 3(c).

Similar dispersion experiments were performed on nanocrystalline Al_2O_3 powders. Alumina powders prepared at Argonne by evaporation of Al into a low pressure of oxygen [9] have an extremely small average grain size of less than 3 nm (Fig. 4(a)). This is approximately an order of magnitude smaller than that of commercial nanocrystalline Al_2O_3 [5]. However, the commercial powder particles have a much more spherical shape (Fig. 4(b)) and show much better dispersion behavior in H_2O than the powders in Fig. 4 (a), as seen in Fig. 4(d). One reason for the poor dispersion behavior of the smaller Al_2O_3 particles is that they appear to actually dissolve in H_2O and re-precipitate as much larger particles, as seen in Fig. 4(c).

The thermal conductivity as a function of nano-particle volume fraction is shown in Fig. 5 for nanofluids of CuO or Al_2O_3 dispersed in deionized water. As expected based on earlier calculations [3], the conductivity increases linearly with increasing particle concentration. Very significant enhancements in thermal conductivity are seen, in particular in the case of CuO where

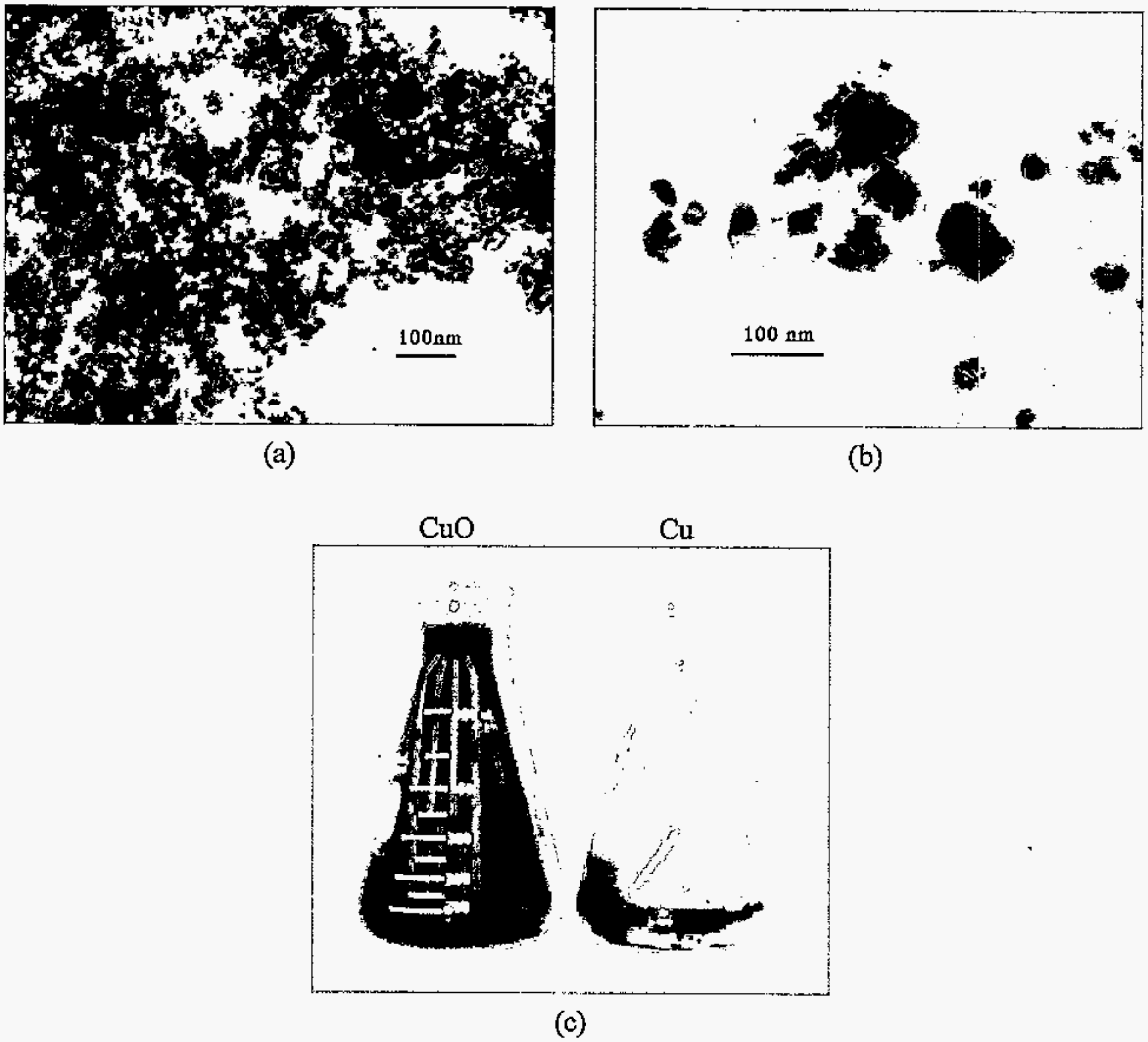


Figure 3. Bright-field micrographs showing the typical agglomeration size of nanocrystalline (a) Cu produced by IGC and (b) CuO [5]. While the Cu in (a) exhibits a smaller grain size of approximately 18 nm compared to the typical grain size of 36 nm for CuO in (b), the CuO agglomerate sizes are smaller than those of Cu and thus CuO forms much more stable dispersions in deionized water, as seen in (c).

increases of approximately 60% are seen for 5 volume % suspensions. Increases in conductivity of Al_2O_3 are also seen, although the effect is less significant than for CuO, which has a higher intrinsic conductivity than Al_2O_3. These results clearly demonstrate the commercial potential for significantly enhancing industrial heating and cooling capabilities through the use of nanofluids.

While a 60% improvement in thermal conductivity is very significant, comparison of the thermal conductivities of oxides and metals (Table 1) suggests that even larger effects can be obtained if metal nanoparticles such as Cu can be successfully suspended in liquids. Attempts to suspend Cu in water by first suspending CuO and then reducing the CuO to Cu by heating the

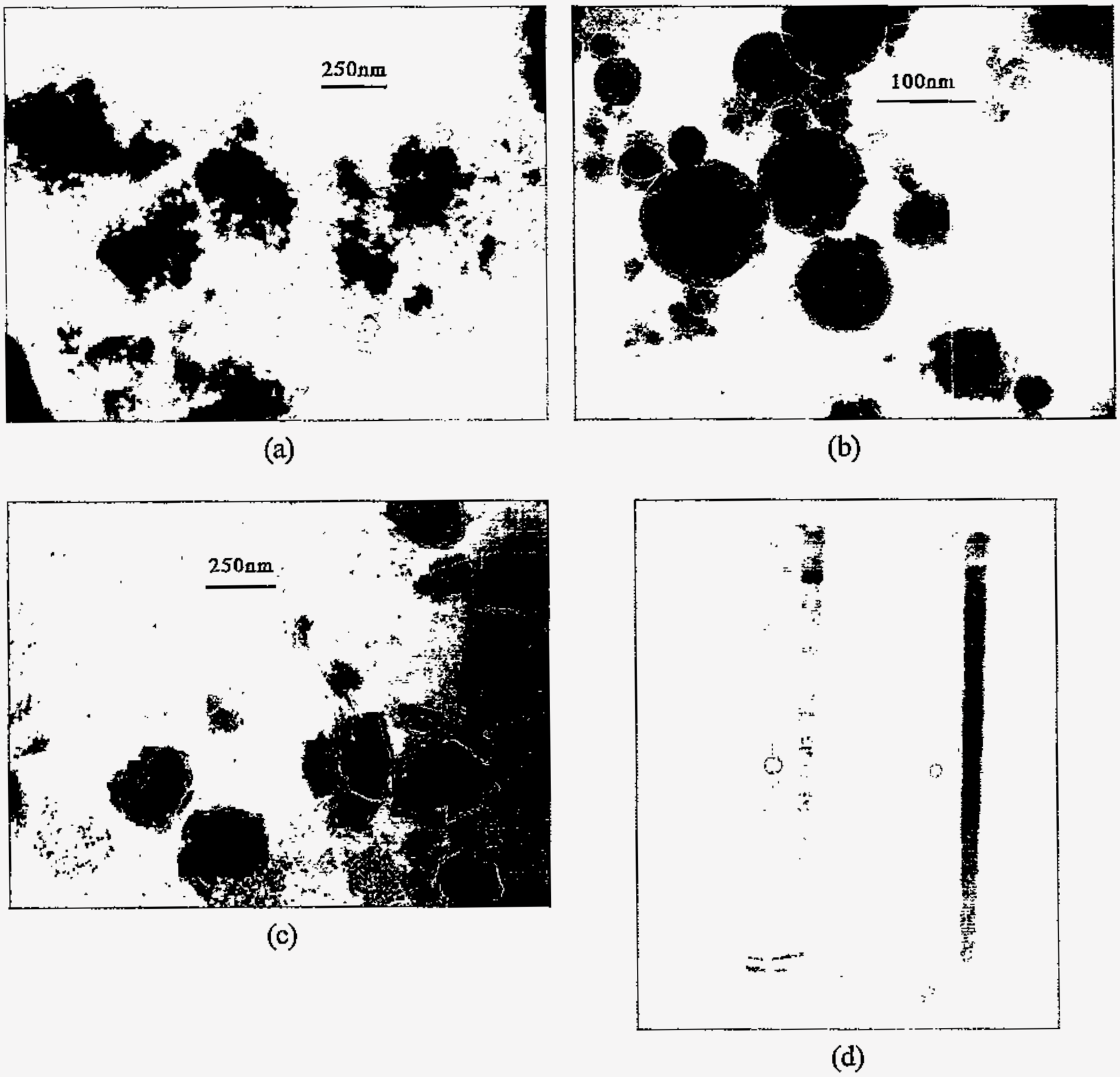


Figure 4. Bright field TEM micrographs of nanocrystalline Al_2O_3 (a) produced by IGC at Argonne (average grain size < 3 nm) and (b) purchased from Nanophase Technologies [5]. The average grain size in (b) is 33 nm. Both (a) and (b) show powders prior to dispersion in deionized water, while (c) shows the powder in (a) after dispersion. Large grains are seen after dispersion. Beakers of Al_2O_3 dispersed in H_2O are seen in (d). The beaker on the right contains a stable solution of powders from (b), while the powders in the beaker on the left (corresponding to (a) and (c)) settle rapidly and are thus unsuitable for heat transfer applications.

fluid while bubbling hydrogen gas through it resulted in the precipitation of large Cu particles that displayed poor suspension behavior. Therefore, an alternative method of nanofluid preparation was undertaken based on the VEROS technique [6,7]. Using a system shown schematically in Fig. 1, Cu was evaporated into two types of low vapor pressure pump oil [8]. A TEM

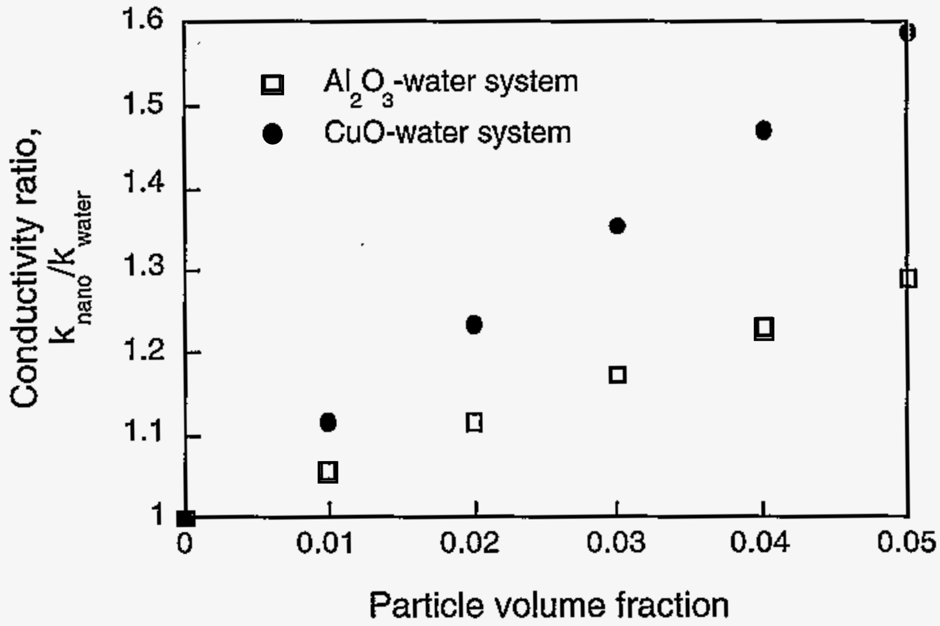
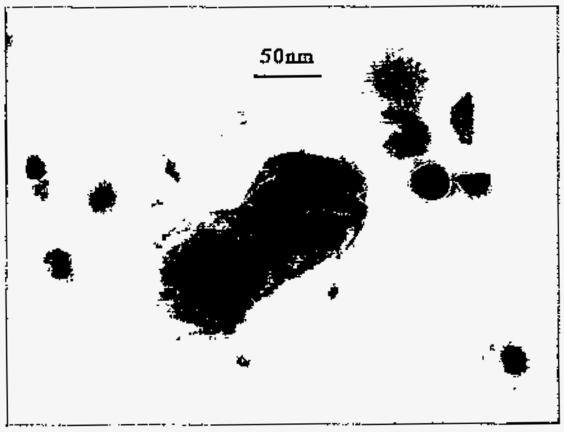
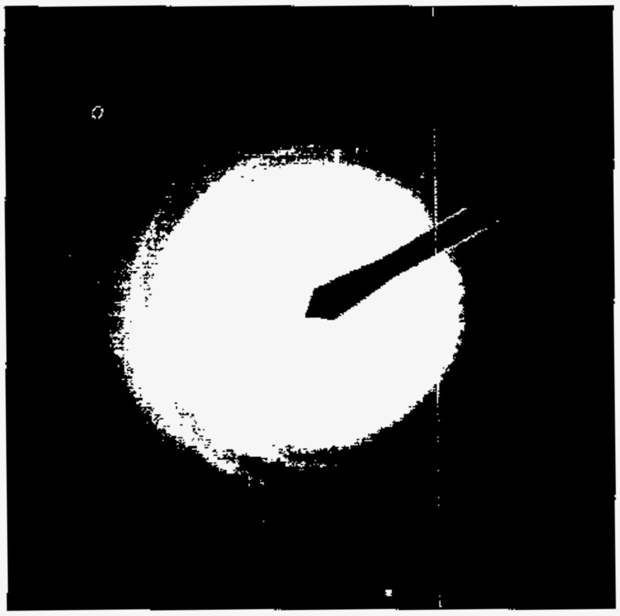


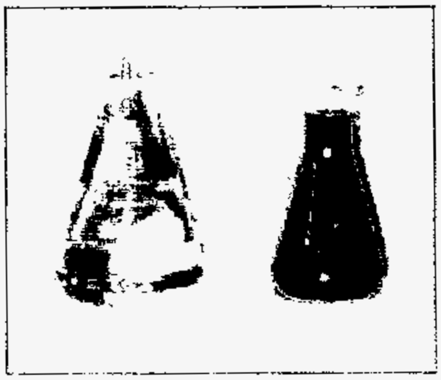
Figure 5. Dramatic improvements in the thermal conductivity of deionized water are observed with increasing volume fraction of dispersed copper oxide or alumina nanoparticles.



(a)



(b)



(c)

Figure 6. (a) Bright-field micrograph of nanocrystalline oil evaporated directly into low vapor pressure pump oil The electron diffraction pattern in (b) shows rings corresponding to the fcc Cu phase. (c) Oil prior to (left) and after evaporation of Cu (right).

micrograph of the resulting Cu nanoparticles is seen in Fig. 6(a). The average particle size in this case is on the order of 35 nm and the particles are quite round with minimal agglomeration. Most importantly, electron diffraction patterns (Fig. 6(b)) reveal that the resulting particles are fcc Cu. Thus, direct evaporation not only results in the formation of a nanofluid with stable suspension properties as seen in Fig. 6(c), but also retains the higher conductivity metallic phase even after subsequent exposure of the fluid to air.

The thermal conductivity behavior of nanofluids formed by direct evaporation of Cu into two types of pump oil are seen in Fig. 7. Particularly for the HE-200 oil, which is a high purity oil designed for use in pumps such as Roots blowers [8], significant enhancements in thermal conductivity are again obtained. Most importantly, in this case the enhancements are obtained with the addition of less than 0.1 volume % particles (i.e. more than a factor of 50 less material than required to produce a similar enhancement in the CuO/H_2O nanofluid system shown in Fig. 5). Further experiments are required to determine if even larger enhancements in thermal

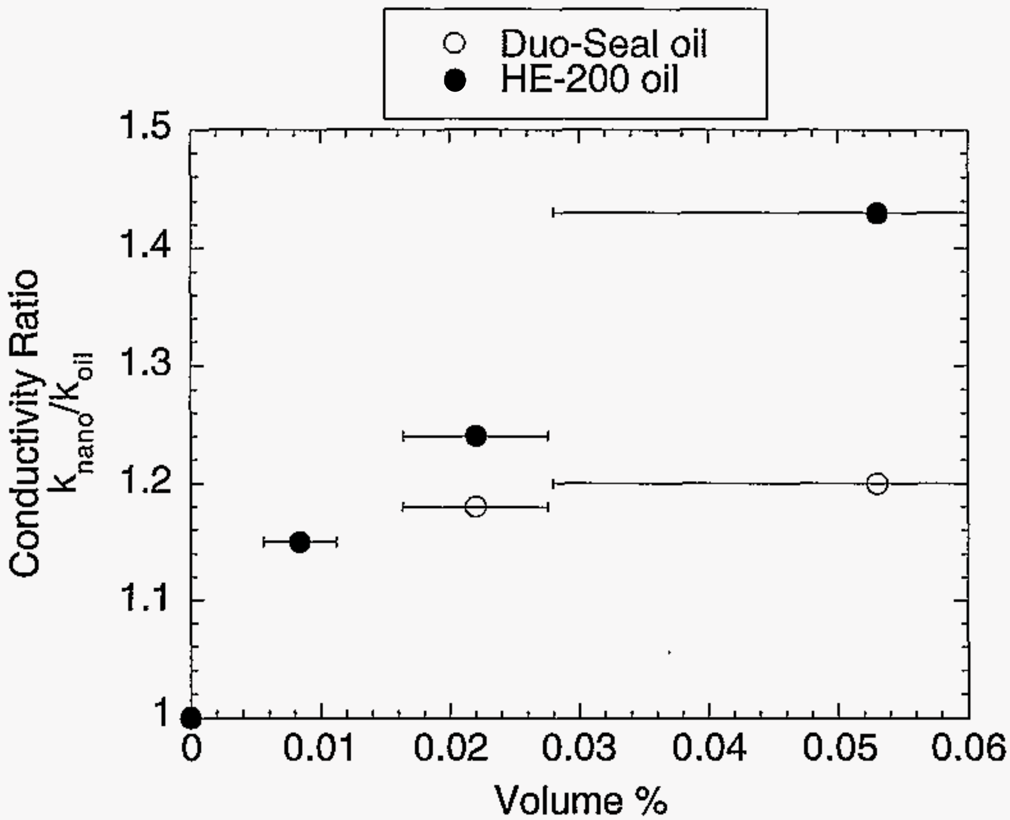


Figure 7. Thermal conductivity of Cu dispersed in oil. Note that similar substantial enhancements in thermal conductivity are seen compared to the oxide-in-water systems shown in Figure 5. However, in the case of Cu-in-oil, this improved behavior is obtained with almost two orders of magnitude less dispersed nanocrystalline powder.

conductivity can be obtained with larger concentrations of Cu nanoparticles. The large enhancement in thermal conductivity with a very small concentration of Cu particles seen in Fig. 7 is also significant because the concentration of particles is small enough that negligible changes in fluid viscosity will accompany the improved thermal behavior.

CONCLUSIONS

These preliminary results demonstrate the feasibility of significantly improving the heat transfer performance of commercial heating and cooling fluids such as water or oil by suspending nanocrystalline particles in the liquid to produce nanofluids. In the case of oxide nanoparticles suspended in water, increases in thermal conductivity of approximately 60% can be obtained with 5 volume % particles. The use of Cu nanoparticles results in even larger improvements in thermal conductivity behavior, with very small concentrations of particles producing major increases in the thermal conductivity of oil.

Further work remains to demonstrate the full potential of nanofluids. In addition to determining if additional improvements in conductivity can be obtained through the suspension of larger volume fractions of Cu particles in oil, numerous other experiments are required to determine other important properties of nanofluids. These include determining the effects of nanoparticle suspensions on the flow, corrosive, and abrasive properties of fluids.

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REFERENCES

1. J.C. Maxwell, A Treatise on Electricity and Magnetism, 2nd Ed., **1**, 435, Clarendon Press (1881).
2. R.L. Hamilton and O.K. Crosser, *I and EC Fundamentals*, **1**, no. 3, 187 (1962).
3. U.S. Choi, in Developments and Applications of Non-Newtonian Flows, eds. D.A. Siginer and H.P. Wang, (American Society of Mechanical Engineers: New York), Vol. 231/MD-Vol. 66, 99 (1995).
4. C. G. Granqvist and R.A. Buhrman, *J. Appl. Phys.*, **47**, 2200 (1976).
5. Nanophase Technologies Corporation , Burr Ridge, IL
6. S. Yatsuya, Y. Tsukasaki, K. Mihama, and R. Uyeda, *J. Cryst. Growth*, **43**, 490 (1978).
7. M. Wagener and B. Günther, these proceedings.
8. HE-200, produced by Leybold-Heraeus Vacuum Products Inc., Export, PA
   Duo-Seal #1407K-11, produced by Welch Vacuum Technology Inc., Skokie, IL.
9. J.A. Eastman, L.J. Thompson, and D.J. Marshall, *Nanostruct. Mater.* **2**, 377 (1993).