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On Synthesis and Characterization of Water Based Cu_9Al_4-Nanofluid

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Nanosized particles of Cu_9Al_4 intermetallic phase, which is hard (HV 403) and can thus be easily reduced to sizes as low as 20–90 nm, have been synthesized by mechanical alloying of elemental powder blend of Cu and Al. It is then evenly dispersed in water to produce the nanofluids. Thermal conductivity of the nanofluids measured by the conventional transient hot-wire method shows significant enhancement compared to that of water. The enhancement increases linearly with low volume fraction loading of nanoparticles. The experimental data on thermal conductivity of the present nanofluid manifests reasonable agreement with the theoretical predictions.

Keywords: Nanofluid, Thermal Conductivity, Enhancement.

Nanofluid, i.e., fluid containing nanoparticles suspended in it, has attractive prospect in the heat transfer applications, because its thermal conductivity can be remarkably higher than that of the base fluid.[1] Experimental investigations have revealed that the enhancement in thermal conductivity of nanofluids depends on the type of nanoparticle and base fluid,[2] volume fraction of nanoparticles,[2] temperature of the liquid medium,[3] size of the nanoparticles,[4] etc. Eastman et al.[5] have measured the thermal conductivity of ethylene glycol (EG) based nanofluids containing Cu particles of mean diameter <10 nm. They have found 40% enhancement in thermal conductivity over that of the base fluid for a loading of 0.3 vol.% Cu nanoparticles. Conventional continuum models, such as Maxwell model,[6] Hamilton and Crosser model,[7] etc., which are based on the effective medium approximation, cannot account for the enhanced thermal conductivity of nanofluids containing well dispersed nanoparticles. Keblinski et al.[8] have explored four possible mechanisms contributing to the enhanced thermal conductivity of nanofluids, namely, Brownian motion of nanoparticles, ordered layering of liquid molecules at the liquid/particle interface, ballistic nature of heat transport in nanoparticles, and nanoparticle clustering effect. However, none of these mechanisms could provide a complete rational explanation for the enhanced thermal conductivity of nanofluids. Several other investigators have developed models of thermal conductivity of nanofluids based on different mechanisms.[9–12] However, a consensus among them is yet to emerge.

Recently, Ghosh et al.[13] have developed a coupled molecular dynamics (MD)-stochastic model on thermal conductivity of water based Cu-nanofluid. The model is based on the fact that evenly dispersed nanoparticles in the nanofluid undergo Brownian motion and collide with the heat source repeatedly with an average frequency, which depends on the Brownian motion parameters. MD simulation shows that during each collision a substantial amount of heat is transferred to the nanoparticle from the heat source within a very short period of a few ps. The combined model yields the characteristic thermal history of nanoparticles in the nanofluid, on the basis of which the thermal conductivity enhancement for a given volume fraction of nanoparticle loading has been estimated.

It is known that copper based intermetallic phase Cu_9Al_4 can be easily synthesized and reduced to nanostructured powder by mechanical alloying[14] (MA) because of the very high hardness (HV 403) of this intermetallic. However, MD simulation of collision of Cu_9Al_4 nanoparticles with the heat source is not practicable due to the non-availability of interatomic potentials in the literature. In the present study, Cu_9Al_4 nanoparticles are first synthesized by MA, then characterized and evenly dispersed in water to produce a nanofluid. The thermal conductivity of the nanofluid measured by transient hot-wire method has been compared with the predictions of the model of Ghosh et al.[13] for the thermal conductivity of water based Cu-nanofluid.

A two-step method has been employed to produce water based Cu_9Al_4 nanofluids. In the first step, nanostructured Cu_9Al_4 particles have been synthesized by high energy ball milling of the elemental powder blend of Cu

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(purity >99.9%) and Al (purity >99.7%) of requisite proportion in a planetary ball mill (Fritsch Pulverisette 5) at a mill speed of 300 rpm using WC grinding media and toluene as the process control agent. The ball to powder ratio was maintained 10:1. The milling has been carried out up to 30 h. The crystallite size and identity of phase(s) of the milled powder have been characterized by a Philips X'pert Pro high resolution X-ray diffractometer. Crystallite size of the Cu-rich phase at different instances of milling has been determined from the X-ray diffraction (XRD) patterns by Williamson-Hall method,[15] which permits elimination of instrumental broadening and microstrain. In order to obtain the chemical composition of the mechanically alloyed Cu_9Al_4 particles, energy dispersive spectroscopic (EDS) analysis has been performed. The size of the dispersed nanoparticles has been verified by a JEOL JEM 2100 transmission electron microscope (TEM).

In the second step, the as-milled nanopowder has been dispersed in distilled water by means of programmed ultrasonic vibration using sodium dodecyl sulfate (SDS) as surfactant. Nanofluids containing different volume fraction of nanoparticles have been produced by this method.

The viscosity of the nanofluids has been measured by Bohlin CVO Rheometer D 100. The schematic diagram of the transient hot-wire set up used in the present experiments for measuring the thermal conductivity of nanofluids has been given in Figure 1. It is basically a Wheatstone bridge circuit, where R_1, R_2, and R_3 are three precision resistances of 3.9 Ω. R_w is the resistance of a coated platinum wire suspended vertically in the liquid, whose thermal conductivity is to be measured. The platinum wire is 70 μm diameter and it serves as a line heat source as well as temperature sensor. V_s is a stable source voltage (6 V). When current is sent through the bridge circuit for a short duration (to avoid convection), the platinum wire gets progressively heated to a level dependent on the thermal conductivity of the surrounding liquid. The output voltage ΔV gives the temperature variation of the platinum wire with time of passing current, which in turn yields the thermal conductivity of the fluid. The transient hot-wire set up has been calibrated using the liquids of known thermal conductivity, namely, distilled water, high purity ethylene glycol, methanol and toluene The error in measurement was found to be <1%.

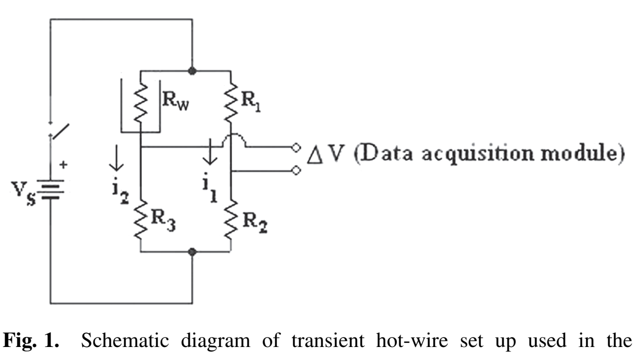

Fig. 1. Schematic diagram of transient hot-wire set up used in the present experiments to measure the thermal conductivity of nanofluids.

The XRD patterns of the mechanically alloyed powder blend of nominal composition $Cu_{69.2}Al_{30.8}$ at different instances of milling up to 30 h are displayed in Figure 2. It is found that the peaks of Al disappear within 10 h of milling, and thereafter peaks of the intermetallic phase Cu_9Al_4 become visible. The Cu_9Al_4 phase remains stable up to 30 h of milling. Analysis of the XRD spectrum of 30 h milled sample has yielded the average crystallite size of the milled product (Cu_9Al_4) as 9 nm, and such a refinement of the crystallite size by ball milling can be attributed to the high hardness of Cu_9Al_4 (HV 403). Figure 3 shows the EDS pattern of the mechanically alloyed product. The chemical composition obtained from the EDS analysis is shown in Table I. It is evident that the mechanically alloyed product has a composition quite close to that of the Cu_9Al_4 intermetallic phase.

The TEM image in Figure 4 shows the particle size and morphology of the Cu_9Al_4 nanoparticles dispersed in distilled water. It shows that the particles are isolated, equiaxed in shape, and their size is in the range of 20–90 nm. The data of average crystallite size of the milled product (9 nm) and the range of particle size (20–90 nm) indicate that most of the as-milled Cu_9Al_4 nanoparticles are polycrystalline.

The thermal conductivity of water based Cu_9Al_4-nanofluids measured in the present experiments has shown a significant enhancement compared to that of the base fluid (water). Figure 5 shows the extent of this enhancement for the water based Cu_9Al_4-nanofluids observed experimentally as a function of the volume fraction loading of nanoparticles. It is to be noted that all the thermal conductivity data reported here have been measured within 5 minutes of synthesis of each nanofluids. The enhancement in thermal conductivity for the water Cu-nanofluid

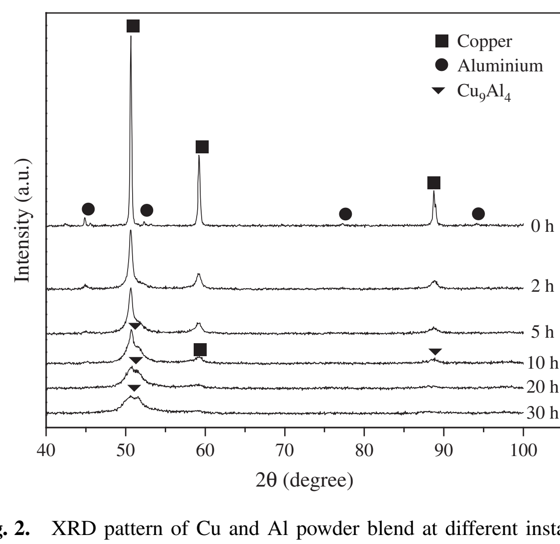

Fig. 2. XRD pattern of Cu and Al powder blend at different instances of milling (Radiation Co-K_α).

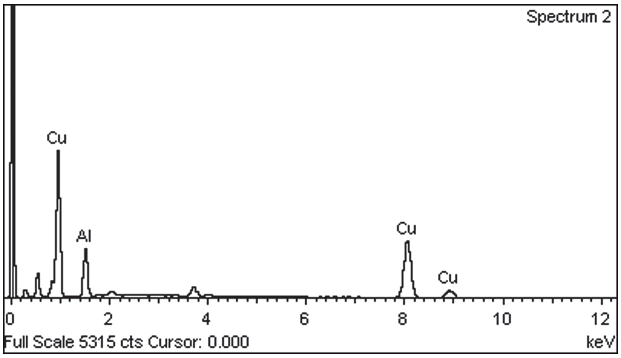

Fig. 3. EDS pattern of the mechanically alloyed product.

predicted by the model of Ghosh et al.[13] as a function of the volume fraction of Cu nanoparticles in water has also been superimposed in Figure 5. It is apparent that the theoretically predicted enhancement in thermal conductivity increases linearly with the volume fraction of nanoparticles. The same type of linear variation in the enhancement is manifested by the present experimental data as well. However, it is found that for a given volume percent of loading (<0.3%), the theoretically estimated enhancement in thermal conductivity is about 20% more than experimentally determined value for water based Cu_9Al_4 nanofluid. This deviation partly arises due to the fact that the size of nanoparticles considered in the model of Ghosh et al.[13] (4 nm) is much smaller than the experimentally prevailing size of Cu_9Al_4 nanoparticles (20–90 nm). The thermal conductivity data for the Cu_9Al_4 intermetallic is not available in the literature. But the available data for the copper based intermetallics of other compositions show that they have conductivity less than that of pure Cu.[16] Hence, when a copper based nanosized intermetallic is dispersed in water, the resultant nanofluid is likely to show lower thermal conductivity compared to that of water based Cu nanofluid. Thus, the present experimental data is in reasonable agreement with the prediction of the model of Ghosh et al.[13] The empirical correlation of the percentage of enhancement in thermal conductivity (E) manifested by present experimental data with the volume% of Cu_9Al_4 nanoparticle loading in water (φ) can be expressed as

$$E = 161.9\varphi \tag{1}$$

Figure 5 also shows the experimental data of Eastman et al.[5] for EG based Cu nanofluid. It is apparent that the enhancement in thermal conductivity of EG based Cu

Table I. Chemical composition obtained by EDS analysis of mechanically alloyed Cu_9Al_4 intermetallic phase.

Element	Weight %	Atomic %
Al	18.25	34.45
Cu	81.75	65.55

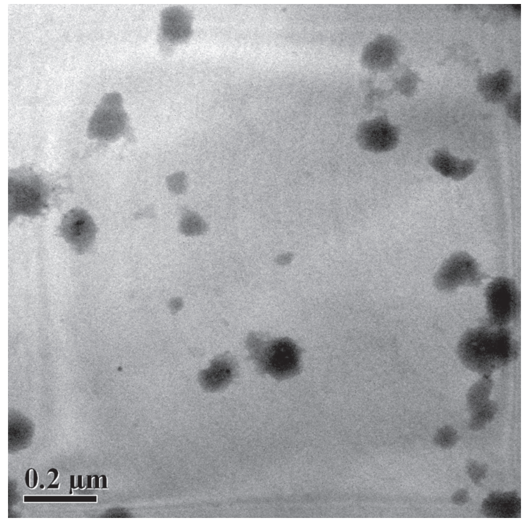

Fig. 4. TEM image of Cu_9Al_4 nanoparticles dispersed in water.

nanofluid produced by Eastman et al.[5] is almost comparable to the water based Cu_9Al_4 nanofluid produced in the present experiment, although the particle size of the former nanofluid (<10 nm) is less than that prevailing in the latter one (20–90 nm). This apparent controversy can be explained on the basis of the model developed by Ghosh et al.,[13] which considers that collision of nanoparticles suspended in a nanofluid with the heat source has profound influence on thermal conductivity of the nanofluid. The viscosity of EG is more than that of water. This would lead to lower frequency of collision of the nanoparticles dispersed in EG with the heat source as compared to that dispersed in water. Due to the opposing effects of the lower size of dispersed particles and higher viscosity of base fluid, the enhancement in thermal conductivity of EG based Cu nanofluid produced by Eastman et al.[5] has possibly become comparable to that of water based Cu_9Al_4 nanofluid produced in the present experiments.

The variation of the enhanced thermal conductivity with the volume fraction of evenly dispersed Cu nanoparticles in water medium, as predicted by the classical Maxwell's model[6] for evenly dispersed nanoparticles has also been shown in Figure 5. It is evident that the predictions based on the Maxwell's model lie far below the experimental data, and therefore, it cannot account for the conductivity of present Cu_9Al_4 nanofluid.

In Figure 5, the variation of experimentally measured viscosity of the present nanofluids with volume% of nanoparticles loading has also been superimposed. It shows only marginal increase in the viscosity, which seems to have insignificant effect on the thermal conductivity, as evidenced by the linear variation of the enhancement in thermal conductivity with loading of nanoparticles. The marginal increase in viscosity of the present nanofluids occurs due to the very small% of nanoparticles loading (<0.35 vol.%).

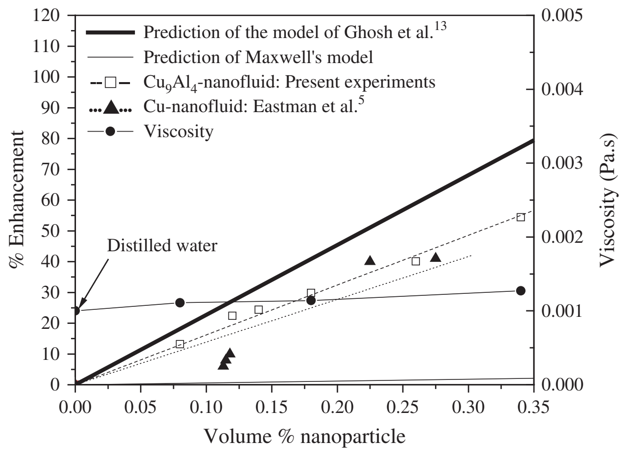

Fig. 5. Enhancement in thermal conductivity of water based nanofluid with volume fraction of Cu nanoparticles as per the prediction of the model of Ghosh et al.[13] (thick line) compared with the present experimental data for water based Cu_9Al_4 nanofluid (- -□- -) and the experimental data for EG based Cu nanofluid produced by Eastman et al.[5] (···▲···). The viscosity data (— • —) have been superimposed in the plot.

In order to assess the stability of the present nanofluids, the variation of their thermal conductivity under stagnant condition with the storage time from the instant of their synthesis has been measured. It showed that after a small initial fall ($<20\%$) within 30 min from the time of its synthesis, the thermal conductivity of the nanofluid remains almost unchanged during prolong holding up to 8 h. The initial fall in thermal conductivity is attributed to settling of relatively coarser nanoparticles. This indicates that the present nanofluid remains stable for more than 8 h under stagnant condition.

In summary, water based Cu_9Al_4-nanofluid has been synthesized and characterized. The experimental data shows a significant enhancement in thermal conductivity of the nanofluid compared to that of water, and the enhancement increases linearly with the volume fraction of nanoparticles. More than 50% enhancement in the thermal conductivity was obtained by loading only $\sim$0.34 vol.% Cu_9Al_4 nanoparticles in water. The measured values of thermal conductivity are in reasonable agreement with those theoretically predicted.

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