PRODUCTION AND STABILITY OF Al AND Cu ULTRAFINE PARTICLES IN NANOFLUIDS

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Abstract

In this paper, a two step approach of synthesis of Al and Cu ultrafine particles by mechanical alloying and then dispersing them in base fluid to prepare nanofluid has been reported. Ultrafine powders were prepared by milling elemental Al and Cu powders for 50 h in a planetary mill. After 50 h of milling, particles size has been reduced to 500nm for Al and 400 nm for Cu. It is also found from transmission electron microscopy (TEM) that each particles consists of large number of crystallites of size around 10-15 nm. Aiming at the dispersion of nano-Al and Cu is regarded as the guide of heat transfer enhancement, the stability of Al and Cu particles in water were studied under different pH values. It has been found from Nanozeta meter that Al suspension is stable at pH 2.5 and 9.5, whereas Cu suspension is stable at pH 2.3 and 9.8.

Introduction

Nanofluid is a stable colloidal suspension of low volume fraction of ultrafine solid particles in nanometric dimension dispersed in conventional heat transfer fluid. The concept of nanofluid was first coined by S.U.S Choi [1] for heat transfer application [1,2]. Since thermal conductivity of solids is orders of magnitude greater than that of liquids, dispersion of solid particles in a given fluid is bound to increase its thermal conductivity. The dispersion of a low volume (<1%) fraction of solid nanoparticles in traditional base fluid drastically increases the thermal conductivity than that of base fluid [3,4]. The enhancement of thermal conductivity of nanofluid over conventional base fluid like de-ionized water, ethylene glycol etc. has several applications starting from closely packed integrated circuits at small scale industry to nuclear reactor at large scale. However, dispersion of milli- and micro- meter-sized particles is prone to sedimentation, clogging and erosion of pipes and channels.

There are two techniques for production of Nanofluids; (i) the one step direct evaporation method represents the direct formation of the nanoparticles in the base fluid; and (ii) the two step method represents the formation of nanoparticles and subsequent dispersion of the nanoparticles in the base fluid. In either of the case, the production of a uniformly dispersed nanofluid is very necessary for obtaining stable and superior properties of nanofluids [5,6].

A two step approach has been adopted here to prepare nanofluids. Several techniques have been developed to synthesize nanoparticles such as Laser ablation, Inert gas condensation (IGC), mechanical attrition, mechanical alloying etc [7]. Here the ultrafine particles were prepared by mechanical alloying (MA) with the help of a Fritsch pulverisette-5 planetary ball mill. High energy ball induces high energy impact on the charged powder by collision between balls and powder causing severe plastic deformation, repeated fracturing and cold welding of charged powder leading to the formation of nanoparticles [8,9]. The prepared nanoparticles were dispersed in de-ionized water by ultrasonic probe and magnetic stirrer to prepare desired nanofluid. Although many experimental studies on nanofluid systems have been performed, the preparation methods for stable nanofluid were not systematically studied yet. In earlier study, stability of carbon black based nanofluid was studied by Kim *et al* [10]. In this paper, the primary objectives are to synthesize elemental nanoparticles (Al, Cu) and preparation of stable dispersion of particles in nanofluid to develop heat transfer fluids.

Experimental

Milling was carried out in Pulverisette-5 planetary ball mill with steel vials and steel balls. Starting materials used for milling were elemental Al and Cu powders with 99% purity. The ball to powder weight ratio (BPR) was 10:1. Milling was conducted at 300 rpm in wet medium (about 50 ml of toluene) to prevent undue oxidation and agglomeration of powder. Powder particles were milled for 50 h in two vials- each containing 35 g powder and 350 g steel balls. Steel balls of diameter 10 mm were used for milling. Powder samples were picked up from the vials after selected interval of milling time to see the change in shape and size reduction of powder samples. Powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

A very small amount of milled powders (approximately 0.04g) were dispersed in de-ionized water (150 ml) by ultrasonication and subsequently magnetic stirring for about 30 minute each to prepare the desired nanofluid. The pH was controlled using acetic acid and ammonium hydroxide. The prepared nanofluids were analyzed by Nano zeta meter to determine the particle size and zeta potential and study the stability of nanofluids at a particular pH value.

Results and Discussion

The morphology and size of initial elemental metallic powders were investigated with the help of scanning electron microscopy (SEM). Figure 1 shows the SEM micrographs of the powder of

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reacting materials are bulky with random shape and size at the initial stage of milling. The average size of initial powders is ~ 28 μm.
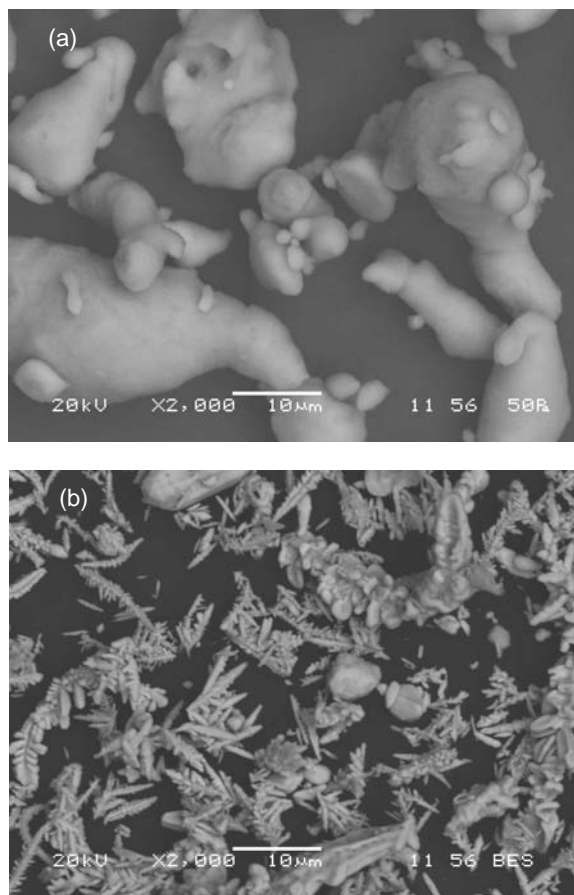

Figure 1. SEM micrographs of elemental metallic powders:
(a) Al; (b) Cu

X-Ray Diffraction (XRD)

The XRD patterns of elemental metallic powder particles after different intervals of milling time are shown in Fig. 2. The final milling product is a single phase nanocrystalline material. It is evident from the figure that the Bragg peaks for milled product (after 50 h of milling) are broad, suggesting accumulation of lattice strain and reduction in crystallite size. These two individual contributions to broadening have been analyzed in the next section.

Crystallite Size and Lattice Strain

The crystallite size can be investigated by analyzing the X-ray diffraction patterns. For this purpose, as received and milled powders were analyzed using X-ray diffraction (XRD) methods with CuK_α radiation. The XRD peak broadening was used to measure the crystallite size and lattice strain. The Phillips Expert High score software has been used here to calculate the crystallite size and lattice strain.
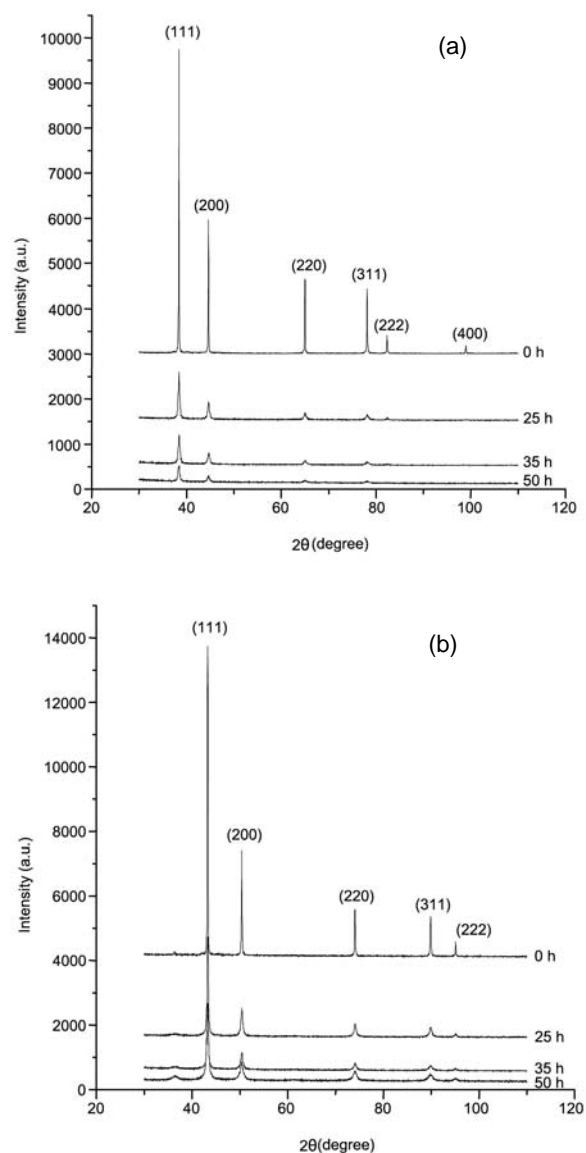

Figure 2. XRD patterns of milled powder at selected milling time: (a) Al; (b) Cu

The decrease of the grain size and lattice strain to characterize the activation process has been determined from the X-ray diffraction patterns. Although the accumulation of lattice strain is a measure of defect formation, determining the defect structure was found to be more difficult. The crystallite size and the lattice strain of the powder, measured from the XRD peak broadening, are shown as a function of milling time in Fig. 3. It can be seen that the crystallite size decreases and internal strain increases rapidly with milling time up to about 25 h. With further milling the crystallite size remains almost constant up to 35 h and then increases slightly up to 50 h, but the lattice strain appears to increase. It is found that the crystallite size has been reduced from 72 nm to 31 nm for both cases. The lattice strain is increased from 0.1196 to 0.372% for Al and 0.1116 to 0.293% for Cu.
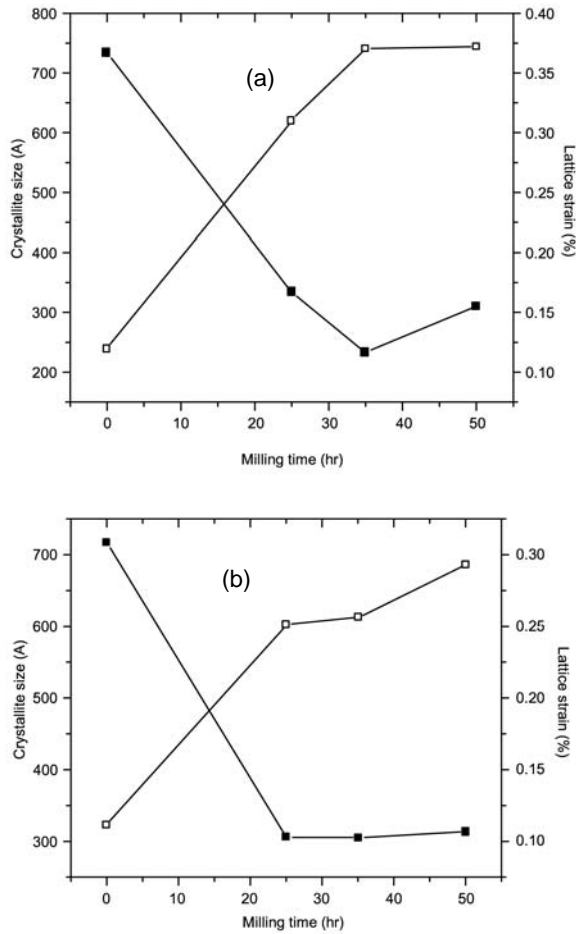
Figure 3. Crystallite size and Lattice strain of the milled powder calculated from XRD patterns Vs milling time: (a) Al; (b) Cu
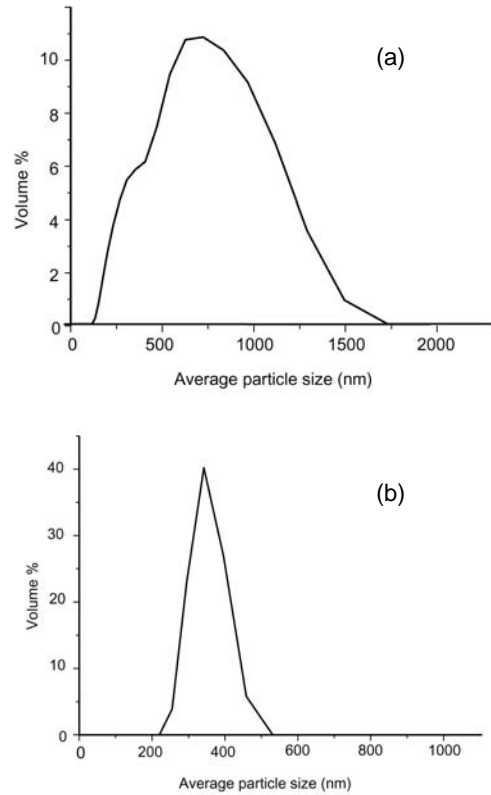

Figure 4. Variation of volume % of the deionized water-based elemental metallic powders nanofluids as a function of the average particle size: (a) Al; (b) Cu

Particle Size Analysis

Particle size of the milled powder was measured by nano particle size analyzer. Particle size of the milled powder is shown in Fig. 4. It is evident from the figure that particle size is reduced from initial size 28 μm to 500 nm for Al and 28 μm to 400 nm for Cu.

Transmission Electron Microscopy (TEM)

The sample for TEM was prepared by adding a pinch of milled elemental metallic powder particles in the beaker containing acetone and kept in an ultrasonic bath for about 15 min to get uniform dispersion of powder particles in the liquid. After that 2 drops of fluid containing dispersed particles were added in carbon coated Cu-grid and then dried. The desired sample was fixed in the sample holder of TEM for analyzing the internal structure of mechanically alloyed powder. Figure 5 shows the bright field TEM micrograph and corresponding selected area diffraction (SAD) pattern of both the powders after 50 h of milling. It is evident from the figure that the particle size is around 300 nm and contains large number of crystallites (size around 15-20 nm) with difference in contrast due to the variation of orientation.
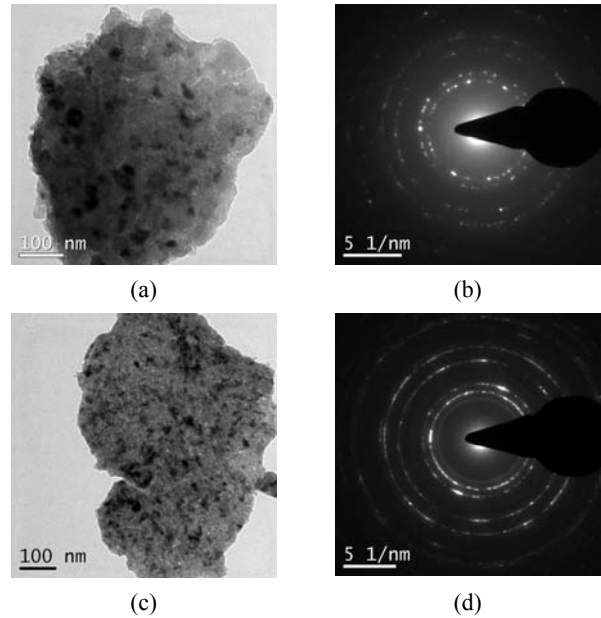

Figure 5. Bright Field TEM micrograph and corresponding SAD pattern: (a) (b) Al; (c) (d) Cu

Stability of Nanofluids

The stability of Nanofluid was determined by measuring zeta potential values of elemental metallic powder dispersed in deionized water. However, for measurement of zeta potential, dilute fraction of metallic nano-suspension was selected here. The values of zeta potential ζ can be calculated by the Helmholtz-Smoluchowski equation :

$$\zeta = \mu\left(U/\varepsilon\right)$$

where U is the electrophoretic mobility, and μ, ε are the viscosity and the dielectric constant of the liquid in the boundary respectively.

In case of Cu powder particles, the zeta potential is zero at pH= 5.1, which is isoelectric point as shown in Fig.6.
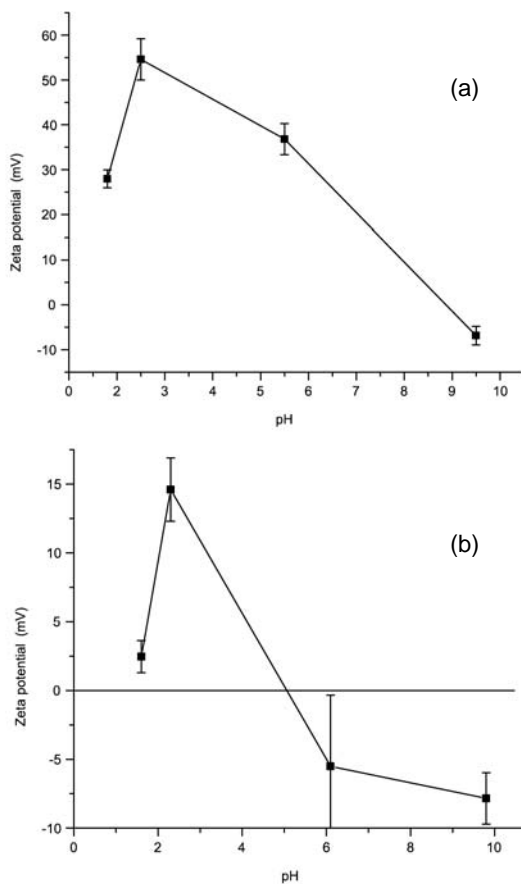

Figure 6. The evolution of zeta potentials of the deionized water-based elemental metallic powder nanofluids as a function of pH without surfactants : (a) Al; (b) Cu

Therefore, the force of electrostatic repulsion between particles is not sufficient to overcome the attraction force between particles and hence the dispersion is least stable. As pH increases or decreases by adding ammonium hydroxide (NH$_4$OH) or acetic acid respectively, then the particles tend to acquire more charge. So, the electrostatic repulsion force between particles becomes sufficient to prevent attraction and collision between particles

caused by Brownian motion. Greater electrostatic force can also lead to more free particles by increasing particle-particle distance so that the distance exceeds the hydrogen bonding range between particles and further reduces the probability of particle coagulation and settling and hence, improving the dispersion stability of copper (Cu).

At pH = 9.8 and 2.3, the zeta potential becomes higher; the electrostatic repulsion force between particles is stronger, and the coagulated particles can redisperse through mechanical force. Therefore, the dispersion stability of copper (Cu) is best at pH = 9.8 and 2.3. If pH-value is more than 9.8 or less than 2.3, then the zeta potential of particle surface and electrostatic repulsion force decreases due to compression of electrical double layer. Therefore, the suspension exhibits a poorer dispersion.

Similarly, for Al powder particles, the zeta potential is zero at pH = 8.9 which is isoelectric point as shown in Fig.6 and hence the dispersion is least stable. With increasing pH value or decreasing pH value by adding reactant reagent, the stability tends to increase and therefore, a pH=2.5 and 9.5, the dispersion of Al is best. If pH-value is more than 9.5 or less than 2.5, then the zeta potential of particle surface and electrostatic repulsion force decreases due to compression of electrical double layer. Therefore, the suspension exhibits a poorer dispersion.

Conclusions

The following conclusions can be drawn from the present investigation:

1. It is possible to prepare ultrafine Al and Cu particles through mechanical alloying process by 50 h of planetary ball milling.

2. The crystallite size decreases and internal strain increases rapidly with milling time up to about 25 h. With further milling, the crystallite size remains almost constant up to 35 h and then increases slightly up to 50 h, but the lattice strain appears to increase. It is found from XRD that the crystallite size is around 31 nm for both and lattice strain is 0.37% and 0.29 % for Al and Cu, respectively.

3. The dispersion stability of Al and Cu nanoparticles in nanofluids is best at pH value of 2.5, 9.5 and 2.3, 9.8 corresponding to zeta potential value 54.63, -6.87 and 14.6, -7.84 respectively.

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