Synthesis and thermal stability of Cu-(2.5-10)vol.%\text{Al}_2\text{O}_3 nanocomposite powders by high energy mechanical milling

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Abstract. High energy mechanical milling (HEMM) of a mixture of Cu powder and \text{Al}_2\text{O}_3 nanopowder has been used to produce Cu-(2.5-10)vol.%\text{Al}_2\text{O}_3 nanocomposite powders with a ultrafine grained or nanocrystalline Cu matrix. The microstructure and microhardness of the as-milled powder particles and the thermal stability and microhardness change of the nanocomposite powder particles caused by annealing at temperatures up to 500°C have been studied. It is shown that HEMM can be effectively used to disperse (2.5-10)vol.% \text{Al}_2\text{O}_3 nanoparticles into a ultrafine grained or nanocrystalline Cu matrix. Using larger diameter balls or increasing the volume fraction of \text{Al}_2\text{O}_3 nanoparticles to 7.5% or higher allows synthesis of Cu-\text{Al}_2\text{O}_3 nanocomposite powders with nanocrystalline Cu matrix. Refining the microstructure of the Cu matrix and increasing the volume fraction of \text{Al}_2\text{O}_3 nanoparticles in the nanocomposite both increase the thermal stability of the nanocomposite structure.

1. Introduction

Metal-ceramic nanocomposites are a class of materials which can be loosely defined as materials which consist of both metallic and ceramic phases and in the meantime have a structure comprising of one or more phase domains with at least one dimension being smaller than 100nm. The motivation behind synthesising metal-ceramic nanocomposites properties lies in the fact that the metallic phases and ceramic phases posses very different mechanical, physical and chemical properties, and a combination of those very different properties may lead to highly desirable materials properties including high strength, good ductility, electrical conductivity and unique magnetica properties. There are two ways of synthesising metal matrix nanocomposites: (a) in-situ formation of nanoparticles in a matrix through chemical reactions or phase transformations [e.g.1-3]; and (b) dispersion of nanoparticles in a matrix through mechanical mixing in solid or liquid state or selective fracturing of secondary particles through mechanical means [e.g. 4-8]. As one of the processes belong to category (b), high energy mechanical milling (HEMM) is widely used to synthesise metal matrix or ceramic matrix nanocomposites. The principle underlying the effectiveness of HEMM in synthesizing metal matrix nanocomposite powders involves: (i) mechanical mixing of powder particles of different compositions; (ii) incorporating nanoparticles into the metal matrix through plastic deformation, fracturing and cold welding of the metallic powder particles and breaking of agglomerates of nanoparticles; (iii) uniformly dispersing ceramic nanoparticles in the metal matrix in each of the powder particles again through randomly moving the nanoparticles by plastic deformation, fracturing and cold welding of the metal matrix composite powder particles. In this study, HEMM was used to
synthesize Cu matrix nanocomposite powder with a dispersion of (2.5-10)vol.% Al$_2$O$_3$ nanoparticles. The microstructure of the nanocomposite powder particles and its thermal stability as a function of annealing temperature was studied in detail to understand the morphological and microstructural evolution mechanisms of the powder particles during HEMM and to determine the effect of various factors on the thermal stability. As additional information for the understanding, microhardness of the powder particles processed under different conditions was also measured.

2. Experimental technique
The starting powders are powders of Cu (99.5% pure; particle size<63µm) and Al$_2$O$_3$ (99.9% pure; average particle size~50nm). A hardened steel vial, stainless steel balls and a Restch PM4000 planetary ball mill with a rotational speed of 400 rpm were used for the milling. The vial containing the balls and 100g of powder mixture was sealed in a glove box filled with high purity argon. Two milling routes were used: in Route 1, the powder mixture was milled for 12 hours using 60 balls with a diameter of 12.5mm; and Route 2 was Route 1 plus further milling for 12 hours using 12 balls with a diameter of 12.5mm and 6 balls with a diameter of 25mm. In both routes, the ball to powder weight ratio was 5:1. The samples of the milled powders were annealed for 1 hour at different temperatures in a tube furnace which has a vacuum of 10$^{-6}$ bar. The analyses and characterization of the samples were performed using X-ray diffractometry (XRD) scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectrometry (EDX) and microhardness testing.

3. Results and discussion

3.1 Microstructure
In using HEMM to produce Cu-(2.5-10)vol.%Al$_2$O$_3$ nanocomposite powders, one challenge comes from the high ductility of Cu powders which can lead to excessive cold-welding that in-turn causes formation of millimetre sized balls or lumps [9,10]. Once the millimetre sized balls or lumps are formed, further milling is not effective in refining the microstructure. Of course, process control agent (PCA) can be used to prevent the excessive cold welding of the powder particles, but in this study, this is avoided as much as possible due to the concern of material contamination (PCA). This study has shown that HEMM of a mixture of Cu powder and Al$_2$O$_3$ powder using route 1 led to formation of either millimetre sized hollow balls or lumps when the volume fraction of Al$_2$O$_3$ was 2.5-5% (Figure 1). When the volume fraction of Al$_2$O$_3$ was 7.5% or 10%, powders with coarse particles were produced. In order to produce Cu-(2.5-10%)Al$_2$O$_3$ nanocomposite powders with fine particles, Route 2 milling was used. The higher kinetic energy of the larger diameter balls allow crushing of the millimetre sized Cu-Al$_2$O$_3$ nanocomposite balls or lumps and coarse particles to form fine particles and facilitate continued cycles of plastic deformation, fracturing and cold-welding, leading to further refinement of matrix microstructure and improve the dispersion of the Al$_2$O$_3$ nanoparticles in the matrix.

Figure 1. Cross section morphologies of Cu-Al$_2$O$_3$ nanocomposite balls/lumps produced by HEMM using route 1: (a) Cu-2.5vol.%Al$_2$O$_3$ milled for 6 hours; (b) Cu-2.5vol.%Al$_2$O$_3$ milled for 12 hours; (c) Cu-5vol.%Al$_2$O$_3$ milled for 6 hours; (d) Cu-5vol.%Al$_2$O$_3$ milled for 12 hours.
Dispersion of Al$_2$O$_3$ nanoparticles uniformly throughout the Cu matrix of each individual powder particle is a major task of the HEMM process in producing Cu-Al$_2$O$_3$ nanocomposite powders. This study has shown that with 5vol.%Al$_2$O$_3$, almost uniform dispersion of Al$_2$O$_3$ nanoparticles in the Cu matrix is achieved with a relatively short time of 6 hours of milling, as shown by the STEM image and X-ray elemental mapping for Al of the 6 hour milled powder particle (Figures 2(a) and (b)). Increasing the milling time to 12 hours causes little change in terms of the dispersion of the Al$_2$O$_3$ nanoparticles (Figure 2(c) and (d)). In the STEM images shown in Figure 2, the bright particles are Al$_2$O$_3$ nanoparticles as confirmed from the X-ray elemental mapping for Al. It appeared that in the powder particles produced with a short milling time of 6 hours, the Al$_2$O$_3$ nanoparticles are predominantly distributed along the grain boundaries, while in the powder particles produced with a short milling time of 12 hours, a large fraction of the Al$_2$O$_3$ nanoparticles are distributed inside the grains. For Cu-5vol.%Al$_2$O$_3$, with Route 1 milling of up to 12 hours, ultrafine grains with sizes in the range of 100-300nm formed due to the severe plastic deformation and recrystallisation during HEMM. The second 12 hours milling using larger balls in Route 2 caused significant refinement of the grains into the size range of 50-150nm, as shown in Figure 2(e).

Increasing the volume fraction of Al$_2$O$_3$ powder in the starting mixture of Cu and Al$_2$O$_3$ powders led to increased effectiveness of milling due to the lack of excessive cold welding which leads to formation of millimetre sized lumps or balls. This was confirmed by the observation of the formation of nanostructure of the Cu-7.5vol.%Al$_2$O$_3$ nanocomposite powder with nanocrystalline matrix as shown by the STEM image, X-ray elemental mapping for Al and TEM bright field image in Figure 3. From Figure 3, it can also be seen that the Al$_2$O$_3$ nanoparticles are uniformly distributed throughout the Cu matrix, and predominantly along the grain boundaries. For Cu-(7.5 and 10)vol.%Al$_2$O$_3$ nanocomposite powder particles produced by milling using Route 1 and Route 2 respectively, a small fraction of Al$_2$O$_3$ particles (~1vol.%) with sizes in the range of 100-500nm were also observed in most of the powder particles, as shown by the SEM backscattererred electron images in Figure 4(a) and (b). It appeared that with increasing the milling time and effectiveness through the use of Route 2 milling, the fraction of the larger sized Al$_2$O$_3$ particles remains almost unchanged, but their sizes became smaller. It would be an intriguing question if one asks how the Al$_2$O$_3$ nanoparticles are entrapped at the Cu matrix grain boundaries or inside grains during HEMM. The possible mechanisms may include: (a) the Al$_2$O$_3$ nanoparticles are trapped at the Cu matrix grain boundaries during their formation through cold welding; (b) the Al$_2$O$_3$ nanoparticles are swept across by the movement of grain boundaries during recrystallisation of the Cu matrix, leaving them inside the newly formed

![Figure 2](image-url). (a)-(d) STEM images and elemental X-ray mapping for Al of the microstructure of typical particles in Cu-5vol.%Al$_2$O$_3$ nanocomposite powders milled for different conditions: (a) and (b): milled for 6 hours; (c) and (d) milled for 12 hours; and (e) TEM bright field image of the microstructure of Cu-5vol.%Al$_2$O$_3$ nanocomposite powder particle milled for 24 hours.

![Figure 3](image-url). (a) STEM image, X-ray elemental mapping for Al and TEM bright field image of the microstructure of Cu-7.5vol.%Al$_2$O$_3$ nanocomposite powder particles milled for 12 hours.
grains; and (c) the Al<sub>2</sub>O<sub>3</sub> nanoparticles may be the result of Al<sup>3+</sup> and O<sup>2-</sup> diffusion through the Cu matrix and recombination to form Al<sub>2</sub>O<sub>3</sub> precipitates or clusters.

**Figure 3.** (a) STEM image; (b) Al elemental X-ray mapping; and (c) TEM bright field image of the microstructure of a Cu-7.5%Al<sub>2</sub>O<sub>3</sub> powder particle produced by milling for 12 hours.

**Figure 4.** SEM backscattered electron images of the cross section of Cu-7.5vol.%Al<sub>2</sub>O<sub>3</sub> nanocomposite powder particles produced by (a) Route 1 milling; (b) Route 2 milling; (c) and (d) Route 2 milling followed by annealing at 300 and 500°C respectively.

### 3.2. Thermal stability of the microstructure

To determine the optimum temperature for consolidation of the nanocomposite powders into fully dense or nearly fully dense and fully bonded bulk solid materials, it is important to study the thermal stability of the as-milled nanocomposite powder particles. In contrast of monolithic alloys, the microstructural stability of the nanocomposite with nanocrystalline metal matrix has three aspects: (a) the stability of the microstructure of the matrix; (b) the stability of the nanoparticles; and (c) the stability of the interface between the nanoparticles and the matrix. This study shows that for Cu-(7.5 and 10)vol.%Al<sub>2</sub>O<sub>3</sub> nanocomposite powders, the fraction of the Al<sub>2</sub>O<sub>3</sub> particles with sizes in the range of 100-500nm clearly increased after the as-milled powder particles produced with Route 2 was annealed at 300°C for 1 hour (Figure 4(c)). With increasing the annealing temperature to 500°C, a substantially higher amount of larger sized Al<sub>2</sub>O<sub>3</sub> particles appeared in the microstructure, as shown in Figure 4(d). This shows that coarsening of the Al<sub>2</sub>O<sub>3</sub> nanoparticles occurs during annealing at temperature in the range of 300-500°C, and the rate of the particle coarsening become quite dramatic at 500°C. This finding suggests that the Cu matrix nanocomposite should not be processed at 500°C or higher if the sizes of the Al<sub>2</sub>O<sub>3</sub> particles are to be kept smaller than 100nm in the bulk nanocomposite materials.

It was found that for Cu-5vol.%Al<sub>2</sub>O<sub>3</sub> nanocomposite powder produced with Route 1, annealing at 150 and 300°C, respectively, caused slight growth of the Cu grains (Figures 5(a) and (b)), but annealing at 500°C caused significant growth of the Cu grains. However, it appears that for Cu-5vol.%Al<sub>2</sub>O<sub>3</sub> nanocomposite powder produced with Route 2 milling, the thermal stability of the Cu matrix was much higher, with the grains only growing slightly (Figures 6(a)-(c)). The possible reason for this might be that with refinement of the grains of the Cu matrix caused by increased milling time and effectiveness, the Al<sub>2</sub>O<sub>3</sub> nanoparticles are more homogeneously distributed along the grain boundaries in the microstructure of the Cu matrix and thus are more effective in pinning the grain boundaries.
Figure 5. TEM bright field images of Cu-5vol.%Al$_2$O$_3$ nanocomposite powder particles milled for 12 hours, and then heat treated at different temperatures: (a) 150°C; (b) 300°C; and (c) 500°C.

Figure 6. TEM bright field images of Cu-5vol.%Al$_2$O$_3$ nanocomposite powder particles milled for 24 hours, and then heat treated at different temperatures: (a) 150°C; (b) 300°C; and (c) 500°C.

3.3 Microhardness

Figure 7 shows the average microhardness of the Cu-(2.5-10)vol.%Al$_2$O$_3$ nanocomposite powder particles produced by Route 1 and Route 2 milling as a function of annealing temperature. The microhardness of pure Cu powder particles produced by Route 2 milling was also plotted in the figure for comparison. For Cu-5vol.%Al$_2$O$_3$ nanocomposite powder, increasing the milling time and effectiveness from Route 1 to Route 2 caused a significant increase in the microhardness of the as-milled powder particles, from 225Hv to 270Hv. Surprisingly, for the same milling condition, increasing the fraction of Al$_2$O$_3$ from 2.5% to 5% caused some increase of the microhardness of the powder particles, but then with further increasing the volume fraction of Al$_2$O$_3$ nanoparticles, the average microhardness even slightly decreased. At this point, it is not clear what the reason is. Figure 7 shows that the microhardness of the Cu-2.5vol.%Al$_2$O$_3$ nanocomposite powder particles only slightly decreased with increasing annealing temperature to 300°C, but then decreased significantly when the annealing temperature was decreased from 300 to 400°C. With a volume fraction of Al$_2$O$_3$ of 5vol.% or higher, the microhardness of the powder particles only decreased slightly with increasing the annealing temperature to 400°C, and then the microhardness decreased sharply with increasing the annealing temperature to 500°C. It appears that the level of microhardness decrease increases with the volume fraction of the Al$_2$O$_3$ nanoparticles. In contrast of the Cu-Al$_2$O$_3$ nanocomposite powders, the microhardness of the 24 hours milled (Route 2) coarse Cu powder particles first increased drastically from 150Hv to 210Hv with annealing for 1 hour at 150°C, and then decreased with increasing the annealing temperature.

For metal matrix nanocomposite with an ultrafine grained or nanocrystalline metal matrix, contributions of the strengthening come from three sources: (i) grain boundary strengthening which can be estimated using the Hall-Petch relationship; (ii) nanoparticle strengthening due to Orowan looping and the higher Young's modulus of the ceramic nanoparticles; and (iii) increase of dislocation...
density in the grains due to thermal stress induced by the mismatch of matrix and ceramic nanoparticles and temperature change associated with cooling from processing temperature. The strengthening contribution from the third source may not be significant for metal matrix nanocomposite with a nanocrystalline matrix due to the difficulty of nucleating new dislocations in the matrix. Similarly, when the metal matrix has a nanocrystalline structure, whether strengthening from the nanoparticles is still significant is a question to be answered. TEM examination of the Cu-5vol.%Al$_2$O$_3$ nanocomposite powder produced with Route 2 milling of 24 hours shows that the Cu matrix grain sizes are in the range of 50-100nm. The Hall-Petch relationship of pure Cu established by Chen et al. [11] based on a large amount of data for the hardness of Cu of a wide range of different grain sizes shows that pure Cu with this range of grain sizes is expected to have a hardness in the range of 100-140HV. Figure 7 shows that the microhardness of the Cu-5vol.%Al$_2$O$_3$ nanocomposite particles is more than 100HV higher than that range. This suggests that the 5vol.% of Al$_2$O$_3$ nanoparticles significantly strengthen the material. However, it appears that further increasing the volume fraction of the Al$_2$O$_3$ nanoparticles does not lead to any stronger effect on the microhardness.

**Figure 7.** Average microhardness of Cu and Cu-(2.5-10)vol.%Al$_2$O$_3$ nanocomposite powder particles produced by Route 2 milling for 24 hours and Route 1 milling for 12 hours, respectively, as a function of annealing temperature

4. Conclusions

High energy mechanical milling (HEMM) can be effectively used to disperse (2.5-10%)vol.% Al$_2$O$_3$ nanoparticles into a ultrafine grained or nanocrystalline Cu matrix. Using larger diameter balls or increasing the volume fraction of Al$_2$O$_3$ nanocomposite powders with nanocrystalline Cu matrix. The study of the thermal stability and microhardness change of Cu-(2.5-10)vol.%Al$_2$O$_3$ nanocomposite powder particles shows that refining the microstructure of the Cu matrix and increasing the volume fraction of Al$_2$O$_3$ nanoparticles in the nanocomposite both increase the thermal stability of the nanocomposite structure.

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