Thermal stability and microhardness of Cu-10vol.%Al₂O₃ nanocomposite produced by high energy mechanical milling

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Abstract. Cu-10vol. %Al₂O₃ nanocomposite powders were produced using two high energy milling routes and heat treated at 150, 300, 400 and 500°C for 1 hour, respectively, to determine the thermal stability of the microstructure and the microhardness change of the materials as a function of the annealing temperature. Annealing of the asmilled powders at 150°C caused recovery and recrystallisation that leads to significant decrease in dislocation density and slight decrease of microhardness. Increasing the annealing temperature to 400°C causes slight coarsening of the Cu grains and corresponding slight decrease of microhardness. Further increasing the annealing temperature to 500°C causes significant coarsening of the Cu grains and cause significant decrease in microhardness. The effects of different factors on the thermal stability and microhardness change of the Cu-Al₂O₃ are discussed.

1. Introduction
The high energy mechanical milling (HEMM), as one of the severe plastic deformation (SPD) processing processes, has been widely used in producing nanostructured powders [1-3]. Since early 1990s, HEMM has also been used to produce high quality bulk ultrafine grained (UFG) and nanostructured materials from ductile powders such as Cu, Zn and Al powders [4-6]. HEMM is the most widely used technique in powder metallurgy for processing copper-based composites. The presence of fine dispersion of Al₂O₃ particles of various sizes and amount in a Cu matrix improves the hardness and strength of the material at room temperature prepared by HEMM [7-9]. Since the ultrafine and nanostructured powders need to be consolidated at elevated temperatures by thermomechanical processing, it is important to understand their microstructural stability at different temperatures. We studied the thermal stability and microhardness changes of Cu-10vol.%Al₂O₃ nanocomposite at different temperatures produced by HEMM of mixtures of Cu and Al₂O₃ powders.

2. Experimental procedure
Mixtures of powders of Cu (99.5% pure; particle size<63μm) and Al₂O₃ (99.9% pure; average particle size~50nm) were milled using a PM 4000 Restch planetary ball mill with a rotational speed of 400 rpm. The hardened steel vial containing balls and 100g of powder mixture was sealed in a glove box filled with high purity argon. The powder mixture was milled using two different routes. In Route 1, the powder mixture was milled for 12 hours using 60 balls with a diameter of 12.5mm, and in Route 2, the 12 hours milled powder was further milled 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 milled composite material was annealed at different temperatures for 1 hour using tube furnace with
vacuum reaching $10^{-6}$ mbar. The analyses and characterization of the samples were performed using standard materials characterisation techniques and Vickers microhardness tester with a load of 25g and a loading duration of 20s.

3. Results and discussion

Coarse and fine powders formed during the first 12 hours (Route 1) and further 12 hours of milling (Route 2), respectively, for the Cu-10vol.%Al$_2$O$_3$ nanocomposite. Figs. 1 and 2 show the XRD patterns of Cu-10vol.%Al$_2$O$_3$ nanocomposite powders produced with Route 1 and Route 2 and after annealing at different temperatures, respectively. The XRD patterns only showed Cu peaks, due to the small fraction and extremely small size of Al$_2$O$_3$ nanoparticles and increasing the annealing temperature caused little change in the broadness of the Cu peaks of the XRD patterns. There is a slight Cu(111) peak shift to a larger angle for the Cu-10vol.%Al$_2$O$_3$ fine powders produced using Route 1 and Route 2, after annealing at 500°C, indicating that the Cu lattice parameter has decreased, and the reason is likely to be that some of the Al$_2$O$_3$ was dissolved in the solution during the milling and then precipitated out after annealing at 500°C.

Figure 1. X-ray diffraction patterns of Cu-10vol.%Al$_2$O$_3$ nanocomposite powder produced using Route 1 and after annealing at different temperatures.

Figure 2. X-ray diffraction patterns of Cu-10vol.%Al$_2$O$_3$ nanocomposite powder produced using Route 2 and after annealing at different temperatures.

Figure 3. SEM micrograph and corresponding Energy Dispersive X-ray elemental (Al and Cu respectively) mapping of the cross section of a powder particle produced using Route 1.

Energy dispersive spectroscopy (EDS) analysis of the as-milled Cu-10vol.%Al$_2$O$_3$ powder particles produced using Route 1 (Figure 3) showed that the Al$_2$O$_3$ nanoparticles were incorporated into each of the as-milled powder particles, forming a Cu-Al$_2$O$_3$ nanocomposite structure. Backscattered electron SEM imaging of the cross section of the powder particles was carried out to determine the volume fraction and distribution of Al$_2$O$_3$ particles of large sizes in the range of 100-400nm in the as-milled powder particles. This revealed that there was approximately 1vol.% of such large Al$_2$O$_3$ particles in the microstructure, as shown in (Figures 4(a) and 5(a)). After annealing at 300°C, the volume fraction of the large Al$_2$O$_3$ particles increased slightly (Figures 4(b) and 5(b)) suggesting coarsening of the
Al$_2$O$_3$ nanoparticles occurred. With further increasing the temperature to 500°C, the volume fraction of the large Al$_2$O$_3$ particles increased significantly (Figures 4(c) and 5(c)). The large sized Al$_2$O$_3$ particles in the 500°C annealed powder particles were homogenously distributed in the Cu matrix.

Figure 4. Backscattered electron SEM images of (a) 12h milled (Route 1) Cu-10vol.%Al$_2$O$_3$ composite; (b) and (c) corresponding composite after annealing at 300°C and 500°C respectively.

Figure 5. Backscattered electron SEM images of (a) 24h milled (Route 2) Cu-10vol.%Al$_2$O$_3$ composite; (b) and (c) corresponding composite after annealing at 300°C and 500°C respectively.

Figures 6 and 7 show the TEM bright field images of as-milled Cu-10vol.%Al$_2$O$_3$ nanocomposite powder particles and those after annealing at different temperatures. For the coarse powders produced with Route 1, TEM examination showed that grains of the Cu matrix decreased from the range of 50-120nm to 30-70nm due to recrystallisation after annealing at 150°C. Increasing the annealing temperature to 300°C an increase of the grain sizes of the Cu matrix to 50-100nm and further increasing the annealing temperature to 500°C caused a significant increase of the Cu matrix grain sizes in the range of 50-150nm. On the other hand, for the fine powder produced with Route 2 the majority of the Cu grains of the as-milled powder particles had sizes smaller than 100nm. After annealing at 150°C, the grain sizes increased very little to the range of 50-150nm. With further increase of the annealing temperature to 300°C, the sizes of the Cu grains increased to the range of 80-180nm. Further increasing the annealing temperature to 500°C caused more significant coarsening of the Cu grains, with the sizes of the Cu grains increasing to 100-350nm.

Figure 6: TEM bright field images of 12h milled (Route 1) Cu-10vol.%Al$_2$O$_3$ composite powder particles after annealing at 150, 300 and 500°C respectively.

Figure 8 shows the change of the average microhardness of the powder particles produced using Route 1 and Route 2, respectively, as a function of annealing temperature. After heat treatment at 150°C, the average microhardness of powder particles produced using Route 1 decreased sharply from 263HV to 240HV, due to decrease of dislocation density, and the average microhardness remained almost unchanged with increasing the annealing temperatures to 400°C. The average microhardness decreased sharply to 180HV after heat treatment at 500°C partly due to coarsening of Cu grains and partly due to coarsening of Al$_2$O$_3$ nanoparticles. On the other hand, the average microhardness of powder particles produced using Route 2 increased to 262HV and 270HV after annealing at 150°C.
and 300°C, respectively, from 255HV for the as-milled powder particles. After heat treatment at 400°C and 500°C, the average microhardness decreased to 245HV and 196HV respectively, again partly due to significant increase of Cu grain sizes and significant coarsening of Al₂O₃ nanoparticles. It appears that the coarsening of the grains and the associated microhardness decrease are not significant after annealing at temperatures up to 400°C. This suggests that the nanostructured powder can be consolidated at temperatures around 400°C without totally losing the nanostructure.

Figure 7: TEM bright field images of 24h milled (Route 2) Cu-10vol.% Al₂O₃ composite powder particles after annealing at 150, 300 and 500°C respectively.

![Figure 7](image)

Figure 8
Average microhardness of Cu-10vol.% Al₂O₃ nanocomposite produced with Route 1 and Route 2, as a function of annealing temperatures.

4. Conclusions
Coarse and fine powders of Cu-10vol.% Al₂O₃ nanocomposite was produced using two high energy mechanical milling routes respectively. The as-milled and annealed nanocomposite powder particles showed little increase of the Cu matrix grain sizes and decrease of the microhardness after annealing at temperatures of up to 300°C and but significant coarsening of the Cu grains and Al₂O₃ nanoparticles and sharp decrease of microhardness with increasing the annealing temperature to 500°C. This confirms that the Cu-10vol.% Al₂O₃ nanocomposite is thermally stable at temperatures up to 400°C.

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