# Mechanochemical synthesis of nanocrystalline $Al_2O_3$ dispersed copper

SEUNG J. HWANG
*Department of Materials Science and Engineering, Daejin University, Pocheon, Kyung-gi, 487-711, South Korea*

D. WEXLER, A. CALKA
*School of Materials, Mechanical and Mechatronics Engineering, University of Wollongong, Northfields Ave., Wollongong NSW 2522, Australia*

Copper alloys dispersion, strengthened with aluminum oxide ($Al_2O_3$), have great potential as a class of oxide dispersion strengthened (ODS) alloys with relatively high strengths, good phase stability and excellent conductivity at elevated temperatures. Applications of ODS Cu alloys include spot welding electrodes for the automotive assembly and electronic packaging industries. ODS Cu alloys can be produced via several processing routes including internal oxidation [1–4], and casting and mechanical alloying [5, 6]. Unfortunately, internal oxidation tends to result in alloys with relatively low volume fractions of $Al_2O_3$ dispersoids, while casting and mechanical mixing both have the limitation that dispersoids produced are generally too large to effectively limit dislocation motion [5].

Several reports have been published confirming that metals and alloys can be synthesized from their own oxides, using the technique of mechanochemical synthesis with an appropriate reductant [7, 8]. In particular, it has been demonstrated that high energy ball milling can induce the reduction reaction between CuO and Al, although, as yet, attempts to turn the powder product into useful ODS Cu alloys have met with problems due to the coarse nature of the final product [9, 10]. The particular reduction reaction is highly exothermic and rapid enough to be self-propagating, and the $Al_2O_3$ dispersoid particles produced in the mill are subjected to such high temperatures that they over-coarsen. Ying *et al.* [11] attempted to overcome this problem by replacing Al with Cu-Al/Cu(Al) powder in order to slow down the reduction reaction. They synthesized a Cu-$Al_2O_3$ nanocomposite precursor powder which, after consolidation, produced $Al_2O_3$ dispersoids less than 200 nm in size. Unfortunately, this was still not fine enough to give rise to significant dispersion strengthening [12].

In the current study it was intended to produce fine $Al_2O_3$ dispersoid particles in a Cu matrix through appropriate mechanochemistry, using two approaches to further decrease the reaction rates and lower the reaction temperatures and energy. First, CuO was to be replaced with $Cu_2O$ for reasons outlined below. Second, excess Cu powder would be added as a diluent and thermal conductor to help remove heat from the system during milling with the aim of a less violent reaction or, at least retardation, of the combustion synthesis reaction in the mill [10, 11].

The reported heats of reaction of Cu oxides and Al are as follows [13]:

$$3CuO + 2Al \rightarrow 3Cu + Al_2O_3 \quad -4.14\ kJ/g$$

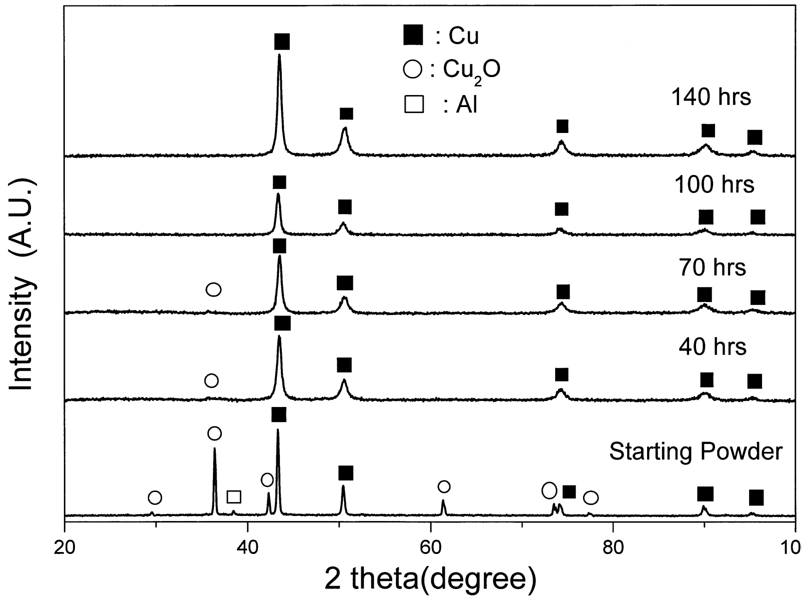

*Figure 1* XRD patterns obtained from the powders as a function of milling time.

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and

$$3Cu_2O + 2Al \rightarrow 6Cu + Al_2O_3 \quad -2.43\ \text{kJ/g}.$$

Differential thermal calorimetry (DSC) studies of both reactions have shown that the major exothermic peaks appear at higher temperatures for the reaction $3Cu_2O + 2Al \rightarrow 6Cu + Al_2O_3$ [11, 14]. Thus, the reduction reaction between $Cu_2O$ and Al is less exothermic and has a higher critical ignition temperature than that between CuO and Al. This suggests that for the same mechanical energy input via mechanical milling, heat-induced particle coarsening might be less of a problem for the reaction between $Cu_2O$ and Al. Furthermore, if the self-propagating high temperature reduction of $Cu_2O$ does occur, then it will likely be less violent than for the case of CuO.

Starting powder ingredients were $Cu_2O$ (Sigma-Aldrich, $-325$ mesh, 97%), Al (Johnson Matthey, $-40 + 325$ mesh, 99.8%) and Cu (Aldrich, $-200$ mesh, 99%). Samples (10 g) were reactively milled in a magneto-ball mill (also called Uniball mill) for 140 h in a He atmosphere with ball to powder ratio 27:1. Details of the magneto-milling technique are described elsewhere [15]. The amount of the reactants and Cu powder were measured to stoichiometry of the reaction:

$$3Cu_2O + 2Al + 7.65Cu \rightarrow 13.65Cu + Al_2O_3.$$

The amount of $Al_2O_3$ expected to be formed is equivalent to 21 vol%.

Consolidation of the milled powders was by uniaxial hot pressing of samples in high-density graphite dies. Samples were induction heated under controlled inert atmosphere to $850\,^{\circ}C$ and held for 4 min under a load of 20 MPa. The microstructure and phases of milled powders and of the consolidated materials were characterized by X-ray diffraction (XRD), using Cu $K_{\alpha}$ radiation and graphite monochrometer; scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The milling process was also periodically monitored by XRD up to completion of the reaction.

Fig. 1 shows XRD patterns obtained after milling times of up to 140 h from powder milled in the proportions, $3Cu_2O + 2Al + 7.65Cu$. The $Cu_2O$ and Al peaks progressively disappeared with increasing milling time and were below limits of detection after 100 h, which represents the nominal completion time of milling. No evidence of $Al_2O_3$ was found in XRD patterns of powders milled for 100 h or longer, although there was evidence of Cu, with peak broadening indicating that this was in nanostructural and/or highly strained from. XRD patterns obtained from the hot pressed material did not reveal additional peaks which are associated with $Al_2O_3$. These XRD results do not necessarily preclude the existence of $Al_2O_3$ in nanocrystalline form, which produces very weak diffraction peaks.

Fig. 2 shows TEM bright field (Fig. 2a), dark field (Fig. 2b) and Selected Area Diffraction (SAD) patterns (Fig. 2c) obtained from a small particle of the nanostructural powder after milling for 140 h. Typical SAD patterns displayed spotty-rings which could be indexed as a mixture of FCC Cu and Rhomboheral $\alpha$-$Al_2O_3$. The fine structure of the spotty rings indicated that both Cu and $\alpha$-$Al_2O_3$ phases took the form of predominantly nanostructural particles. Dark field imaging confirmed this and indicated a bimodal size distribution of nanocrystallites, with an average size of around 2–5 nm for the smaller crystals and around 10–20 nm for the larger ones.

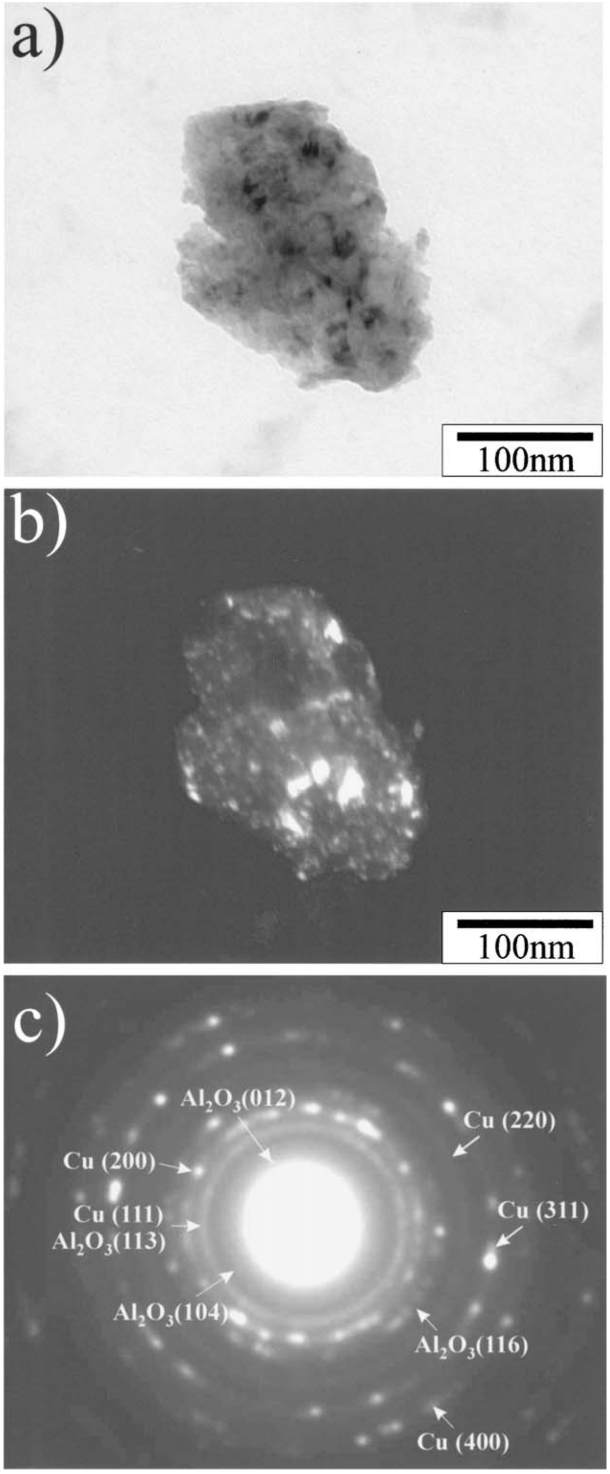

*Figure 2* TEM study of nanostructural powder particle produced by magneto-milling for 140 h, (a) bright field image, (b) dark field image and (c) SAD pattern.

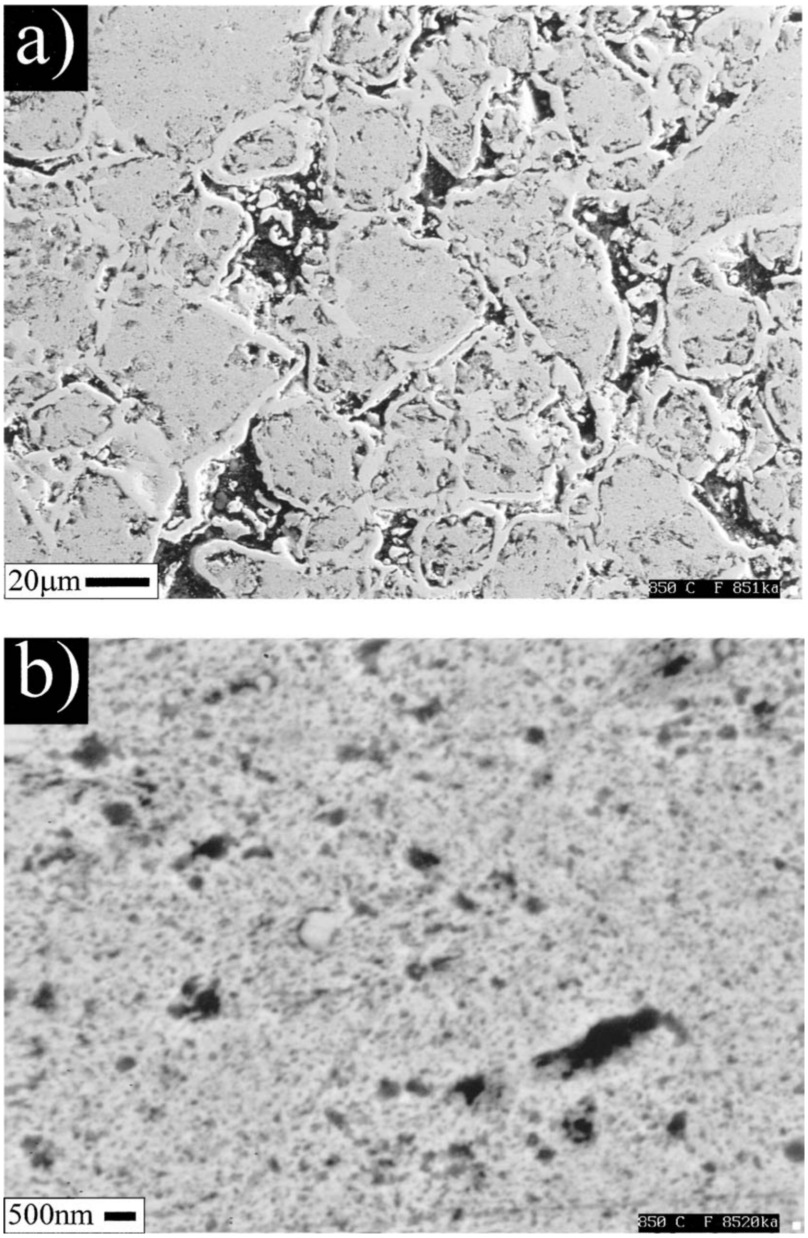

*Figure 3* SEM images of the consolidated material showing the distribution of Cu and Cu/$Al_2O_3$ dispersoid particles: (a) low magnification and (b) high magnification.

Fig. 3 shows SEM images obtained from material milled for 140 h and hot pressed at 850 °C. Low magnification images (Fig. 3a) revealed separation of Cu into bright regions (particle free Cu) and darker grey regions (dispersions of other material in a fine Cu matrix), with additional regions (grey-black) of porosity. SEM examination at higher magnifications (Fig. 3b) confirmed that the darker grey regions comprised a low porosity, predominantly nanostructural mixture, presumably containing nanocrystalline alumina particles in a Cu matrix. The presence of the particle free Cu layers (light, continuous phase in Fig. 3a) around the nanostructural regions of Cu and alumina indicate that some of the Cu diluent powder was not caught up in the reduction reaction between the $Cu_2O$ and Al.

The size distribution of the particles in the grey-black regions of Fig. 3 was also investigated by TEM (Fig. 4). Typical bright field (Fig. 4a) and dark field (Fig. 4b) images of those regions confirmed that they comprised a mixture of nano-crystalline Cu and alumina particles, both of which were still less than 20 nm in diameter. The nanocrystalline Cu grains were found to be slightly more rounded in morphology than the alumina and were also observed to have high dislocation densities, even after consolidation at such a high temperature. This suggests that these ODS Cu alloys produced by mechanosynthesis might have an extra Hall-Petch contribution to strengthening, which would not occur in conventionally produced ODS Cu alloy containing microcrystalline Cu [3].

The current research results clearly demonstrate that the synthesis of ODS Cu powder at room temperature can successfully be achieved through mechanochemistry using $Cu_2O$ and Al as reactants. It seems to be feasible, in view of the current preliminary microstructural observations, to produce nano-sized $Al_2O_3$ dispersed in ~20 nm sized Cu grains, by appropriate control of the in-situ formation process.

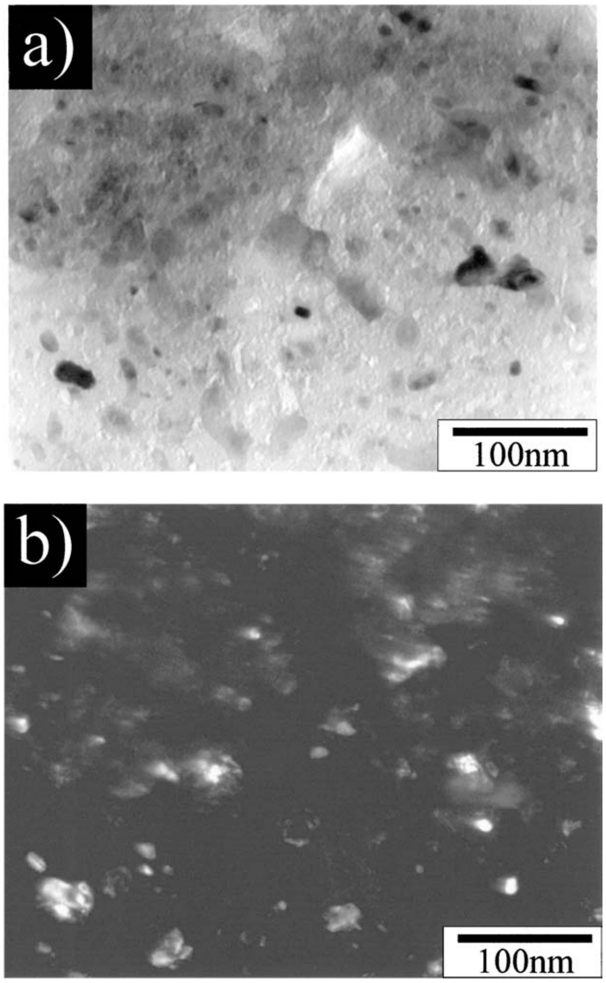

*Figure 4* TEM study of nanostructural Cu/$Al_2O_3$ region in consolidated sample: (a) bright field image and (b) dark field image.

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