

MECHANOSYNTHESIS OF NANOCRYSTALLINE Cu WITH Al_2O_3 DISPERSION BY CRYOGENIC MILLING

Jin-Hyung Lee and Seung J. Hwang

Dep't of Materials Sci. and Eng., Daejin University, Pocheon, Kyung-gi, 487-711, Rep. of Korea

Received: March 29, 2008

Abstract. Nanocrystalline Cu with Al_2O_3 dispersoid (Cu-4.1 vol.% Al_2O_3) was successfully produced by a simple cryo-milling at 210K with a mixture of Cu_2O , Al, and Cu powders, followed by hot pressing at 1123K. The results of microstructural analysis showed that the hot pressed materials comprised a mixture of Cu matrix (25.1 nm) and Al_2O_3 (<10 nm) with a homogeneous size distribution of the dispersoid. Grain sizes of Cu were estimated by XRD (Scherrer's formula) and TEM; dispersoid sizes of Al_2O_3 were confirmed by STEM-EDS (Scanning Transmission Electron Microscopy-Energy Dispersive Spectroscopy) and TEM (Transmission Electron Microscopy).

1. INTRODUCTION

Several reports have been published confirming that the nanocomposites of Cu - Al_2O_3 could be synthesized from Al and $\text{Cu}_2\text{O}/\text{CuO}$ by milling at room temperature [1-4]. The suppression of self propagating reaction between Al and copper oxides is recently the most challenging issue in the mechanochemical synthesis of Cu - Al_2O_3 nanocomposite by reactive milling for the refinement of dispersoids [5,6].

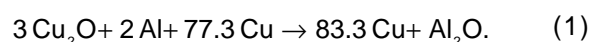
In previous report, nanocrystalline Cu matrix with much finer Al_2O_3 dispersoid with bimodal size distribution (20 and 100 nm) was successfully produced by reactive milling using a less exothermic oxidant (Cu_2O) [7,8]. The purpose of this work is to produce a finer and more homogeneously distributed Al_2O_3 dispersoid in nanocrystalline Cu using liquid nitrogen (LN2) flowing around the mill to remove the heat generated while both of the reaction and milling.

2. EXPERIMENTAL

A batch of powdered ingredients mixture (100 g) was reactively milled in a high energy attritor mill

Corresponding author: Seung J. Hwang, e-mail: sjhwang@daejin.ac.kr

for 8 h in Ar atmosphere with ball to powder ratio of 15:1. Milling temperatures of 210K was obtained by flowing LN2 (liquid nitrogen) to cool down the outside of milling chamber. The powder mixture of the reactants was prepared in a molar proportion according to reaction (1).



Button type samples (16 mm ϕ \times 7 mm) were compacted by electric resistant heating at 1123K for 2 h in vacuum hot press (HPed) under 50MPa. To make a compare with the cryo-milled materials, another batch of powder milled at 283K (using cooling water instead of LN2) was also prepared under the same milling and hot pressing conditions. Cu - 4.1 vol.% Al_2O_3 in the materials was estimated by calculation, assuming that all Al and O react to form Al_2O_3 by the reactive milling. Materials designations for different process conditions are given in Table 1. The microstructures and hardness of the materials were characterized by XRD (X-ray Diffraction), TEM, STEM-EDS, and micro Vickers hardness test. The details of the processing and characterizing techniques are described in elsewhere [8].

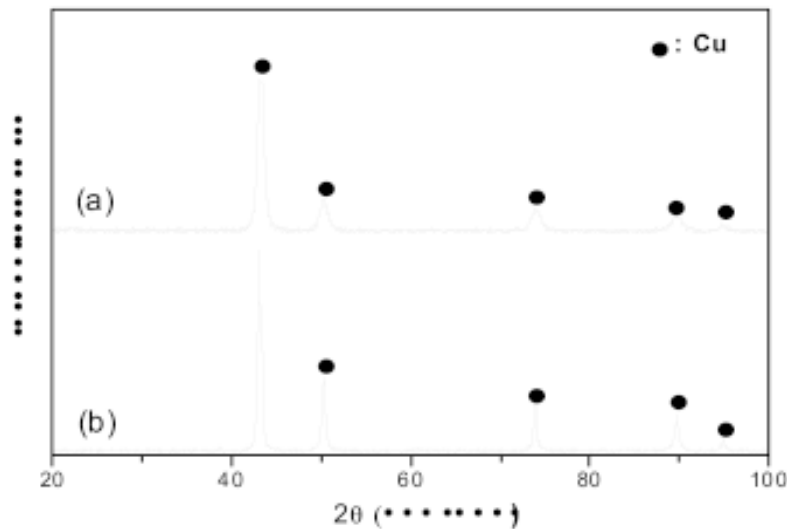


Fig. 1. XRD intensity-angle (2θ) patterns obtained from the A1 (Fig. 1a) and A2 (Fig. 1b).

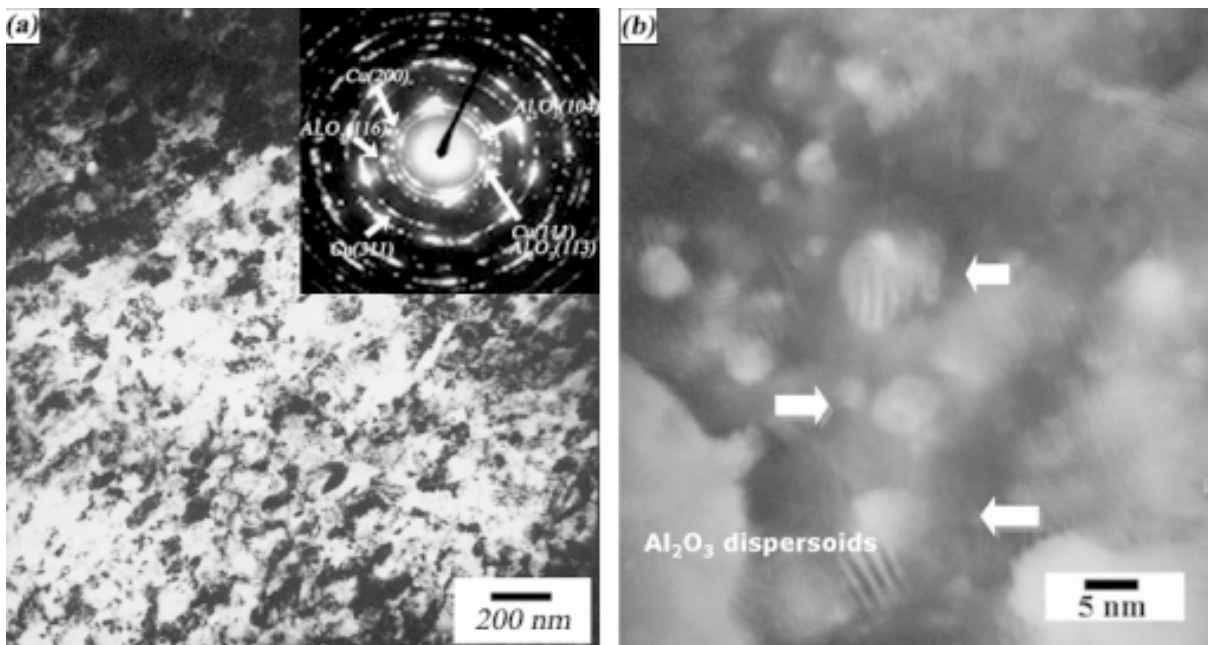


Fig. 2. TEM bright field images (Fig. 2a and 2b) and corresponding electron diffraction pattern (inset of Fig. 2a) obtained from the A2. (See the arrows marked).

3. RESULTS AND DISCUSSION

Insignificant evidence of Al_2O_3 was found on XRD pattern of the materials while Cu peaks are with strong intensity (Figs. 1a and 1b). Such a result may be attributed to the difference in absorption coefficient of the components (Cu and Al) as proposed by Koch [9].

The grain sizes of Cu matrix of the samples (A1, A2, B1, and B2, Table 1) were estimated by measuring the full width at half maximum (FWHM)

of Cu (111) diffraction peak using Scherrer's formula (Table 1) [10]. The results show that the sizes of Cu grains in the samples retain the nanocrystalline even after hot pressing at 1123K. Insignificant difference between the grain size of powder and bulk after hot pressing is presumably due to the Al_2O_3 dispersoids which is effective to prevent the Cu grain growth. These results are in agreement with the estimated grain size from the TEM observation of the A2 below (Fig. 2a).

Table 1. Materials designations, process conditions, grain sizes of Cu, and micro Vickers hardness numbers for Cu-4.1 vol.% Al₂O₃ powders and alloys.

Materials designations	Process conditions	Grain size of Cu (nm)	Vickers hardness number (VHN)
A1 (Powder)	Cryo-milled powder (using LN2 for cooling)	12.7 ± 0.3	253 ± 7
A2 (Bulk)	Cryo-milled and HPed at 1123K	25.1 ± 0.3	265 ± 8
B1 (Powder)	RT-milled powder (Using tap- water for cooling)	16.7 ± 0.4	217 ± 6
B2 (Bulk)	RT-milled and HPed at 1123 K	30.5 ± 0.5	219 ± 9

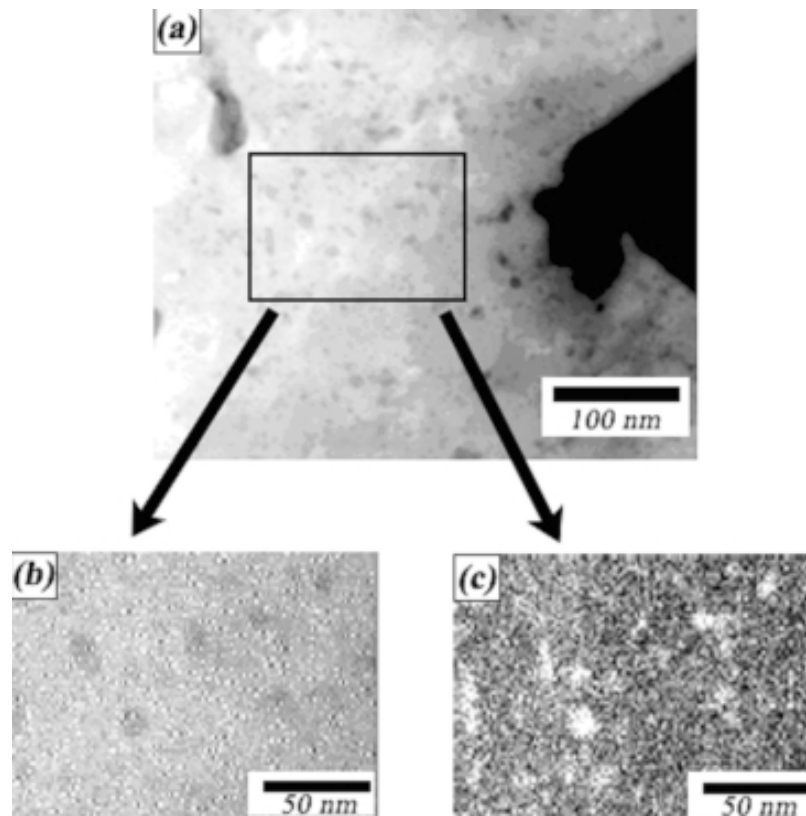
**Fig. 3.** STEM image (Fig. 3a) and EDS element mapping images of Al (Fig. 3b) and Cu (Fig. 3c) collected from the A2.

Fig. 2 illustrates TEM bright field images (Figs. 2a and 2b) and corresponding electron diffraction pattern (inset of Fig. 2a) obtained from the A2. The diffraction analysis revealed that most of the diffracted beams (spotty-rings) were attributed to the

nanocrystalline mixture of Cu and Al₂O₃ (see the arrows marked).

In order to ensure the size of Al₂O₃ dispersoids, STEM-EDS mapping for elements of Al and Cu was carried out on the sample A2 (STEM image

(Fig. 3a) and element mapping images of Al (Fig. 3b) and Cu (Fig. 3c). The micrographs clearly show that the size distribution of Al_2O_3 in A2 is fairly uniform and fine (<10 nm) while that in B2 is bimodal with coarse one (20 and 100nm, see [8]). The results of grain sizes of Cu and micro Vickers hardness test are given in Table 1; they show that the hardness number of the cryo-milled is considerably higher than the RT-milled. This difference in the hardness is most likely due to the size and distribution of Cu and Al_2O_3 .

In summary, nanocrystalline Cu - 4.1 vol.% Al_2O_3 alloy has been successfully produced by cryo-milling and consolidated by hot pressing, resulting in a nanocrystalline mixture of Cu (~25 nm) with a homogeneous, uniform distribution of Al_2O_3 (< 10 nm). Future quantitative analysis of the relationship between the mechanical properties and microstructure of Cu - Al_2O_3 nanocomposite is required to understand the strengthening mechanisms of these materials.

ACKNOWLEDGEMENT

This work was supported by the Daejin University Research Grants in 2006

REFERENCES

- [1] I. G. B. Schaffer and P. G. McCormick // *Scripta Metall.* **23** (1989) 835.
- [2] G. B. Schaffer and P. G. McCormick // *Metall. Trans.* **21A** (1990) 2789.
- [3] A. Bakhshai, R. Pragani and L. Takacs // *Met. Mat. Trans.* **33A** (2002) 3521.
- [4] T. F. Grigorieva, A. P. Barinova and N. Z. Lyakhov // *J. Nanoparticle Research* **5** (2003) 439.
- [5] D. Y. Ying and D. L. Zhang // *Mater. Sci. Eng. A* **286** (2000) 152.
- [6] T. Venugopal, K. Prasad Rao and B.S. Murty // *Mater. Sci. Eng. A* **393** (2005) 382.
- [7] Seung J. Hwang, D. Wexler and A. Calka // *J. Mat. Sci. Let* **39** (2004) 4659.
- [8] Seung J. Hwang and Jin-hyung Lee // *Mater. Sci. Eng. A* **405** (2005) 140.
- [9] R.T. Leonard and C.C. Koch // *Scripta Mat.* **36** (1997) 41.
- [10] B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd ed.* (Prentice Hall, Upper Saddle River, NJ, 2001).