EFFECT OF DISPERSED OXIDE (MgO, Al_2O_3) PHASES ON MICROSTRUCTURE EVOLUTION OF Cu -BASED COMPOSITES

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Abstract

The study is centred on preparation and microstructural analysis of Cu composites containing different volume contents of secondary phases (MgO, Al_2O_3). The microstructure evolution is observed during the preparation of a nanocrystalline powder and after its processing into a compact. Effect of the dispersed oxide phases on preservation of the initial nanostructure is analyzed. The composites were prepared by thermo-chemical transformations of precursors (CuO+MgO, CuO+Al_2O_3) and mechanical milling followed by spark plasma sintering technique. The microstructure development of the powders during their preparation and subsequent compaction is characterized by metallographic observations and X-ray diffraction analysis. Mechanical properties were tested by micro and macro-hardness measurements. From the study follows that the Cu materials containing Al_2O_3dispersoid exhibit improved thermal stability and higher hardness values compared to the Cu materials dispersion strengthened by MgO particles.

Keywords: Dispersion strengthening, mechanical milling, X-ray diffraction analysis, thermal stability

1. INTRODUCTION

Nanocrystalline copper is an interesting material for investigation primarily due to markedly improved mechanical and physical properties compared to coarse-grained copper. The observed improvement in properties is attributed to an interaction of grain size refinement (below 100 nm) and increased grain boundary area. However, the monolithic Cu material tends to be unstable with respect to grain growth. It is urgent to develop novel materials with a high thermal stability of the nanostructure. The cold working hardened and precipitation hardened copper alloys are easily softened at high temperatures. On the other hand, presence of uniformly dispersed oxide nanoparticles - dispersoids in the metal matrix inhibits the grain boundary migration and thus it stabilizes the structure up to temperatures close to the melting point of the matrix [1-3]. The dispersion strengthened (DS) materials on the Cu base are characterized by interesting and technologically important properties (excellent thermal stability, special optical, electrical, chemical and mechanical properties). Dispersion strengthening is achieved by introducing a small volume fraction of thermodynamically stable secondary phase (oxides, carbides, nitrides) into the soft copper. Alumina DS Cu offers an unique combination of high strength and electrical as well thermal conductivity over a wide range of temperatures. These materials are developed for modern applications in electrical engineering [4-7]. In recent years, amount of research effort has been expanded into studying and understanding the fabrication characteristics, mechanical and electrical properties of nanocrystalline (nc) Cu-MgO materials [8-12]. Maintaining the nanostructure of starting powder after its thermal exposure is very important owing to achieving unique properties of the final product [13, 14].

The objective of this work was to obtain the nanocrystalline Cu-MgO and Cu-MgO-Al_2O_3 powders by mechano-chemical preparation followed by compaction using a spark plasma sintering technique. The study analyses the structural and mechanical characteristics of the materials.

2. EXPERIMENTAL PROCEDURE

Experimental materials consisting of the Cu-5 vol.% MgO, Cu-3 vol.% MgO-2 vol.% Al2O3 and Cu-1 vol.% MgO-4 vol.% Al2O3 were prepared by powder metallurgy technology. Ultrafine composite powders were prepared by modification of the original mechano-chemical method based on the mechanical milling in an attritor and a vibrate mill and chemical reduction of CuO precursor by a hydrogen. The starting CuO was prepared by annealing of electrolytic copper powder a purity of 99.7 % at a temperature of 250 °C.

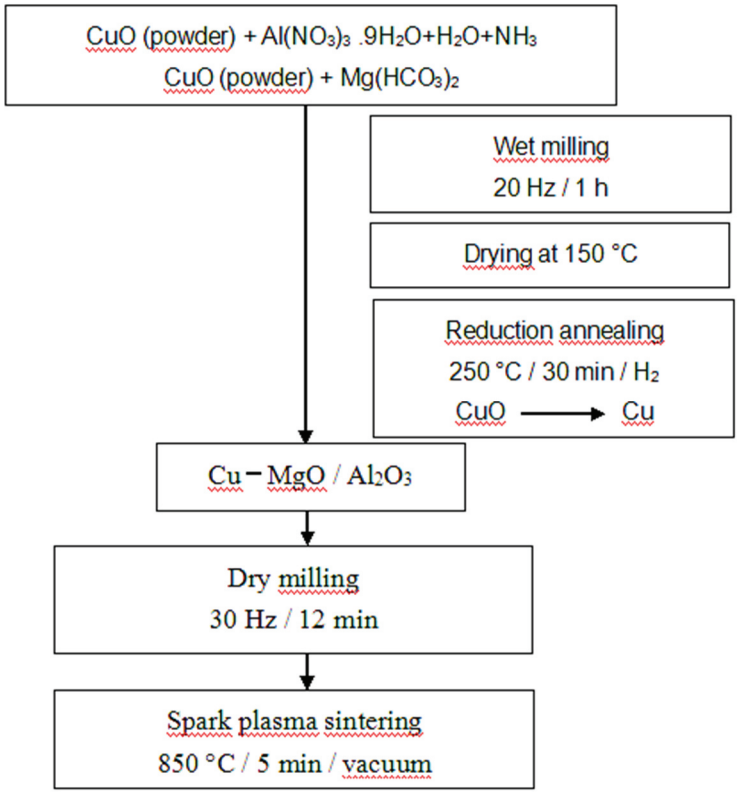

Figure 1 Scheme of powder materials preparation

The MgO and Al_2O_3 particles were prepared inside the CuO powder by in situ method as it is shown in **Figure 1**. The mixtures containing CuO matrix and 5 vol.% of dispersoids were wet high-energy milled in an attritor at a frequency of 20 Hz for 1 h. The milling process ensured thoroughly homogenization of the CuO and the secondary phases. The mixtures were next dried and treated at a temperature of 150 °C in a hydrogen atmosphere to obtain Cu matrix. The as-prepared Cu composite powders were 12 minutes milled in a vibrate mill at a frequency of 30 Hz and sintered in a vacuum at a temperature of 850 °C by means of a spark plasma sintering (SPS) device.

Microstructure of the powders and sintered samples was analyzed by methods of X-ray diffraction and scanning electron microscopy (SEM) (JEOL JSM 7000F). X-ray diffraction patterns were obtained by Philips X´Pert Pro powder diffractometer equipped with Ni-filtered Cu Ká radiation at 40 kV and 40 mA using the positional sensitive detector X´Celerator. Mechanical properties were tested by hardness according to Vickers (HV 10) and micro-hardness measurements.

3. RESULTS AND DISCUSSION

As can be clearly seen in **Figures 2** and **3**, the SEM images of the as-sintered Cu-5 vol.% MgO and Cu-1 vol.% MgO-4 vol.% Al_2O_3 materials are different. The Cu-5 vol.% MgO microstructure is coarser compared to

the Cu-1 vol.% MgO-4 vol.% Al_2O_3 one. The EDX data in **Figure 2** confirm that elements of the material are Cu, Mg and O without any other impurities. The Cu grains in the Cu-MgO composite range from 500 nm to 1 ěm and MgO particles with sizes between 50 - 200 nm in diameter are non uniformly distributed in the matrix. However, the particles with size above 50 nm are too large to strengthen the grain boundaries at elevated temperatures by dispersion strengthening mechanisms what has resulted in the coarser microstructure. The large MgO particle formation is supported by a poor Cu/MgO interface bonding [15] inducing an undesirable clustering/agglomeration of some particles during the hot consolidation. On the other hand, the Cu-1 vol.% MgO-4 vol.% Al_2O_3 microstructure is fine, **Figure 3**, the Cu grains are in the 150-300 nm range. The EDX analysis shows that the material is composed of Cu, Al, Mg and O elements. The MgO dispersoids present here coarser particles of size about 100 nm. These particles can not inhibit recrystalization processes of the copper matrix. However, Al_2O_3 dispersoids exhibit here the sizes about 30 nm and they are located mostly at grain boundaries. Therefore, these well-dispersed and thermodynamically stable nanoparticles can be effective in the process of crystallite/grain stabilization at elevated temperatures by hindering dislocation movements as well as by suppressing diffusion needed for the grain growth. As can be seen, the SEM study of both experimental materials containing the same amount of dispersoid (5 vol.%) suggests that primarily the Al_2O_3 nanoparticles are effective in dispersion strengthening of the copper matrix during the hot processing of the powder.

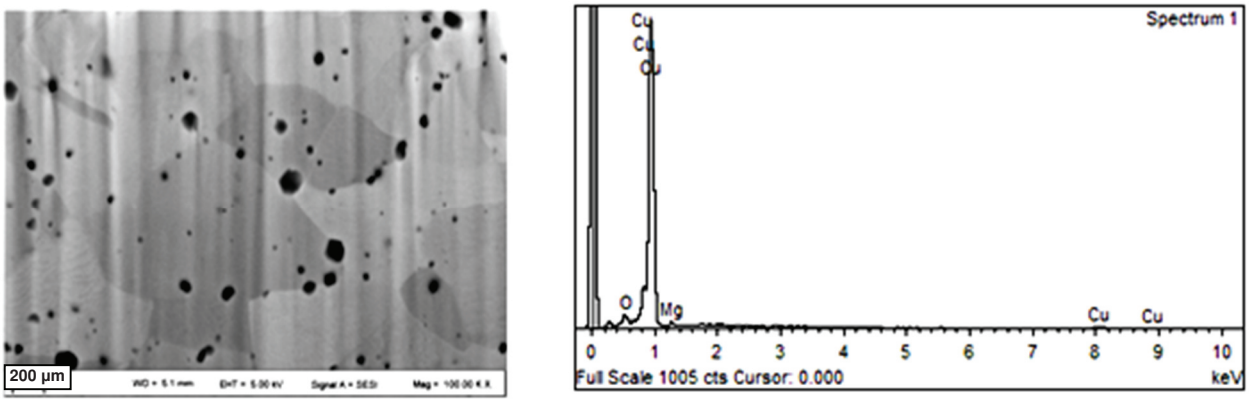

Figure 2 SEM microstructure of the Cu-5 vol.% MgO material and EDX analysis

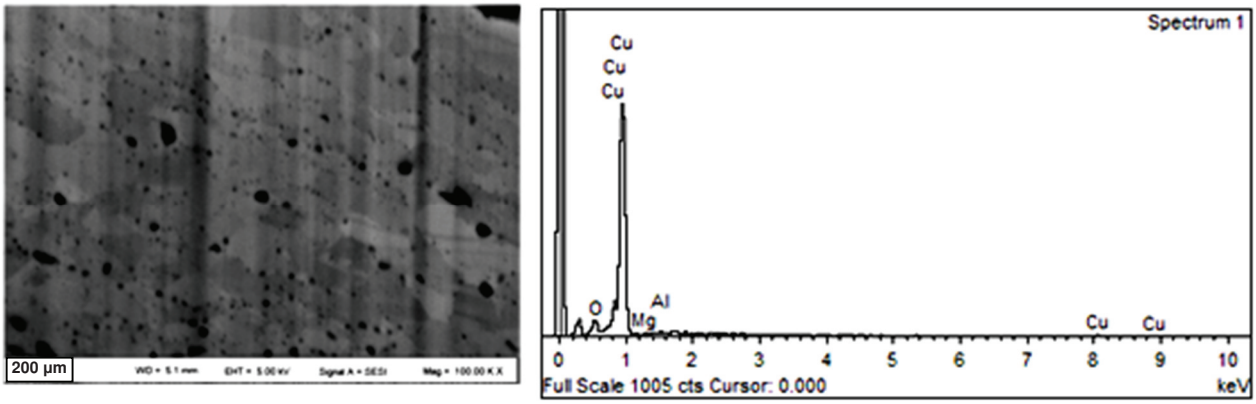

Figure 3 SEM microstructure of the Cu-1 vol.% MgO-4 vol.% Al_2O_3 material and EDX analysis

The mean crystallite/grain size was calculated by the well-known Voigt function [16] that was used for detailed analysis of the (111) diffraction line profile. The changes in mean crystallite size of the as-prepared powder and the as-sintered material documented in **Table 1** reveal that the hot densification by SPS has resulted in coarsening of the initial grains of the powders but newly formed grains have remained in nanometric scale

(below 100 nm). The finest microstructure was formed in the Cu-1 vol.% MgO-4 vol.% Al_2O_3 composite and this result is consistent with the SEM observations, **Figure 3**. As can be seen in **Table 1**, the higher Al_2O_3 content, the lower copper crystallite size of the as-sintered material and consequently the higher hardness, as it is expected from an extrapolation of the well-known Hall-Petch relationship. The higher volume fraction of the MgO in the Cu-5 vol.% MgO and Cu-3 vol.% MgO-2 vol.% Al_2O_3 materials has caused that the coarse MgO particles did not strengthen the grain boundaries as effective as the Al_2O_3 nanoparticles. It has negatively affected microstructural evolution during the hot densification resulting in the lower hardness of the both composites.

Table 1 Mean crystallite size of the Cu matrix and hardness of the experimental materials

Material	Crystallite size (nm)		Hardness (HV)	Microhardness (HV)
	as-prepared powder	as-sintered material	as-sintered material	as-sintered material
Cu-5 MgO	20	75	115	130
Cu-3 MgO-2 Al_2O_3	19	64	122	143
Cu-1 MgO-4 Al_2O_3	22	53	154	192

4. CONCLUSION

From the study follows that the Al_2O_3 nanoparticles dispersed in the Cu matrix are effective in the process of subgrains/grains stabilization during hot densification by the SPS method. The high hardness of the Cu-1 vol.% MgO-4 vol.% Al_2O_3 results from the dispersion strengthened nanostructure of the material. On the other hand, the MgO particles are less efficient barriers against the copper grain growth due to their agglomeration into coarser particles (>50 nm) during the hot consolidation of the Cu-5 vol.% MgO and Cu-3 vol.% MgO-2 vol.% Al_2O_3 powders. The results indicate that choice of a suitable dispersoid for a given matrix is very important factor for thermal stabilization of nano-grains.

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