

## THERMAL STRUCTURE STABILITY OF Cu-MgO NANOCOMPOSITES

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### Abstract

The study compares the microstructure of the dispersion strengthened Cu - MgO composites prepared by thermo-chemical transformations of precursors and mechanical milling followed by spark plasma sintering technique. The effect of two different MgO contents (3 and 5 vol.%) on formation and stability of the copper matrix nanostructure is analysed. The structure development of the powder during its preparation and compact is characterised by metallographic observations and X-ray diffraction analysis. From the results follows that both the MgO contents are sufficient for effective strengthening the Cu - MgO nanostructure.

**Keywords:** Dispersion strengthened Cu - MgO, mechanical milling, X-ray diffraction analysis, thermal stability

### 1. INTRODUCTION

Copper is an interesting material for investigation primarily because of its attractive properties at the microstructural length scale of nanometers. The observed improvement in properties has been attributed to the conjoint and mutually interactive of grain size refinement and increased grain boundary area. The cold deformation hardened and precipitates hardened copper alloys are easily softened. It is urgent to develop novel materials with a high thermal stability of the microstructure. The presence of dispersoid in the matrix inhibits the grain boundary migration and it thus stabilizes the structure up to the temperatures close to the melting point of the matrix. Chemical stability in relation to the matrix, fineness and distribution homogeneity in the matrix are the most important demands on the secondary phases [1-3]. In recent years, amount of research effort has been expanded into studying and understanding the fabrication characteristics, mechanical and electrical property characterization of nc Cu-MgO materials [4-8]. The objective of this work is to obtain the nanocrystalline (nc) dispersion-strengthened (DS) Cu - MgO powder material by mechano-chemical preparation and to analyse the structural characteristics of bulk materials.

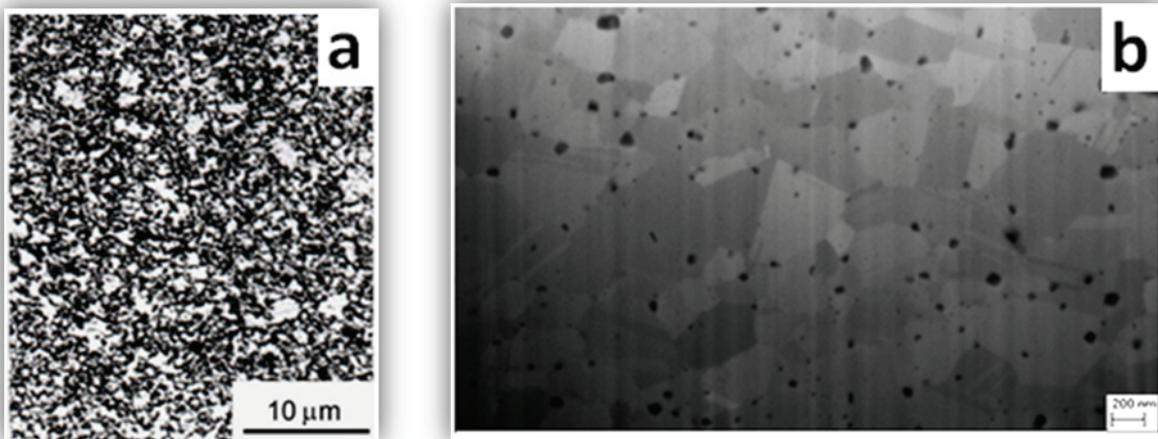
### 2. EXPERIMENTAL PROCEDURE

Experimental materials were dispersion strengthened Cu - 3 vol. % MgO and Cu - 5 vol. % MgO, prepared by powder metallurgy technology. The composite powder was prepared by the modification of the original mechanical-chemical method based on the mechanical milling in an attritor and a vibrate mill, chemical reduction by hydrogen [9]. CuO was prepared by annealing electrolytic copper powder with a purity of 99.7% at 250°C in air. The formation of CuO and a fraction of Cu<sub>2</sub>O can take place during oxidation, therefore the conditions of Cu oxidation were optimized in such a way that the full conversion of Cu into CuO was ensured. MgO was added to CuO during the crystallization of magnesium hydrogen carbonate from the CO<sub>2</sub> supersaturated aqueous solution of Mg(HCO<sub>3</sub>)<sub>2</sub> [10]. The stability of the Mg(HCO<sub>3</sub>)<sub>2</sub> decreased by expelling of the excessive CO<sub>2</sub> by heating the solution. The mixture of CuO with 3 and 5 vol.% MgO was prepared by high-energy milling brittle oxidic matrix (CuO) with the addition of MgO phase that represented the dispersoid [11]. Mixture was prepared by wet milling CuO with crystallised hydrogenmagnesite in the attritor at 700rpm for 1 hour. After milling, the mixture was dried. Homogenization process took place during milling. Then both mixtures were then annealed at 550°C under inert atmosphere of 100 % N<sub>2</sub> for 30 minutes, after this a reduced atmosphere of 100% H<sub>2</sub> were applied which was followed a second annealing at 150°C in reduced atmosphere of 100 % H<sub>2</sub>. The mixtures were analyzed by the methods of X-ray diffraction, TEM and SEM

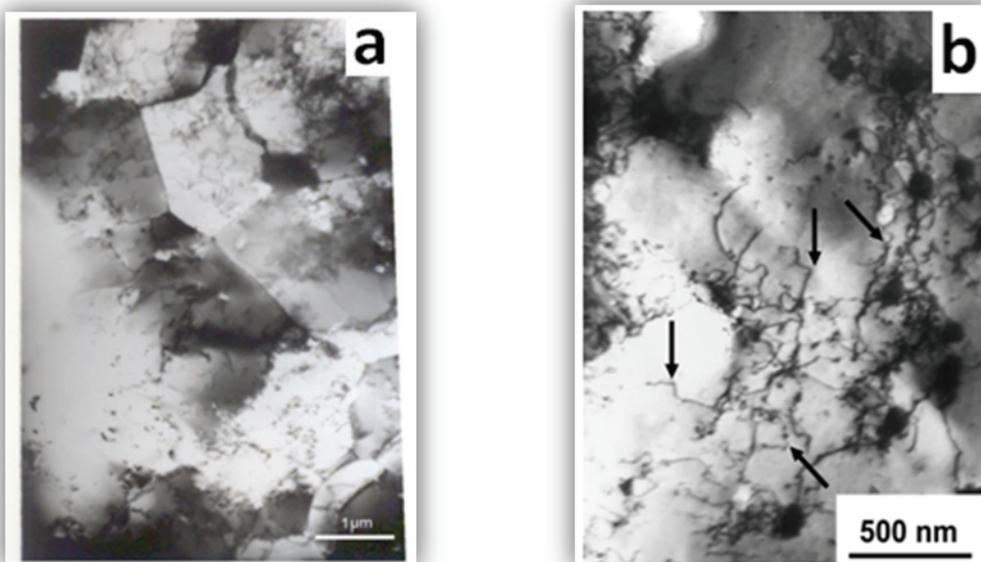
(materials prepared by FIB). The qualitative phase analyses were performed using X-ray diffraction method. X-ray diffraction patterns were obtained by Philips X'Pert Pro powder diffractometer equipped with Ni-filtered Cu K $\alpha$  radiation using the positional sensitive detector X'Celerator. Qualitative phase analyses were determined using the High Score program.[12]

### 3. RESULTS AND DISCUSSION

The microstructure of the compacted Cu-MgO material shows homogenous structure with a high proportion of interfaces under light microscopy as it is shown in **Fig. 1a**. The presence of twins in copper was rarely observed. A detailed view of the microstructure obtained by SEM is indicated in **Fig. 1b**.



**Fig. 1** Microstructure of the Cu-MgO material: (a) light microscopy (b) SEM prepared by FIB



**Fig. 2** The microstructure of the material Cu-3 vol.% MgO material by TEM: (a) detailed view, (b) the interaction of particles with dislocation

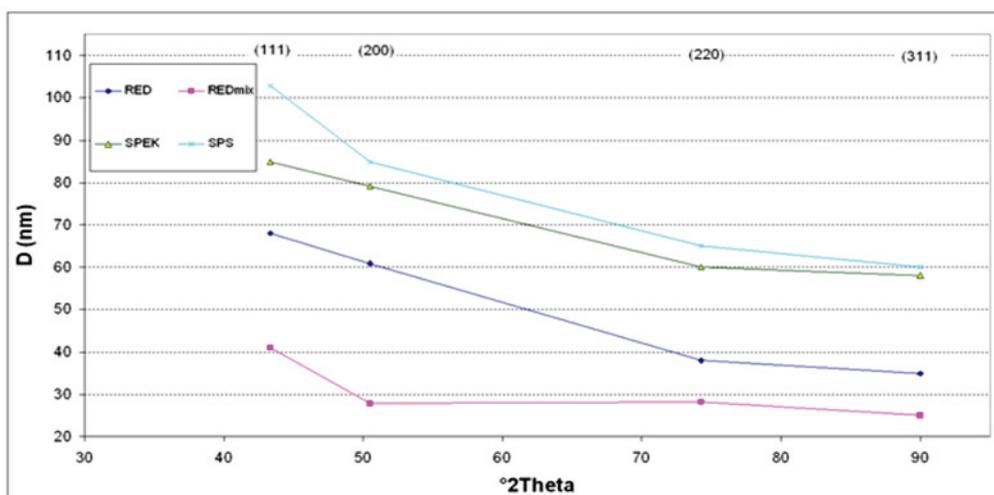
The TEM micrograph, **Fig. 2**, documents typical microstructure of the studied compact material. The microstructure of the composite can be characterized by the presence of dual grain groups. The coarser - fully

recrystallized grains **Fig. 2a** with a mean crystallite size above 1  $\mu\text{m}$  have straight, well-defined high-angle boundaries. Boundaries of non-equilibrium finely fragmented nano-grains are different curved and they are less visible. They are formed by grain fragmentation. As it is shown in **Fig. 2b**, fine particles of MgO secondary phase with sizes about 20 nm are uniformly dispersed in the Cu matrix and they are located at boundaries and inside the grains. Dislocation-particle interactions are very common, and this is clearly documented in SEM images, **Fig. 2b**. However and the same time also shows the presence of areas in which are coarser spherical MgO particles with size about 200 nm. These particles are in form of the loosely aggregated nano particles or as a large globular particles and they are located mostly at the boundaries of larger grains. These particles are formed by agglomeration and subsequently sintering of initially fine nanoparticles during powder mixture preparation, as well as in the process of compaction. Coarse particles of MgO are ineffective to ensure the thermal stability of the structure of Cu matrix by disperse strengthening mechanism.

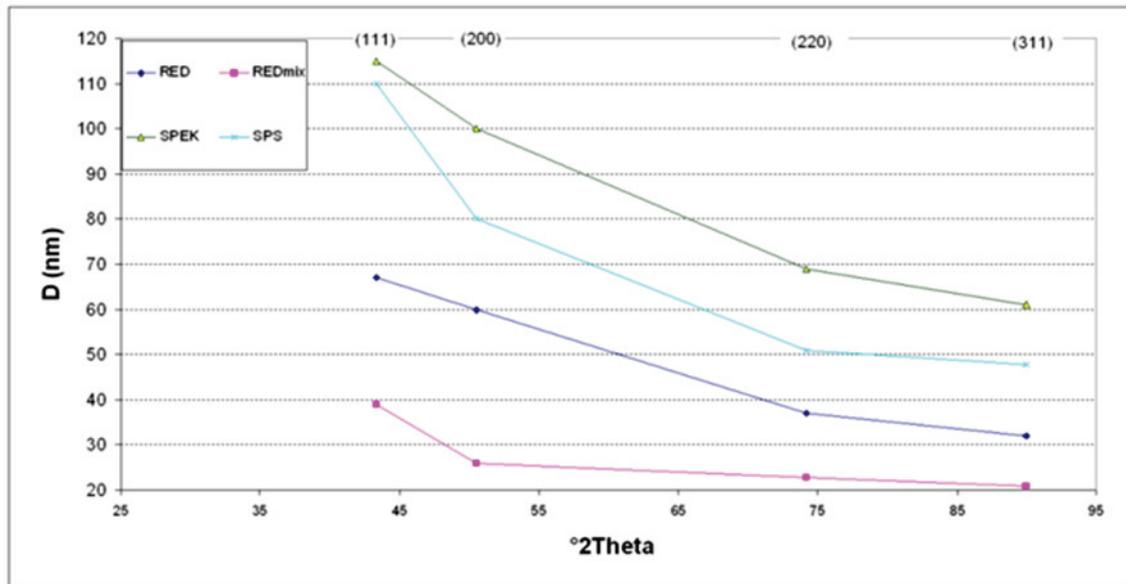
The effect of the secondary phase amount of the copper matrix crystallite size ( $D$ ) was evaluated in different stages of materials preparation. The crystallite size was calculated from the the diffraction pattern in planes (111), (200), (220) and (311). The evolution of the crystallite size was analysed after each sequential steps:

- powder after reduction (RED),
- powder after milling in a vibration mill 18Hz / 1hour (REDmix),
- after pressing and sintering at 850 ° C (SIN),
- after spark plasma sintering (SPS).

The comparison of the calculated values shows that the crystallites size changes during of the powder processing on the composite. The minimal values of crystallite size are reached after powder milling consequently a massive deformation, **Fig. 3** and **Fig. 4**. Similar changes of the crystallite size were demonstrated for the system Cu-Al<sub>2</sub>O<sub>3</sub> in the works [13], [14]. The consolidation process leads to structural changes. The crystallites size of Cu matrix increases as a consequence of heat-initiated processes as diffusion and recrystallization during sintering. From comparison of the crystallites size after milling and the consolidation results that the crystallites size increases in material with 3 vol.% MgO from 39 nm to 115 nm and in Cu-5 vol% MgO material from 41 nm to 102 nm. The maintaining of the nanostructure of the starting powder after the thermal exposure is very important owing to achieve the unique properties of the final product [15], [16].



**Fig. 3** Crystallite size of the material Cu 3 vol.% MgO material after various stages of preparation for the plane (111), (200), (220) and (311)



**Fig. 4** Crystallite size of the material Cu 5 vol.% MgO material after various stages of preparation for the plane (111), (200), (220) and (311)

#### 4. CONCLUSION

The experimental results indicated that the addition of MgO secondary phase in the copper matrix is suitable. The increase of the Cu grain size in both materials (3 and 5 vol. % MgO), after the heat treatment could be related with the non-homogeneous distribution of dispersoid particles and particles agglomeration. The appropriate solution of this problem is creation of only effective dispersoid particles and reduction in volume fraction of particles of the secondary phase. For the preparation of ultrafine powder mixture the intensive mechanical milling attritor is suitable, which will provide adequate fineness of the particles and the uniform distribution of dispersoid in the matrix.

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