

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF NANOCRYSTALLINE DISPERSION STRENGTHENED COPPER

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Abstract

The study compares the evolution of the microstructural characteristics of dispersion strengthened Cu–3 vol. % MgO and Cu–3 vol. % Al₂O₃ composites. Aim of the investigation is to analyse the influence of the two different oxide dispersoids on the stabilization of the copper nanostructure after thermo-deformation processing of powder into a compact. Investigated were structural stability of the materials at elevated temperatures and tensile properties. The results indicate that alumina particles more effectively strengthen the Cu matrix and that the choice of a suitable dispersoid for a given matrix is one of the deciding factors for thermal stabilization of the nano-grains.

Keywords: *nanocrystalline copper composite, oxide dispersion strengthening, Cu–MgO, Cu–Al₂O₃, dispersoid, microstructure, thermal stability, tensile properties*

INTRODUCTION

Nanocrystalline dispersion strengthened copper alloys are particularly attractive for high temperature applications in electrotechnical industry due to excellent thermal stability of microstructure and combination of high strength and conductivity over a wide range of temperatures. Thermodynamically stable, fine (< 50 nm) oxide secondary particles – dispersoids uniformly distributed inside the copper matrix grains and at grain boundaries contribute significantly to stabilization of the microstructure and strengthen the material by an attractive direct interaction of the particles with moving dislocations. In addition, a good wettability between the particulate and the matrix and a suitable interface particle/matrix bonding strength are thought to be major factors controlling the properties of the composites.

The study is centred on the comparison of the microstructural evolution in the Cu–MgO and Cu–Al₂O₃ composites after processing of the nanocrystalline powders into macroscopic compacts and thermal loading of the solids at elevated temperatures. Aim of the investigation is to analyse the influence of the two different oxides on the strengthening of the copper matrix nanostructure.

MATERIAL PREPARATION AND METHODS

The initial Cu–3 vol.% of MgO and Cu–3 vol.% of Al₂O₃ powders were prepared by the in situ thermo-chemical technique and high energy mechanical milling. The preparation method resulted in the formation of nanocrystalline powders with the average Cu crystallite size of 9-15 nm both in the Cu–MgO and Cu–Al₂O₃ mixtures. In our previous reports [1,2] there are detailed studies on the formation of the composites in this way.

Both the powders were processed by a modified conventional procedure into bar form. The consolidation consisted of pressing at 150 MPa in a protective atmosphere,

sintering in H_2 at $850^\circ C$ for 1h, forging and subsequent extrusion at $950^\circ C$ with a 95% cross-section area reduction. In order to preserve their unique properties, consolidation of nanocrystalline powders into fully dense material requiring elevated temperatures/elevated pressures must not destroy their initial nanostructure. Therefore, stabilization of the nanocrystalline structure already in the powder by a dispersion strengthening mechanism and also further heat treatments are of critical importance.

The powders and the samples prepared from the extruded bars were analyzed. The evolution of the nanostructure was examined by light microscopy, transmission electron microscopy (TEM), as well as X-ray diffraction (XRD) using Cu $K\alpha$ radiation. The crystallite/grain size was determined by the well-known Scherrer formula [3]. Structural stability after 1h annealing of the samples in H_2 at 200 at $900^\circ C$ was tested indirectly, by Brinell hardness measurements. Tensile testing was carried out at room temperature on an universal test machine Tiratest 2 300 at a crosshead speed of 2 mm min^{-1} .

RESULTS AND DISCUSSION

The XRD patterns in Figs.1 and 2 and the data in Table 1 demonstrate the obvious changes of relative intensities of the (111), (200) and (220) copper peaks which have occurred by compacting of both the Cu-MgO and Cu- Al_2O_3 composites, compared with the initial powders. They confirm the formation of a deformation texture in both the as-extruded materials. The absence of MgO and alumina peaks may be due to their very low contents, fine particle size and low crystallinity of the dispersoids prepared by the sol-gel processes. The consolidation process has caused also a movement of the interfaces and the nanocrystalline Cu-MgO powder matrix has changed into an inhomogeneous nanocrystalline/ultrafine grained compact matrix (Table 1). On the other hand, the changes in the average crystallite size of the Cu- Al_2O_3 powder and the compact reveal that the densification has resulted in some coarsening of the structure, but the newly formed grains have remained in the nanometric range, Table 1.

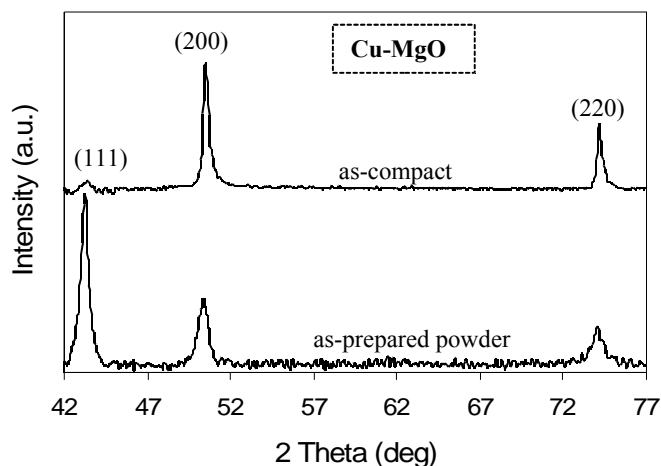


Fig.1. Comparison of the XRD patterns for the Cu-MgO composite.

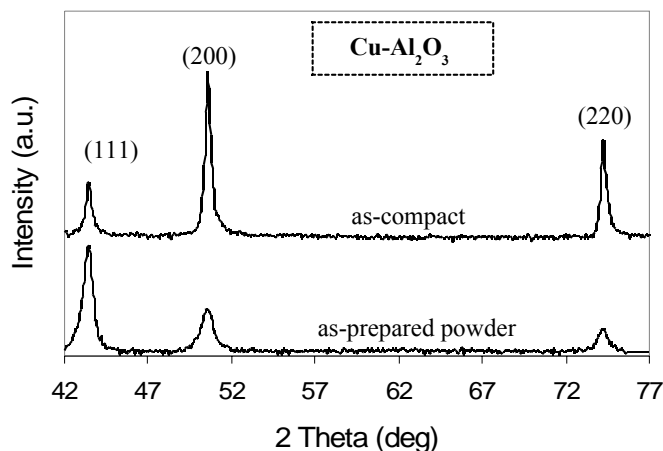


Fig.2. Comparison of the XRD patterns for the Cu–Al₂O₃ composite.

Tab.1. Changes of relative intensity I_{rel} of the Cu peaks and crystallite sizes D after compaction of the powders.

	(111)		(200)		(220)	
	I_{rel} [%]	D [nm]	I_{rel} [%]	D [nm]	I_{rel} [%]	D [nm]
Cu-MgO powder	100	14	45	10	32	9
Cu-MgO compact	6	>150	100	46	55	107
Cu-Al ₂ O ₃ powder	100	15	45	9	25	9
Cu-Al ₂ O ₃ compact	36	24	100	31	59	26

The general metallographic microstructure of the Cu–MgO composite shown in Fig.3(a) is characterised by a bimodal grain size distribution. TEM analyses reveal that the inhomogeneous microstructure consists of micrometer-sized grains embedded inside a matrix of nanocrystalline/ultrafine grains, Fig.3(b). The grains are often fragmented into a fine dislocation cell substructure. The MgO particle size is in the wide range from 15 to 250 nm. The very fine particles are at the cell boundaries and inside the grains. The coarse oxides are located mostly at the boundaries of larger equilibrium grains and they are in the form of loosely clustered nano-MgO particles or as a large globular MgO particle. The particle-dislocation interactions are frequent. On the other hand, the metallographic microstructure of the Cu–Al₂O₃ composite in Fig.4(a) is homogeneous with a high fraction of the interfaces. The detailed TEM microstructure in Fig.4(b) documents polygon grains of copper matrix with a size in the 100 to 500 nm range. The grains are finely fragmented and they consist of dislocation cell interiors. The cell size is in accord with the crystallite size measured by XRD. The Al₂O₃ particles from 20 to 50 nm in diameter are uniformly dispersed over the whole matrix and the particle-dislocation interactions are very frequent.

The Cu–MgO composite hardness is only 90 HB, and decreases above 200°C, Fig.5. The decrease in the range 200–400°C takes place due to the recovered and partially recrystallized grains of the initial nanocrystalline matrix. The constant hardness between 400 and 500 °C can be explained by the presence of recrystallized grains which do not grow due to the dispersoids. Above 500°C, a further softening starts as a result of the abnormal grain growth (secondary recrystallization). The very good initial Cu–Al₂O₃

hardness of 160 HB exhibits no/minor hardness changes after annealing and cooling to room temperature, thus suggesting an excellent thermal stability of the microstructure over the examined temperature range, Fig.5.

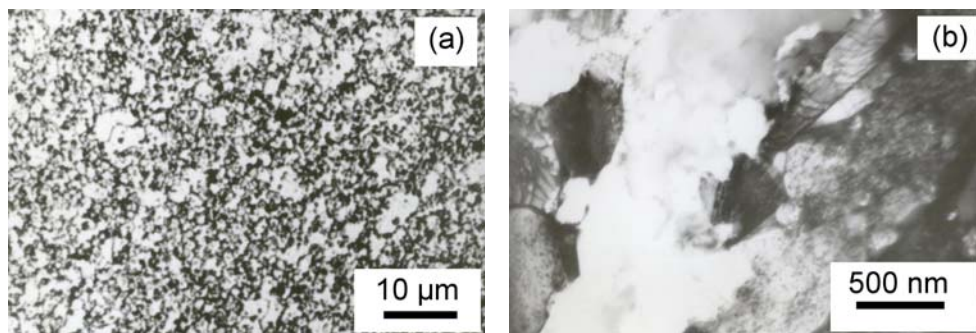


Fig.3. The Cu–MgO microstructure with bimodal grain size distribution: (a) general microstructure and (b) detailed TEM microstructure.

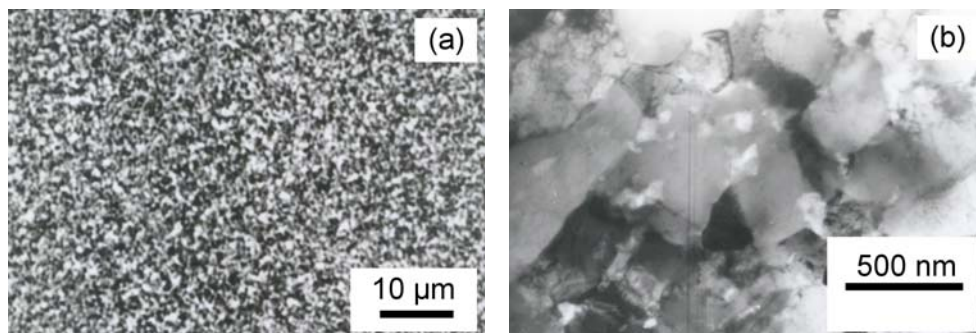


Fig.4. The homogeneous Cu–Al₂O₃ microstructure: (a) general microstructure and (b) detailed TEM microstructure.

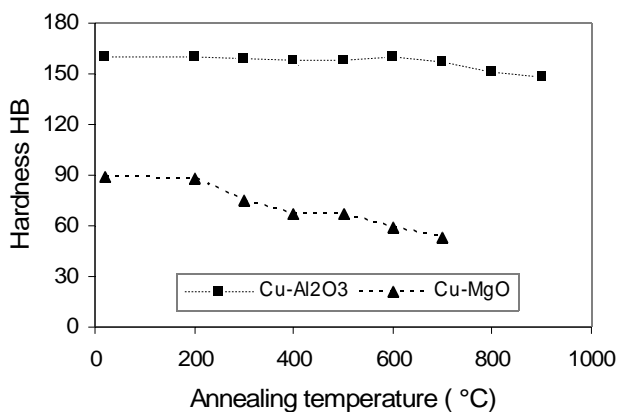


Fig.5. Brinell hardness of the Cu–MgO and Cu–Al₂O₃ materials after 1 h annealing in H₂ at different temperatures.

The tensile test results of both the experimental materials are summarized in Table 2. The Cu–Al₂O₃ nanocomposite shows very good strength due to the dispersion strengthened copper grains ranging from 24 to 31 nm (see Table 1). The ductility is low, only 2 %, which is the usual value for nanomaterials with an homogeneous structure. On the other hand, the reduced strengths of Cu–MgO, compared to the Cu–Al₂O₃ result from a coarser microstructure with the grain sizes from 46 to over 150 nm (Table 1). A good uniform elongation of 22% is attributed to the bimodal microstructure in the copper matrix which stabilizes tensile deformation, because reduction of the dislocation density in the micron-sized grains increases the strain-hardening capacity of the composite.

Tab.2. Comparison of the mechanical properties and hardness.

	Yield strength [MPa]	Ultimate tensile strength [MPa]	Ductility [%]	Brinell hardness HB
Cu – MgO	145	240	22	90
Cu – Al ₂ O ₃	397	436	2	160

The compaction of the Cu–Al₂O₃ and Cu–MgO powders with comparable nanocrystalline structures has resulted in materials with different structures. The homogeneous, thermally stable structure with the nanometric grain size was formed in the Cu–Al₂O₃ compact. The Al₂O₃ nanoparticles uniformly distributed in the matrix powder [3] remained fine and dispersed also in the compact. They play a key role in the process of subgrains/grains stabilization at elevated temperatures by inhibiting dislocations movements as well as by suppressing diffusion needed for matrix grain growth. The enhanced hardness and strength result from the nanostructure. In the Cu – MgO compact clustering and subsequent agglomeration of a portion of the originally fine secondary particles [1], into particles with above 50 nm size, has occurred during the densification. The coarse particles do not strengthen the grain boundaries, which has affected the microstructural evolution and consequently the strength and hardness of the composite.

As can be seen, the selection of a suitable dispersoid type in relation to the matrix is very important. Detailed analysis of the Cu/Al₂O₃ interface investigated by the authors [4,5,6] indicates creating of a third phase such as CuAlO₂ and/or CuAl₂O₄ in the material and the spinel phase forms a strong bond at the interfaces. The chemical interaction between Cu and MgO does not occur [1,7]. The result is a poor particle/matrix bond strength. In both the Cu–Al₂O₃ and Cu–MgO materials the interfacial shear stress rises during sintering and hot extrusion at 950 C. This will continue until sliding occurs at the interface, which can cause debonding of the dispersoid. The weak Cu/MgO interface will break at a relatively lower temperature than the stronger Cu/Al₂O₃. The “disconnected” MgO can be shifted, clustered and agglomerated into particles with sizes above 50 nm and, as a result, these coarser dispersoids will not hinder the recrystallization processes.

The important factor supporting a quality interphase coupling at temperature change is an absolute difference $\Delta\alpha$ of thermal expansion coefficients. The difference causes the misfit strains at the interface and induces thermal stresses capable of influencing the microstructural stability and mechanical properties. The high temperature strengthening by particle-dislocation interaction is more effective when the interface provides the highest stress relaxation and thus produces the greatest inhibition to dislocation motion. From this point of view the alumina dispersoid is preferable to MgO, because the $\Delta\alpha$ value for the Cu/Al₂O₃ is sufficient, but for the Cu/MgO interface is too small ($\alpha_{Cu} = 17.3 - 20.9 \times 10^{-6} K^{-1}$, $\alpha_{MgO} = 12 - 17.3 \times 10^{-6} K^{-1}$ and $\alpha_{alumina} = 7 - 8 \times 10^{-6} K^{-1}$).

CONCLUSIONS

The selection of a suitable dispersoid type in relation to the matrix is one of the deciding factors for thermal stabilization of nano-grains. The uniformly distributed Al_2O_3 nano-particles with a good bond to Cu fulfil their main role - to limit grain growth and maintain it in the nanometric size during thermo-deformation processing of the powder into a compact. They ensure excellent structural stability of the material at elevated temperatures.

Acknowledgement

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