JOURNAL OF MATERIALS SCIENCE **36** (2001) 3675–3678

Preparation of nanocrystalline Cu-xMgO mixture

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Nanocrystalline dispersion systems on the Cu-base belong to the progressive materials that have particularly found their applications in the fields that place demands, besides specific physical and chemical properties of copper (electrical conductivity, thermal conductivity), on improved mechanical properties or on the resistance of mechanical properties against thermal degradation. The process of the formation of the secondary phase in the preparation process, as well as its stability after reduction of the CuO-MgO system to the Cu-MgO system are studied in the presented paper. © *2001 Kluwer Academic Publishers*

1. Introduction

Pure ultra-fine materials are noted for their high thermodynamic instability caused by the accumulation of free energy at the grain boundaries. It can therefore be expected that a reduction in the grain boundary energy will take place at relatively low temperatures [1]. A basic pre-condition for maintaining a fine, thermally stable structure is establishing such conditions in the system that will prevent the migration of the interfaces. Dispersion strengthening using the optimum amount of fine and uniformly distributed strengthening particles of the secondary phase (dispersoid) in the matrix is one of the most advantageous methods that ensure the thermal stability of the interfaces and contribute to the improvement of the mechanical properties of the compact material [2].

Nanocrystalline dispersion systems on the Cu-base belong to the progressive materials that have particularly found their applications in the fields that place demands, besides specific physical and chemical properties of copper (electrical conductivity, thermal conductivity), on improved mechanical properties or on the resistance of mechanical properties against thermal degradation [3, 4]. The nanocrystalline dispersion system Cu-MgO is noted for a high stability of the secondary phase formed by MgO particles, as well as by a possibility of its relatively simple and environmentally friendly preparation. In technical literature we did not find, any references to the investigation of nanocrystalline copper dispersion-strengthened with MgO have been made.

In the preparation process, the nanocrystalline CuO-MgO system represents a mechanically alloyed precursor for the dispersion Cu-MgO system. The process of the formation of the secondary phase in the preparation process, as well as its stability after reduction of the CuO-MgO system to the Cu-MgO system are studied in the presented paper, using the methods of X-ray diffraction analysis, infrared spectroscopy (IR), differential-thermal analysis (DTA) and thermogravimetric analysis (TG).

2. Experimental procedure

CuO was prepared by annealing electrolytic copper powder (Kovohuty Krompachy, 99,7%) at 800°C in air. The oxidation reactions are expressed by Equations 1 and 2 [5]:

$$2\mathrm{Cu} + \mathrm{O}_2 \rightarrow 2\mathrm{CuO} \quad \Delta H_{25} = -155,3\ \mathrm{kJ/mol} \qquad (1)$$

$$4\mathrm{Cu} + \mathrm{O}_2 \rightarrow 2\mathrm{Cu_2O} \quad \Delta H_{25} = -166,8\ \mathrm{kJ/mol} \qquad (2)$$

The formation of CuO and a fraction of Cu_2O can take place during oxidation, therefore the conditions of Cu oxidation (oxidation temperature, time) were optimized in such a way that the full conversion of Cu into CuO could be ensured. MgO was added to CuO by the crystallization of magnesium hydrogen carbonate (hydromagnesite) from the CO_2 supersaturated aqueous solution of $Mg(HCO_3)_2$ [6], according to the Equations 3 and 4:

$$\text{dissolution}: \mathrm{MgO} + \mathrm{H_2O} + 2\mathrm{CO_2} \rightarrow \mathrm{Mg(HCO_3)_2} \qquad (3)$$

$$\text{crystallization}: \mathrm{Mg(HCO_3)_2(aq)} \rightarrow x \cdot \mathrm{MgCO_3} \times \mathrm{Mg(OH)_2} \cdot y \cdot \mathrm{H_2O} + \mathrm{H_2O} + \mathrm{CO_2} \qquad (4)$$

The stability of the $Mg(HCO_3)_2$ decreases by expelling of the excessive CO_2 by heating of the solution and crystallization of the non-stechiometric magnesium hydrogen carbonate (hydromagnesite) $x \cdot MgCO_3 \cdot Mg(OH)_2 \cdot y \cdot H_2O$ takes place.

The mixture of CuO with a 10 vol.% MgO (CuO10MgO) was prepared by high-energy milling brittle oxidic matrix (CuO) with the addition of MgO phase that represented the dispersoid. The CuO10MgO mixture, with a particle size <100 nm, was prepared by wet milling CuO with crystallised hydromagnesite in the attritor (co. Netzsch, type PR 1 S) at 400 rpm for 8 hours. After milling, the mixture was dried at a temperature 120°C for 6 hours.

A reference mixture of CuO + MgO (mole ratio 1 : 1, CuO_MgO) was prepared for obtain more accurancy analysis of the qualitative changes in the CuO-MgO system during preparation. The reference mixture was prepared by continuously mixing by slowly crystallized hydromagnezite in powder CuO during drying. The mixture was then partially homogenized in a mortar. Both the mixtures were then annealed at 800°C for 1 hour in air and consequently they were reduced at 360°C for 1 hour in an atmosphere of 25% vol. $H_2/75\%$ vol. N_2. The mixtures were analyzed by the methods of X-ray diffraction and infrared spectroscopy in each stage of the preparation process.

In the X-ray diffraction analysis, the range of $2\theta \sim 30$–80° was used in which the diffraction of the CuO crystallite planes (002), $(\bar{1}11)$, (111), (200), $(\bar{2}02)$, $(\bar{1}13)$, $(\bar{3}11)$ and $(\bar{2}20)$ can be measured. It should be stated that the planes (002), $(\bar{1}11)$, as well as (111), (200), have the positions of their diffraction maximums practically identical (the diffraction maximums are overlapping) and they are not distinguished apart in the X-ray spectra of the measured samples. The background formed by the diffusion X-ray radiation of the sample and the radiation resulting from the design of the measuring device was appropriately eliminated from the diffraction spectra. The diffractions from Cu $K_{\alpha 2}$ component of the radiation was deducted from the spectra using the Rachinger method [7, 8] and the Cu $K_{\alpha 1}$ diffractions were only evaluated.

IR analysis of the samples was carried out by the KBr technique (400 mg KBr + 1 mg sample, Carl-Zeiss Jena SPECORD M80). Infrared spectroscopy has a lower detection limity than X-ray analysis and a lower dependence of the band shape on the particle size.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the X-ray diffraction spectra of CuO after oxidation of the Cu and the CuO_MgO mixture before and after annealing at 800°C in air. As it is confirmed by phase analysis, in the cases of the oxidized Cu and the CuO_MgO mixture before annealing the diffraction spectra are only formed by the reflections of the copper oxide. In both the spectra, the presence of the Cu_2O fraction was not confirmed. In the XRD spectrum of the CuO_MgO mixture before annealing, phase analysis confirmed the full conversion of the initial MgO. In the spectra of the CuO_MgO mixture after annealing, distinct diffraction maximums are observable of the planes (200), (220) of MgO formed by decomposition of hydromagnesite.

Fig. 2 shows, the X-ray diffraction spectra of the mixture of the initial CuO and CuO10MgO after milling and the subsequent annealing at 800°C in air. In the spectrum of the CuO10MgO sample after annealing at 800°C for an hour (in comparison with the mixture CuO_MgO), no reflections from the planes of MgO were observed (the detection limit of the occurring phases using X-ray phase analysis in coarse-grained materials is above 5 vol. % in the analyzed mixture). Probable reasons for this difference are a very small particle size of MgO, as well as a high homogeneity of distribution of this dispersion phase in the volume of material formed by CuO particles.

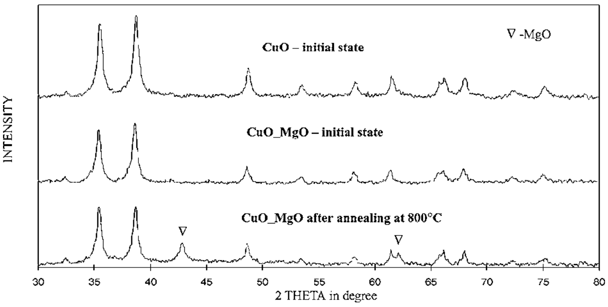

Figure 1 X-ray spectra of CuO_MgO mixture during processing.

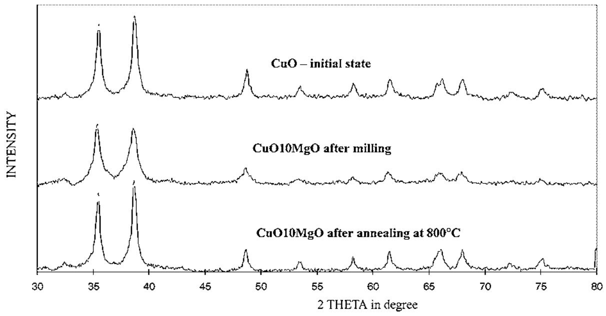

Figure 2 X-ray spectra of CuO10MgO samples during processing.

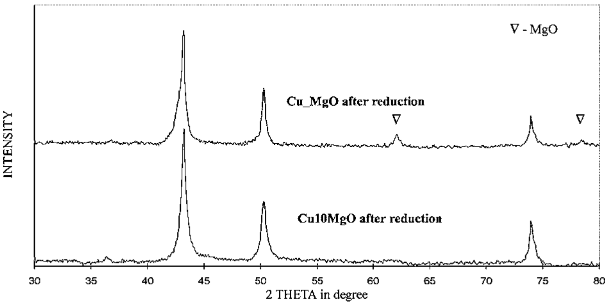

Figure 3 X-ray diagrams of CuO10MgO and CuO_MgO samples after reduction at 360°C/1 hour in hydrogen.

In Fig. 3, the X-ray spectra of the mixture of the Cu_MgO dispersion system and Cu10MgO after reduction of its precursors at 360°C for 1 hour in the atmosphere of 25% vol. $H_2/75\%$ vol. N_2 are shown. Diffraction pattern corresponding to the reflections of the crystalline planes of copper.

The reflections corresponding to the planes (220), (222) of the MgO were only found in the spectrum of Cu_MgO, while they were not observed in the spectrum of the Cu10MgO. This fact is in accordance with the results of analysis of the spectra in Figs 1 and 2. X-ray diffraction analysis did not confirm the presence of other phases that could arise by interaction of the copper matrix and the particles of the MgO dispersoid.

The Voigt deconvolution method [9] was used to determine the size of the diffraction of the coherent areas (crystallites). This method allows estimate crystallites size and stresses influence on broadening of diffraction profile separately. After excluding of stress influence on broadening profile the crystallite size of the milled Cu10MgO mixture was estimate on 30 nm.

In the diagrams of differential thermal analysis (DTA) of the CuO_MgO mixture (Fig. 4) endoeffects can be observed with the maxima 260°C, 410°C and

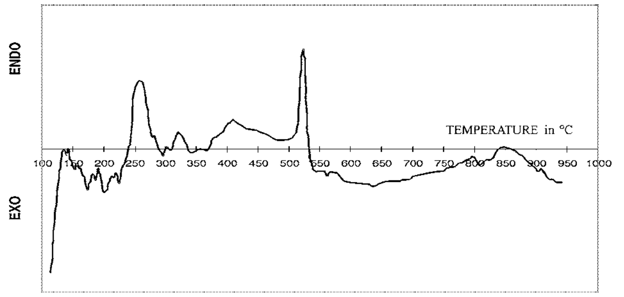

Figure 4 DTA diagram of CuO_MgO system.

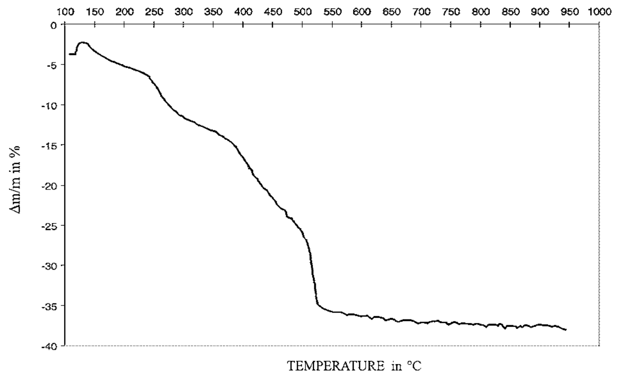

Figure 5 TG diagram of CuO_MgO mixture.

520°C, which corresponds with the weight losses in the TG curve (Fig. 5). It is obvious that the mentioned curves characterize the decomposition of hydromagnesite, while at 550°C practically no changes occur in the weight of the system, and up to the temperature of 900°C no thermal effect was recorded in the DTA curve. Thus, DTA analysis of the CuO_MgO mixture did not confirm the formation of other phases arising by the interaction of CuO and MgO up to 900 °C.

3.2. Results of infrared spectroscopy

Fig. 6 shows the IR spectra of the CuO_MgO mixture after aggitation (Fig. 6a.) and after annealing at 800°C (Fig. 6b). The comparison of the spectra in Fig. 6a and b reveals that the full decomposition of hydromagnesite (the loss of the carbonate doublet in the region of wave numbers 1400–1500 cm^{-1}) takes place during annealing at 800°C. The band in the region from 800–300 cm^{-1} is also modified. The band within the region of 800–300 cm^{-1} corresponds to vibrations of CuO and MgO (Fig. 7) - CuO (Fig. 7e) is characterized by multiple band with the maximum at 500 cm^{-1}, MgO (Fig. 7f) is represented by the spectrum composed of two bands with different intensities and half-widths with the maximums at approximately 615 cm^{-1} (the band with a lower intensity) and 420 cm^{-1} (the peak with approximately double intensity). IR analysis of the spectra of the non-milled CuO_MgO mixture (Fig. 7a–c) confirms the fact observed in the spectra in Fig. 6, that the IR spectrum of the CuO_MgO mixture (Fig. 7b) is simplified by decomposition of hydromagnesite during calcination. The IR spectrum of annealed CuO_MgO mixture (Fig. 7a) represents the superposition of the spectra of CuO (Fig. 7e) and MgO (Fig. 7f). The position of the maximum of the band at the wave number of 430 cm^{-1} remains unchanged even after reduction of calcinate (Fig. 7c). The intensity of the band significantly decreases around the wave number of 500 cm^{-1}, which corresponds with reduction of CuO. The IR spectrum of the CuO_MgO mixture after annealing and reduction (Fig. 7c) is characterized by two bands with the maximums at approximately 615 cm^{-1} and 440 cm^{-1}. By linear approximation of the base line, the measured out peak heights at maxima of bands correspond with a ratio of approximately 1 : 2. The hard-reducible MgO is kept in the mixture with negligible interaction with the Cu-matrix after reduction of the CuO_MgO precursor. This result is in accordance with the results of X-ray analysis. A similar situation can be observed in Fig. 7d where the IR spectrum of the milled CuO10MgO mixture after reduction is shown. It is obvious from Fig. 7d that fine MgO particles occur in the Cu matrix which cannot be determined by X-ray analysis. However, the MgO spectrum is not very intensive (low content of MgO) and it is significantly deformed by the shift of the base line.

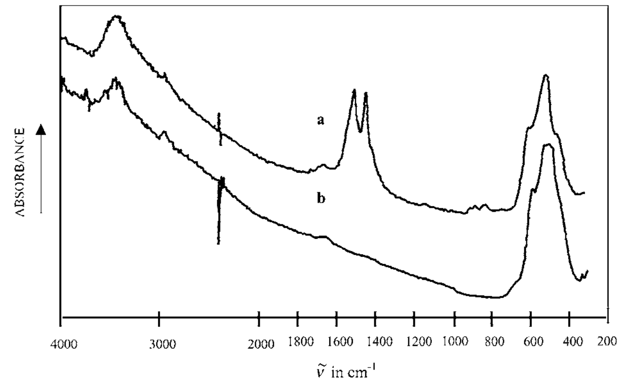

Figure 6 IR complete spectra of CuO_MgO mixture after agitation (**a**), after annealing at 800°C (**b**).

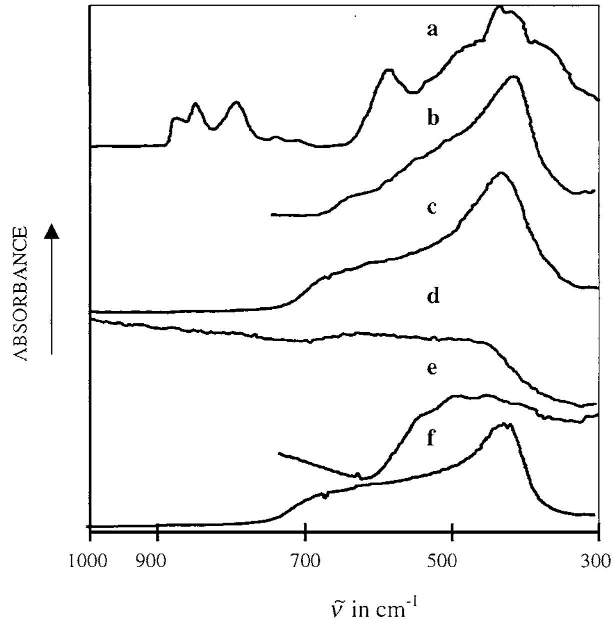

Figure 7 IR details of the spectra of CuO_MgO mixture after agitation (**a**), after annealing at 800°C (**b**), after reduction at 360°C in hydrogen (**c**), CuO10MgO after 8 hours of milling, annealing and reduction at 360°C in hydrogen (**d**), CuO non-milled state (**e**), MgO after decomposition of hydromagnesite at 800°C (**f**).

4. Conclusions

The results of the presented work can be summarized into the following points.

1. By high-energy milling of the CuO10MgO oxidic precursor, nanocrystalline mixtures were prepared with the crystallite sizes of about 30 nm.
2. In the CuO_MgO mixture, the presence of the MgO dispersion phase by the decomposing of hydromagnesite was demonstrated using X-ray diffraction analysis. The XRD phase analysis of the CuO10MgO mixture did not confirm the presence of the MgO phase (which has been found by IR spectroscopy), which is probably caused by a small particle size of MgO and a high homogeneity of distribution of this phase in the CuO matrix.
3. XRD phase analysis, IR analysis and DTA analysis of both mixtures did not confirm the presence of phases arising by the interaction of the CuO matrix and the MgO dispersoid either after calcination of the precursor at 800 °C or after its reduction at 360 °C.

Acknowledgements

The work arose with the support of The Scientific Grant Agency of the SR within the investigation of the project No. 2/5164/98.

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Received 27 June 2000
and accepted 28 March 2001