Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 24
ISSUE 2
October
2007

Microstructure and properties of nanocrystalline copper - yttria microcomposites

J.P. Stobrawa [a,b,*], Z.M. Rdzawski [a,b], W.J. Głuchowski [b]
[a] Division of Materials Processing Technology, Management and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
[b] Non-Ferrous Metals Institute, ul. Sowińskiego 5, 44-100 Gliwice , Poland
* Corresponding author: E-mail address: wojtekg@imn.gliwice.pl

Received 28.03.2007; published in revised form 01.10.2007

Materials

ABSTRACT

Purpose: The objective of the work was to investigate changes in structure and properties of Cu – yttria microcomposites which take place in the process of controlled sintering and deformation of materials of nanometric initial structure.
Design/methodology/approach: Tests were made with the Cu-yttria micro-composites containing up to 3 % of a hardening phase. These were obtained by powder metallurgy techniques and further deformation. The mechanical properties and microstructure (by the optical, scanning and transmission electron microscopy) were examined.
Findings: Analysis of the initial nanocrystalline structure of these materials was made, and its evolution during deformation process was investigated with an account of the changes in the mechanical and electrical properties.
Research limitations/implications: The powder metallurgy techniques make it possible to obtain copper-based bulk materials. Globular structure, high porosity and low sintering temperature of this materials result in their limited mechanical properties.
Practical implications: A growing trend to use new copper-based functional materials is observed recently world-wide. Within this group of materials particular attention is drawn to dispersion hardened microcomposities with nanometric or submicron grain size of a copper matrix, which exhibit higher mechanical properties.
Originality/value: A controlled process of milling compacting, sintering and cold deformation, allow to obtain nanocrystalline copper based materials with improved functional properties.
Keywords: Nanomaterials; Functional materials; Metallography

1. Introduction

Besides high mechanical properties and high electric and thermal conductivity it is more often required that properties of the copper alloys remain stable during their use at elevated temperature. The dispersion – hardened materials, usually by the particles of oxide and carbide phases, obtained by powder metallurgy techniques, are becoming increasingly frequently used for such applications [1-5]. Within this group of materials particularly promising are those of nano - metric size of the matrix hardening phase grains [6-10]. This paper is concentrated on this problem. Investigation into fabrication, properties and microstructure of a copper matrix, dispersion - hardened with yttria, microcomposites are presented.

2. Experimental procedure

The tests were made with Cu – (1,2 and 3 wt.Y_2O_3) microcomposites. These were obtained by powder metallurgy technique, i.e. milling the input powders in the planetary ball mill, compacting and sintering. The mixtures of powders of electrolytic copper and hardening phase were subjected to milling in a ball planetary mill (250 ml containers with 50 balls 10 mm in diameter). After preliminary milling tests the following optimal parameters of the process, suitable to obtain nanometric size of the powder grains, were established: rotary speed of 250 rev/min and milling time – 30 hours. Milling was performed in the atmosphere of argon and methanol. From the obtained powder mixtures solid samples were prepared for compression tests, microstructure examination and for density, hardness and electrical conductivity measurements. Low-temperature sintering at 550 - 570^{O}C for 1 hour was applied and next, the samples were subjected to sizing. The compression tests were made using the Instron test machine at a speed of the cross-head of 1 mm/min. The plastic samples, which had not been damaged before, were subjected to the upsetting test conducted until a true strain of about 0,8 was reached.

Nanostructure of the alloy powders and sintered samples was examined using LEO 1525 scanning electron microscope and JEM 2000 FX analytical transmission microscope linked with the Oxford Instruments' ISIS facility for chemical composition micro-analysis in micro-areas.

3. Results and discussion

Results of the examination of microstructure of the input powders have shown that size of electrolytic copper particles along the main axes of the dendrites was of an order 10-20 µm, and the length of arms and branches ranged from fractions to ten µm. The grains of yttria powder were more regular and their average size was of an order of a micrometers.

During milling the mixtures of copper and yttria powders were disintegrated (fig. 1). It is seen in Fig. 1a and 1b that disintegration was very effective and spherical like or polyhedral nanoparticles were obtained. These are mainly monocrystalline particles and their size ranged from 10 to 190 nm.

After milling in a planetary mill, followed by compacting and sintering, the powder samples were taken for the examination of structure and mechanical properties. The results obtained have been presented in figs. 2 and Table 1.

Figs. 2 shows microstructure of the alloys after sintering. During low-temperature sintering process, grains of a matrix remain stable (Figs 1 and 2). The grain size measurements showed that an average grain size over the whole alloy volume is clearly shifted towards lower values. This apparent reduction of a grain size over the material volume results from the fact that thickness of the most of the particles in a powdered material is smaller compared to the measured values on the photo – plane.

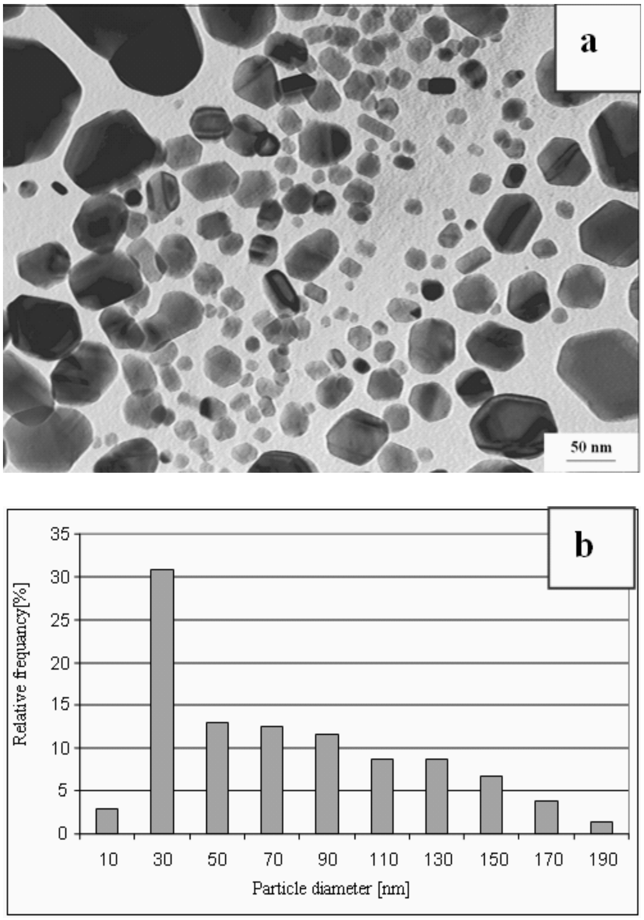

Fig. 1. The Cu+ Y_2O_3 particles after disintegration in a planetary ball mill; a – TEM, b – grains size distribution

The investigations results have shown (Table 1) that it is the difficulty of compacting to high densities, avoiding retained porosity, and at the same time ensuring good powder particle bonding for investigated materials. Agglomeration is a definite problem in consolidated nanopowders.

Results of hardness, density and electrical measurements for the sintered samples are shown in Table 1. The obtained hardening effect (in comparing with hardness of nanocrystalline copper) exceeds 30 and 47% in the Cu - 1% Y_2O_3 and Cu - 2% Y_2O_3 alloys respectively. The obtained mechanical properties appeared to be much lower than expected from the Hall – Petch relationship and Orowan mechanism [11 – 13]. Particularly small was an effect of nanocrystalline size of the matrix grains. Similar results were obtained for Cu – WC microcomposites [14, 15] Electrical conductivity of these materials (as it was expected) is lower than in nanocrystalline copper (table 1). Decrease is ranged from 30 to 50%.

In table 2 values of 0,2 yield strength and elongation after compression test have been presented.

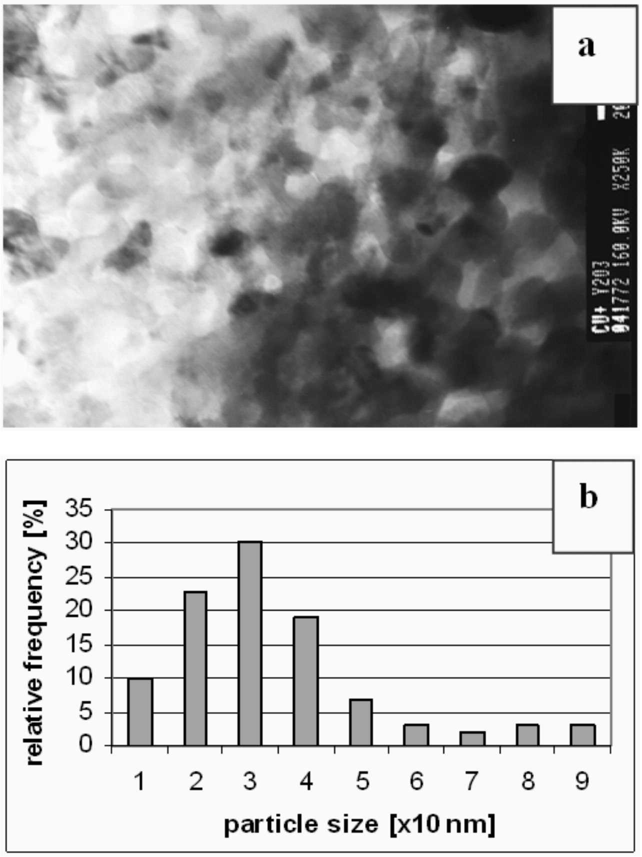

Fig. 2. Microstructure of the Cu+ Y_2O_3 alloys after sintering; a – TEM, b – grains size distribution

Table 1.
Density, microstructure parameters and hardness of the sintered materials

Material	Hardness HV	Electrical Conductivity [MS/m]	Density [g/cm^3]
Cu	55	49,00	7,77
Cu-Y_2O_3 (1%)	72	32,17	7,72
Cu-Y_2O_3 (2%)	76	34,15	7,65
Cu-Y_2O_3 (3%)	81	23,85	7,41

This results show that with the increase of the yttria content in a nanocrystalline matrix the yield strength YS0,2 also increases. It is worth noting that in the materials containing up to 1 % of a hardening phase this increase can be reached with no harm for the material plasticity. It is easily possible to obtain in these materials a true strain of an order of 0.8 and a high strength . However, at higher content of yttria (2 %) a yield strength increase is accompanied by clear decrease in plastic properties. The Cu – 3% yttria materials become brittle and their strength becomes increasingly lower. Due to low plasticity it is difficult to additionally harden them by cold working.

Table 2.
Values of yield point and elongation obtained in compression test.

Material	$R_{0,2}$	Ac [%]
Cu	102,5	-55,7
Cu-Y_2O_3 (1%)	189,5	-46,3
Cu-Y_2O_3 (2%)	190,0	-18,0
Cu-Y_2O_3 (3%)	Brittle	

Table 3.
Values of density, hardness and electrical conductivity after compression test

Material	Hardness HV	Electrical Conductivity [MS/m]	Density [g/cm^3]
Cu-Y_2O_3 (1%)	114	43,5	8,37
Cu-Y_2O_3 (2%)	118	38,8	8,25
Cu-Y_2O_3 (3%)	116	35,5	8,11

Evolution of a structure during deformation of these materials was investigated. Results of these investigations are shown in Figs 3 and 4. A typical, high density fibrous microstructure is seen in Fig. 3, which results mainly from deformation of powder agglomerates during compression tests of Cu-Y_2O_3 (1%) material.

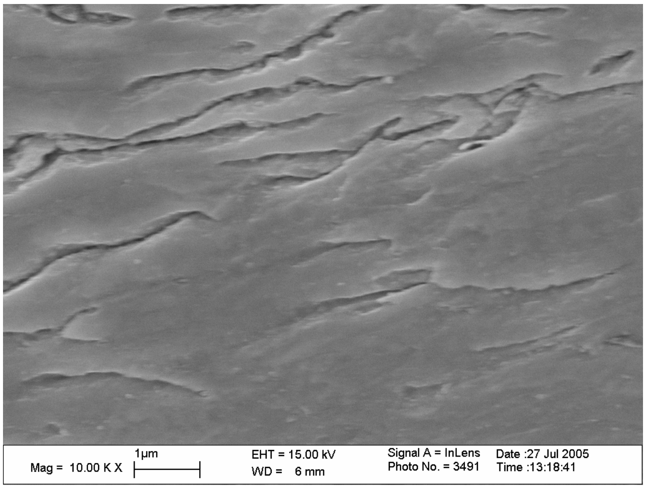

Fig. 3. Microstructure of deformed sample of Cu-Y_2O_3 (1%) microcomposite

The structure of micro-composites with higher content of a strengthening phase is not conducive to their cold working. Because hardness of these materials is very high their plastic deformation is smaller (Figs 4), and small cracks of high density appear during cold working between the agglomerates and in the voids and pores, which results in rapid propagation of cracks and degradation of the compressed samples.

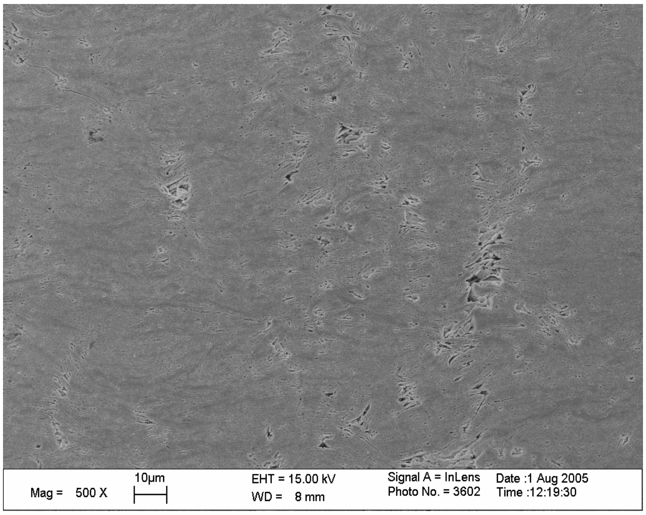

Fig. 4. Microstructure of deformed sample of Cu-Y_2O_3 (3%) microcomposite

Therefore, the materials containing up to 1,5 % yttria seem to be the most suitable for future applications. Follow this results these materials could be cold worked and after this obtain increased density (about 98% of theoretical density) and improved hardness (about 115HV) and electrical conductivity (above 40 MS/m, table 3).

4. Conclusions

In this work results of an investigation into fabrication, properties and microstructure of the copper-based materials, dispersion hardened with yttria, are presented. Based on these results, the following conclusions can be drawn:

- Mechanical alloying is a very efficient technique for fabrication of mixture of copper and yttria powders of a nanometric grain size. This method was used to produce several batches of these powders with predominant presence of a fraction significantly below 100 nm,
- The powders obtained can be used to fabricate products of a nanocrystalline structure by compacting and low-temperature sintering,
- materials containing up to 1,5 % yttria seem to be the most suitable for future applications. Follow this results these materials could be cold worked and after this obtain increased density (about 98% of theoretical density) and improved hardness (about 115HV) and electrical conductivity (above 40 MS/m).

Acknowledgments

This work was supported by the State Committee for Scientific Research under the project KBN-1003/T08/2004/27.

References

[1] J.P. Stobrawa, Z. M. Rdzawski, Formation of a stable nanostructure n the copper-based materials, Proceedings of the 11th International Scientific Conference on Contemporary Achievement In Mechanics, Manufacturing and Materials Science, CAM3S'2005, Gliwice-Zakopane (2005) 909-914, (CD-ROM).

[2] J.P. Stobrawa, Z.M. Rdzawski, Formation of a stable nanostructure in the copper-based materials, Journal of Materials Processing Technology, (2007), (in press).

[3] V. Rajkovic, Copper matrix strengthening in Cu-Al_2O_3 system by mechanical alloying and milling of pure copper and prealloyed copper powders. Advanced Science and Technology of Sintering (1998) 537-543.

[4] D.Y. Ying, D.L. Zhang, D.Y, D.L (2000) Processing of Cu-Al_2O_3 metal matrix nanocomposite materials by using high energy ball milling, Materials Science and Engineering, 1 (2000) 152-156.

[5] A. Zuniga, R. Palma, A. Sepulveda, T. Lobel, L. Nunez, Microstructure and mechanical behavior of Cu-based composites reinforced with WC and TiC particles, prepared by spray forming. Proceedings of the Second International Latin American Conference on Powder Technology, Foz do Iquacu, Brasil, 1999, 542-547.

[6] N. Wang, Z. Wang, K.T. Aust, U. Erb, Effect of grain size on mechanical properties of nanocrystalline materials, Acta Metalurgica Materiallia 2c (1995) 519-528.

[7] Y.J. Li, X.H. Zeng, W. Blum, Transition from strengthening to softening by grain boundaries in ultrafine-grained Cu, Acta Materialia 52(2004) 5009-5018.

[8] R. Suryanarayanan, A.C. Frey, S.M.L. Sastry, B.E. Waller, W.E. Buhro, Plastic deformation of nanocrystalline Cu and Cu-0,2 wt.% B, Materials Science and Engineering A 264 (1999) 210-214.

[9] H. Conrad, Grain size dependence of the plastic deformation kinetics in Cu, Materials Science and Engineering A 341(2003) 216-228.

[10] K.S. Kumar, H.Van Swygenhoven, S. Suresh, Mechanical behaviour of nanocrystalline metals and alloys, Acta Materialia 51(2003)5743-5774.

[11] S.H. Yoo, T.S. Sudarshan, K. Sethuram, G. Subhash, R.J. Dowding, Consolidation and high strain rate mechanical behaviour of nanocrystlline tantalum powder, Nanostructured Materials 12 (1999) 23-28.

[12] D.V. Kudashov, H. Baum, U. Martin, M. Heilmaier, H. Oettel, Microstructure and room temperature hardening of ultra-fine-grained oxide-dispersion strengthened copper prepared by cryomilling, Materials Science and Engineering A 387-379 (2004) 768-771.

[13] U.F. Kocks, The theory of an abstacle-controlled yield strength, Materials Science and Engineering 27(1977)198 - 291.

[14] J.P. Stobrawa, Z. M. Rdzawski, Deformation behaviour of dispersion hardened nanocrystalline copper, Journal of Achievements in Materials and Manufacturing Engineering, 17 (2006) 153-156.

[15] J.P. Stobrawa, Z.M. Rdzawski, Characterization of nanostructured copper – WC materiale, International Journal of Materials and Product Technologies (IJMPT) (2007), (in press).