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Deformation behaviour of dispersion hardened nanocrystalline copper

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Materials

ABSTRACT

Purpose: The aim of this work was to describe deformation behaviour of nanocrystalline copper dispersion-hardened with nanoparticles of tungsten carbide and yttria.
Design/methodology/approach: Tests were made with the Cu, Cu-WC and Cu-Y_2O_3 micro-composites containing up to 3 % of a hardening phase. These were obtained by powder metallurgy techniques, i.e. milling the input powders in the planetary ball mills, compacting and sintering. The mechanical properties (hardness, 0,2 YS, elongation during compression test) and microstructure were examined by the optical, scanning and transmission electron microscopy.
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 hardening effect and the changes in the mechanical and plastic properties. Results of this analysis have been discussed based on the existing theories related to hardening of nanocrystalline materials.
Research limitations/implications: The powder metallurgy techniques make it possible to obtain copper-based bulk materials by means of milling input powders in the planetary ball, followed by compacting and sintering. Additional operations of hot extrusion are also often used. There is some threat, however, that during high-temperature processing or using these materials at elevated or high temperatures this nanometric structure may become unstable. The studies have shown the importance of “flows” in the consolidated materials such as pores or regions of poor powder particles joining which significantly deteriorate mechanical properties of compacted and sintered powder micro composites.
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 those with nanometric grain size of a copper matrix, which exhibit higher mechanical properties than microcrystalline copper.
Originality/value: The paper contributes to the elucidation of deformation behaviour of high-porosity nanocrystalline copper dispersion hardened with tungsten carbide and yttria.
Keywords: Nanomaterials; Mechanical properties; Electron microscopy; Powder metallurgy

1. Introduction

A growing trend to use new copper-based functional materials is recently observed world-wide. Within this group of materials particular attention is drawn to those with nanometric grain size of a copper matrix, which exhibit higher mechanical properties than microcrystalline copper.

The powder metallurgy techniques make it possible to obtain copper-based nanocrystalline bulk materials by means of milling input powders in the planetary ball mills (often at a reduced temperature), followed by compacting and sintering. Additional operations of hot extrusion are also often used. There is some threat, however, that during high-temperature processing or using these materials at elevated or high temperatures this nanometric structure may become unstable. In such cases stabilization of copper nanostructure can be accomplished by means of the dispersed phase particles, most frequently by the oxide or carbide phases [1-4].

Efficiency of nanostructure stabilization depends usually on a volume fraction of these phases and on the degree of dispersion. The same parameters influence hardening degree of these materials during their deforming as a result of the development of deformation structure with the change of the content of hardening phases and dispersion degree, which in turn influences their cold workability. This paper is concentrated on this problem in high-porosity Cu-WC and Cu-Y_2O_3 micro-composites obtained from the processes of disintegration, pressing and sintering of powders. It can be expected that the real mechanical properties of these materials differ from those predicted theoretically [5-9].

2. Experimental procedure

The tests were made with the Cu, Cu-WC and Cu-Y_2O_3 micro-composites containing up to 3 % of a hardening phase. These were obtained by powder metallurgy technique, i.e. milling the input powders in the planetary ball mills, compacting and sintering. Sintering was performed at the temperature of 550 - 570^{O}C for 1 hour in a hydrogen atmosphere. Their nanostructure was examined using LEO 1525 scanning electron microscope and JEM 2000 FX transmission electron microscope.

3. Results and discussion

The consolidation behaviour and microstructure evolution during consolidation and sintering of nanocrystalline copper and nanocrystalline Cu – WC and Cu-Y_2O_3 micro - composites are shown as an example in Figs 1 and 2.

The investigation results have shown that it is difficult to obtain high-density powders of low porosity and good bonding between particles, particularly in the case of nanocrystalline micro-composites. Agglomeration of consolidated nanopowders is a serious problem. The particles are very small by their nature and are, therefore, strongly influenced by relatively small forces (mostly Van der Waals forces) [10]. These forces are caused by a temporary charge distribution in each individual nanopowder, and can cause rapid agglomeration into a branched body. These agglomerates are difficult to break up during compacting and sintering, which results in the formation of inter-agglomerate voids and residual porosity in the samples.

The results of transmission electron microscopy observations of the initial samples are presented in Fig. 2. As an example, the micro-composites containing 2 wt. % of hardening dispersoids have been chosen. The grain size of agglomerate particles is nanometric, and the carbide and oxide particles, as it was reported previously [1,2], are mostly spherical in shape and rather homogeneously distributed within a copper matrix. All the disperdsoids and parameters of the matrix grains in the investigated micro-composites are listed in Table 1.

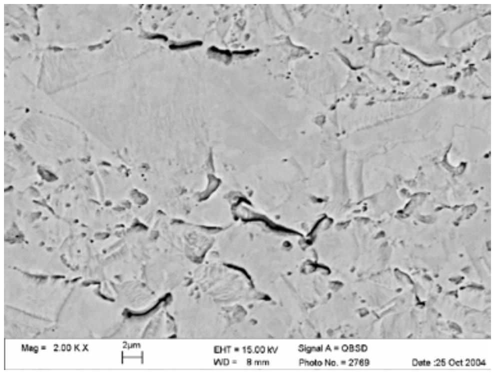

Fig. 1. Exemplary microstructures of the sintered nanocrystalline copper; SEM

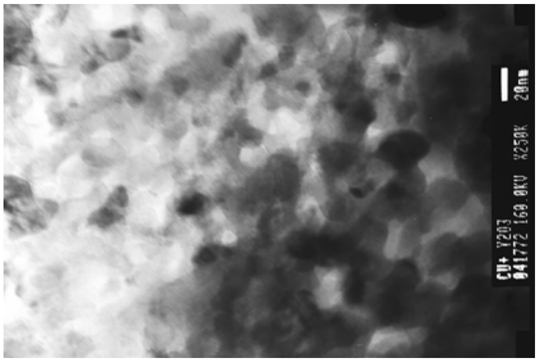

Fig. 2. Exemplary microstructure of the sintered nanocrystalline Cu – Y_2O_3 micro-composite containing 2 wt.% of the hardening dispersoids; TEM

Table 1
Results of compressive deformation experiments performed at room temperature

Sample	R0,2	Ac [%]	matrix - grain size [nm]	size of dispersoids [nm]
Cu	102,5	-55,7	72,15	-
Cu-0,5% WC	165	-53	36,91	10,05
Cu-1% WC	205	-59	60,55	14,09
Cu-1,5% WC	229	-56	62,45	15,24
Cu-2% WC	278	-28	40	-
Cu-3% WC	240	-12,8	-	-
Cu-1% Y_2O_3	189,5	-46,3	68	12
Cu-2% Y_2O_3	190	-18	65	13

The applied sintering parameters were optimal for the Cu-WC and Cu-Y_2O_3 powder mixture. After sintering, most of the grains were much below 100 nm in size and they were highly homogeneous. The average size of carbides and oxides ranged from 10-15 nm. A small amount of them was of a sub-micron size, as it had already been reported previously [1,2]. The same sintering parameters for copper do not enable obtaining such homogeneous nanostructure. In spite of the fact that homogeneous nanostructure is present over the most of the material volume, growth of the grains to the size of several hundred nanometers was observed in some areas. Table 1 show the results of compressive deformation experiments performed at room temperature with the samples from Cu, Cu-WC and Cu-Y_2O_3.

The nanocrystalline copper as well as Cu-WC and Cu-Y_2O_3 micro-composites containing less than 2 wt% of hardening dispersoids exhibit similar stress-strain behaviour. They were clearly hardened although high mechanical properties were preserved. Length of the samples of these materials could be reduced even by 50 %.

It is evident that yield strength increase in the copper-matrix composites is due to the grain refinement, and that the presence of strengthening particles may contribute to work hardening and additional strengthening in the plastic regime by the Orowan mechanism. Kudashov at al. [11] studied a combined effect of the grains size (Hall-Petch relationship), phase fractions and dispersion degree of the yttria and calcium oxide (Orowan mechanism) on the yield point of the Cu-Al_2O_3, Cu-Y_2O_3 i Cu-CaO micro-composites. Taking into account an allowance for the volume fraction of particles, which due to their great size cannot contribute to hardening by the Orowan mechanism, he obtained good agreement between experimental and theoretical results, although the calculated values were, to some degree, underestimated. In our case it should be expected, in accordance with the Hall-Petch relationship, that since density of a nanocrystalline matrix was close to 100 % and the grain size ranged from 60 to 70 nm, then the yield point should be of an order of several hundreds MPa. Moreover, low plasticity might also be expected, e.g. elongations of an order of several %. However, these values appeared to be quite different from those obtained experimentally. Our results have shown that such deviations, mainly from the Hall-Petch behaviour, may result from extrinsic factors such as high porosity and flows.

Results of this investigation have also shown that, at the grain size of 60-70 nm, deformation of nanocrystalline Cu and nanocrystalline Cu-WC and Cu-Y_2O_3 proceeds in a way characteristic for dislocation-controlled processes. Supporting evidence for this have been found during work hardening and compression tests as well as observations of deformation microstructure development during these processes.

The calculated values of hardening of the investigated micro-composites by the Orowan mechanism (according to the equation proposed by Kocks [11, 12]) added to the value corresponding to the yield point of the porous nanocrystalline copper give, for plastic materials containing up to 1 % of a hardening phase, the values close to the experimental ones (Fig. 3). The alloys with higher content of a hardening phase become brittle, and the hardening mechanism starts to diverge from dislocation-based hardening model.

Development of a structure during deformation of these materials was investigated with an account of the hardening effect and of the changes in the mechanical and plastic properties.

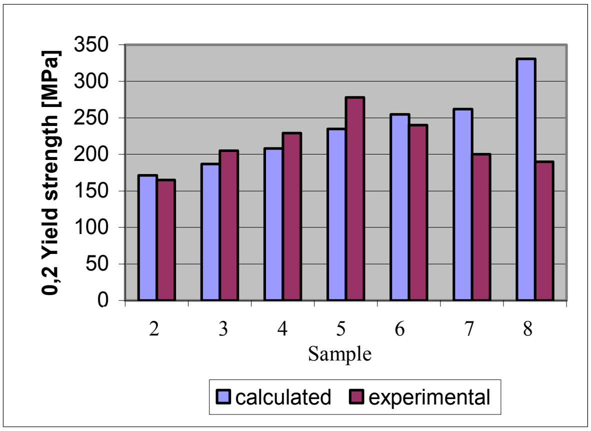

Fig. 3. Comparison of experimental and calculated values for the compressive 0.2% yield stress for the Cu micro-composites

Figures 4 a-b show microstructure of the deformed nanocrystalline copper.

Fig. 4a. Microstructure of the deformed nanocrystalline copper; TEM

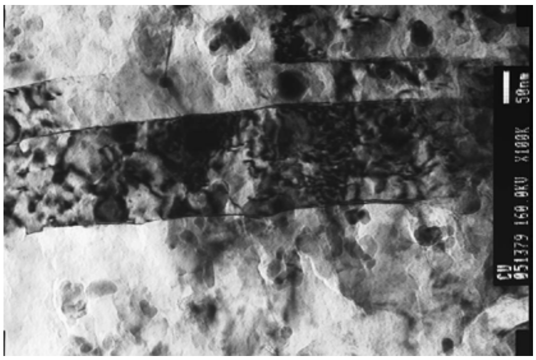

Fig. 4b. Microstructure of the deformed nanocrystalline copper; TEM

The increase of dislocations density, occurring without the change of the shape of nanocrystallites, is observed mainly in greater grains (Fig. 4a). In the micro-areas with finer grains mainly deformation bands are visible (Fig. 4b), which indicates that grain boundary slip contributes to the deformation mechanism. Both mechanisms were found during studies of the deformation processes in nanocrystalline copper, confirming that the grain boundary slip prevails in nanocrystalline materials having smaller grains, within a range of 15-20 nm. After the saturation state is reached, this mechanism should be accompanied by a permanent decrease in a true stress on the $\sigma - \varepsilon$ curve with the increase of a strain.

Microstructure in the deformed micro-composites with low content of a hardening phase develops in a similar way.

The structure of micro-composites with higher content of a hardening phase is not conducive to their cold working. Because hardness of these materials is very high their plastic deformation is smaller (Fig. 5), and small cracks of high density appear during working between the agglomerates and in the voids and pores, which results in rapid propagation of cracks and degradation of the compressed samples.

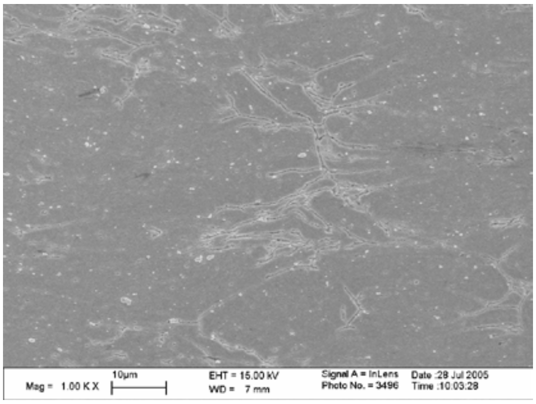

Fig. 5. Exemplary microstructure of deformed microcomposite with 3% wt.WC SEM

4. Summary and conclusions

This study was aimed to investigate mechanical properties and microstructure of nanocrystalline copper and copper-based micro-composites (Cu-WC, Cu – Y_2O_3) obtained by powder metallurgy techniques. The nanocrystalline copper and copper – based micro-composites with a grain size below 100 nm were expected to exhibit the strength and hardness increase by several times as a is direct consequence of the predictions based on the Hall-Petch relationship and Orowan mechanism. Samples of the investigated materials had higher mechanical properties than those of similar materials with microcrystalline size of grains. However, the obtained properties appeared to be much lower than expected. Particularly small was an effect of nanocrystalline size of the grains. Analysis of the initial nanocrystalline structure of these materials was made, and its evolution during deformation process was investigated with an account of the hardening effect and of the changes in the mechanical and plastic properties. The studies have indicated the importance of flows in the consolidated materials such as pores or regions of poor bonds between powder particles, which considerably reduced yield strength of the compacted and sintered powder materials.

The deformation mechanism of nanocrystalline copper is quite complex. Its deformed microstructure exhibits both the areas with high density of dislocations and the deformation bands characteristic for grain boundary slip. Plastic deformation in the micro-composites containing small amount of a hardening phase (up to 2 %) proceeds by similar mechanism. At the higher content of the hardening phase, cold workability of these micro-composites is limited and their plastic deformation is small. Many small cracks appear between the agglomerates and in the voids and pores, which propagate and make that the compressed samples are quickly damaged.

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