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Structure and properties of dispersion hardened submicron grained copper

J.P. Stobrawa [a,*], Z.M. Rdzawski [a], W. Głuchowski [b]
[a] Non-Ferrous Metals Institute, ul. Sowińskiego 5, 44-100 Gliwice
and 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: jerzys@amme.com

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Materials

ABSTRACT

Purpose: The objective of the work was to investigate changes in structure and properties of Cu – WC microcomposites which take place in the process of controlled hot deformation of materials of nanometric initial structure.
Design/methodology/approach: Tests were made with the Cu-WC micro-composites containing up to 2% of a hardening phase. These were obtained by powder metallurgy techniques and further hot 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 hot 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 and high porosity of this materials result in their limited mechanical properties. This is the reason why additional operations, should be applied. The investigations have revealed that controlled hot deformation, within the temperature range of 500 – 550°C, gives possibility for obtaining submicron grain size and more advantageous mechanical properties of Cu-WC microcomposites.
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: The paper shows instability of nanostructure of Cu-WC microcomposites in the processes of hot deformation. A controlled process, which can lead to destruction of globular structure, significant improvement of density and obtaining of submicron size, gives possibility for significant improvements in functional properties of the materials.
Keywords: Nanomaterials; Functional materials; Metallography

1. Introduction

Properties of semi-products manufactured from copper-based materials are strongly related to the foreseen application of those materials. They have also influence on the technologies used for their production and processing. Most often the materials are required to have, beside high mechanical properties, also appropriately high electrical conductivity and heat conductivity [1-3]. Additionally, when used in components operating in elevated temperatures the materials should also present temperature stability of those properties.

These are the reasons why the increasing tendency for application of the dispersion hardened copper based materials is observed [4-8].

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The materials are usually made by powder metallurgy methods often with mechanical synthesis of copper matrix and strengthening phase to obtain nanometric size of matrix and strengthening phase grain size.

According to the results of the research to date, the effect of strengthening in the materials of nanometric matrix grain size is hard to be predicted. There are some deviations from the Hall–Petch [9-14] and Orowan [15] relations observed, which are a consequence of changes in mechanism of deformation in nanocrystalline materials, influence of non-uniform flowing of the material during consolidation and calibration after sintering related to the presence of grain agglomerates, pores etc.[4, 5, 9-13] as well as to the effects related to solution or precipitation strengthening resulting from impurities from elements of wearing containers and balls of mills [4-5]. There is also a danger that during sintering, further hot processing or use of those materials in high temperature, the nanometric structures and subsequently their functional properties can also become unstable.

Taking under consideration the above, authors focused on examination of materials of submicron matrix grain size strengthened with particles of nano size. Such materials were obtained in a process of controlled hot deformation of materials of nanometric grain size.

2. Experimental procedure

The tests were made with Cu-WC micro-composites containing up to 2 % 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. Milling was performed in the atmosphere of argon and methanol. From the obtained powder mixtures samples were prepared in a form of rollers, 10 mm in diameter and 30 mm in length. Sintering was performed at the temperature of 550 - 570°C for 1 hour in a hydrogen atmosphere.

Sintered samples were subjected to compression test within the temperature range of 400 – 550°C. Samples taken from individual stages of production of the materials were used for determination of their basic functional properties and microstructure.

The microstructure was examined using Olympus optical microscope, LEO 1525 scanning electron microscope and JEM 2000 FX transmission electron microscope.

3. Results and discussion

The microstructure evolution during consolidation and sintering of nanocrystalline Cu – WC micro–composites (using an example of Cu – 1 % WC) are shown in Figs 1-2.

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.

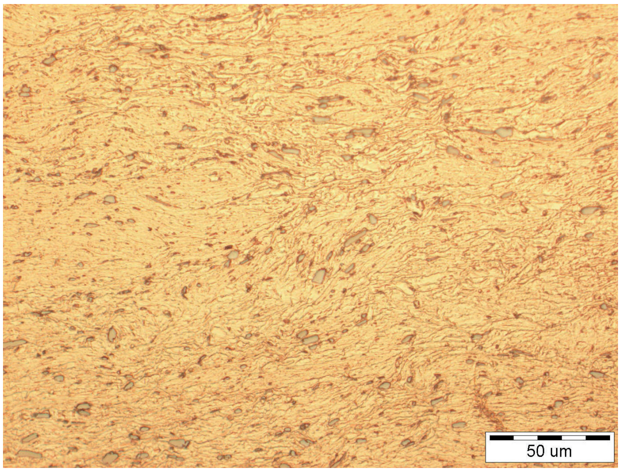

Fig. 1. Exemplary microstructures of the sintered nano-crystalline Cu-WC micro-composites containing 1 wt. % of the hardening dispersoids; optical microscope

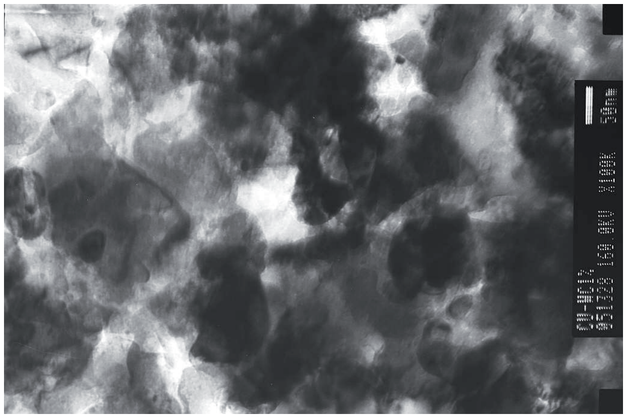

Fig. 2. Exemplary microstructures of the sintered nanocrystalline Cu – WC_3 micro-composites containing 1 wt. % of the hardening dispersoids;. TEM

The results of transmission electron microscopy observations of the sintered samples are presented in Fig. 2. As an example, the micro-composites containing 1 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, are mostly spherical in shape and rather homogeneously distributed within a copper matrix.

The applied sintering parameters were optimal for obtaining a nanocrystaline matrix from the Cu-WC 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 ranged from 10-15 nm. A small amount of them was of a sub-micron size, as it had already been reported previously.

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. [15] 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.

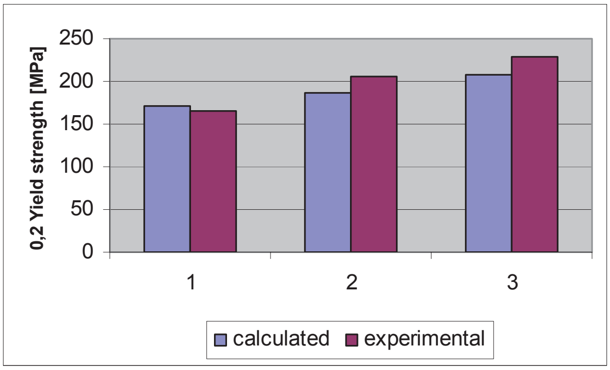

Fig. 3. Comparison of experimental and calculated values for the compressive 0,2% yield stress for Cu micro composites

The calculated values of hardening of the investigated micro-composites by the Orowan mechanism [15] added to the value corresponding to the yield point of the porous nanocrystalline copper (about 100 MPa) give, for plastic materials containing up to 2 % of a hardening phase, the values close to the experimental ones (Fig. 3).

The examinations show that in the investigated Cu – WC microcomposites in the sintered state, even though the microstructure of nanoscale grain size was obtained, the strengthening effect is clearly limited. The major reasons are: formation of a globular structure of weak grain binding and low density. In the result the materials present low hardness after sintering, which – depending on the hardening phase content — can vary within range of 65 – 83 HV. They advantage is high resistance to softening [4].

The consequence of low density and nanometric grain size of the examined sintered materials is their low electric conductivity. With the decrease of the hardening phase content the conductivity increases to about 21 to 47.5 MS/m.

To obtain more advantageous set of functional properties some trials for hot plastic treatment of the materials were performed. The conditions for plastic treatment were selected basing on the performed hot compression tests. Results of the trials, as exemplified by Cu – 1% WC microcomposite, are presented in Fig. 4.

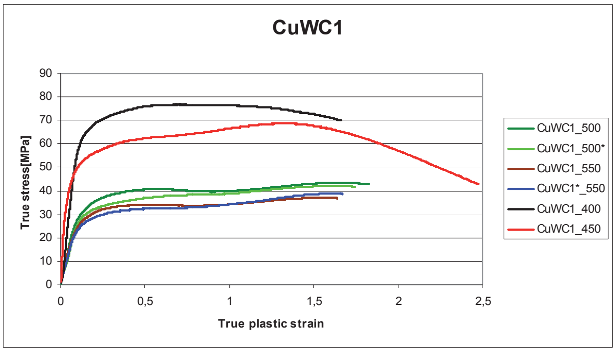

Fig. 4. True stress σ as a function of true plastic strain ε_{pl} for hot compressed nanocrystalline Cu – WC microcomposites

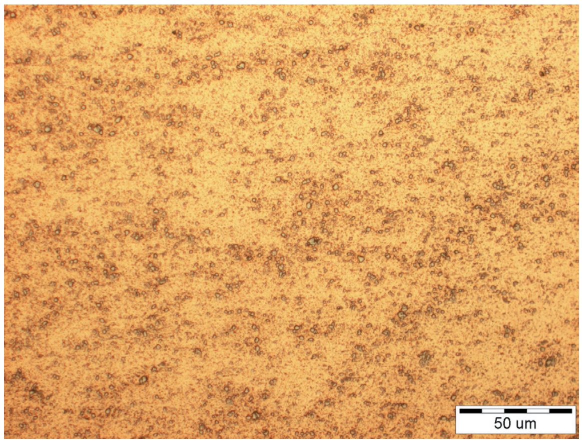

Fig. 5. Microstructure of the hot deformed (500 ^{o}C) nanocrystalline Cu – 1 % WC; Optical microscopy

The diagram shows that the materials are easily deformable in hot conditions, especially in the temperature of 500^{o}C and higher. Already after small strengthening in those temperatures a clear effect of dynamic recovery can be observed. After deformation of the Cu - 1 % WC microcomposite in the temperature of 500^{o}C, no significant grain growth in microstructure of the matrix was observed (Fig. 5).

4. Summary and conclusions

This study was aimed to investigate mechanical properties and microstructure of nanocrystalline and submicrocrystalline micro-composites Cu-WC obtained by powder metallurgy techniques with the use of the operations of milling, pressing and sintering as well as after additional hot deformation by compression or extrusion. The nanocrystalline Cu - WC 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. The earlier 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.

To eliminate the influence of those factors some tests for hot deformation of those materials were conducted. Assuming the possibility that during deformation the process of dynamic recrystallisation takes place, in the test of hot compression the optimum temperature, in which it is possible to obtain structure of submicron grain size at the same time maintaining nanometric particles strengthening phase, was defined. The temperature is within the range of 500 – 550^{o}C. After compressing in that temperature, a distinctly formed subgrained structure was obtained of average grain size at the level of 300 - 500 nm. Hot deformation significantly improved density and functional properties (especially electrical conductivity) of the examined materials. For example, in the material of 2 % WC content the density increased to the value close to the theoretical one and conductivity by about 40% when compared to the sintered material. In that case the increase in hardness exceeded 20 %. After compressing in the compression temperature a much higher hardness was obtained, even by 50%.

The obtained within the scope of this work results show a possibility for significant improvement of properties of sintered Cu- WC microcomposites by way of controlled hot plastic treatment as well as by cold plastic treatment processes with controlled annealing.

Acknowledgments

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