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Characterisation of nanostructured copper - WC materials

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Materials

ABSTRACT

Purpose: The aim of this work was to determine the microstructure and properties stability of nanocrystalline copper dispersion hardened with nanoparticles of tungsten carbides.
Design/methodology/approach: Tests were made with Cu and Cu – WC micro – composites containing up to 3% of a hardening phase. The materials were fabricated by powder metallurgy techniques, including milling of powders, followed by their compacting and sintering. The main mechanical properties of the materials were determined from the compression test, and, moreover, measurements of the HV hardness and electrical conductivity have been made. Analysis of the initial nanocrystalline structure of these materials was made and its evolution during sintering was investigated.
Findings: It was found that an addition of up to 1.5 wt % of a WC significantly improves mechanical properties of the material and increases its softening point.
Research limitations/implications: The powder metallurgy techniques make it possible to obtain nanocrystalline copper-based bulk materials. Additional operations of hot extrusion are also often used. There is some threat, however, that during high temperature processing or application these materials this nanometric structure may become unstable.
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.
Originality/value: The paper contributes to the determination of WC nanoparticles content on the mechanical properties and the nanostructure stability of Cu-WC micro-composites.
Keywords: Nanostructure; Cu-WC micro-composite; Dispersion hardening; Mechanical properties; Structure stability

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1. Introduction

Because of their high electrical and thermal conductivity copper and its alloys have found widespread applications, such as resistance welding electrodes, high voltage switches, motor commutators, continuous casting moulds and others. The required properties of semi-products from copper depend most frequently on the conditions, in which the final products made from them are to work. Besides high mechanical properties and high electric and thermal conductivity it is increasingly more often required that properties of the copper alloys remain stable in different operating conditions, and often also that they are resistant to varying force, current and thermal loads. Some compromise in this regard can be achieved using precipitation hardened alloys, which have to be sometimes subjected to the additional thermo-mechanical treatment [16-20]. However, a serious drawback of these materials is instability of their mechanical properties and electric and thermal conductivity at elevated and high temperatures, resulting from temperature instability of their microstructure. This instability is mainly due to the changes of solvability of the alloy components with temperature and from the processes of recovery, recrystallisation and coagulation of precipitates. The recrystallisation processes are also accompanied by discontinuous precipitation. Therefore, a rising trend to use new copper-based functional materials is being observed world-wide. In the discussed applications, the materials dispersion-hardened, usually by the particles of oxides [6,8,12,13,15,27], carbides [2,5,13,29] and others [1,7,11,14,24,25], obtained by powder metallurgy techniques, are becoming used increasingly frequently. Within this group of materials particular attention is being drawn to those of a nanometric size of copper matrix grains. Investigations carried out so far on the relationship between mechanical properties and the copper grains size showed that the hardness and yield strength increase according to Hall-Petch dependence with the grain size decrease to about 15 nm. At smaller grain size, particularly below 10 nm, the yield strength commences to decrease with further grain refinement, which is called an inverse Hall-Petch relationship [3,4,9,10,18,21,26,28]. Therefore, it is possible to obtain clearly higher mechanical properties of the materials with grain sizes over 10 nm than in those of micro-crystalline grain sizes.

The powder metallurgy enables fabrication of the copper-based bulk materials with nanocrystalline grain size by milling the input powders in planetary ball mills (often at a reduced temperature), compacting and sintering [21-23]. Moreover, additional operations of hot extrusion are often used. There is some threat, however, that during high-temperature processing of these materials or during their use at elevated or high temperatures this nano-metric structure may become unstable. This paper has been concentrated on this problem. The investigation into stability of nanocrystalline copper matrix grains hardened with nano-particles of tungsten carbides has been carried out. Stability of the nano-metric structure of a matrix during the process of sintering and stability of the dispersion hardening effect during annealing at different temperatures for different time of the alloys of different contents of a hardening phase were studied.

2. Experimental procedure

The tests materials studied in this work were based on copper matrix micro-composities reinforced with WC particles. The WC content was 0.5; 1; 1.5; 2 and 3 wt % respectively. These were obtained by powder metallurgy techniques, i.e. milling the input powders in planetary ball mills, followed by their compacting and sintering. The mixed powders of electrolytic copper and tungsten carbide were subjected to milling and mechanical synthesis in a planetary ball mill with 250 ml attritors with 50 balls 10 mm in diameter. After preliminary milling tests the following optimal parameters of the process, suitable to obtain nano-metric size of the powder grains, were established: rotary speed of 250 rev/min and a milling time – 30 hours. Milling was performed in the atmosphere of argon and methanol. Next, mixed powder samples were taken in a form of pellets, 20 mm in diameter and 5 mm high, and in a form of rollers, 10 mm in diameter and 30 mm high. The pellets were used to examine material’s hardness, electric conductivity and microstructure, whereas the rollers were used in compression tests. Sintering was performed at the temperature of 570^{O}C for 1.5 hour in a hydrogen atmosphere and next, the samples were subjected to sizing. Microstructure of the alloy powders and sintered samples was examined using LEO 1525 scanning electron microscope (linked with the Rőntec facility for chemical analysis in micro-areas) and JEM 2000 FX analytical transmission microscope. Hardness measurements were made after sintering of the samples and after additional annealing conducted at the temperatures of 550, 600, 650 and 700^{0}C for up to 8 hours. 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.

3. Results and discussion

Results of the examination of microstructure of the input powders are presented in Fig. 1. Fig. 1a shows SEM images of the powders from electrolytic copper. Their grain size, 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 tungsten carbide powder were regular and their average size was of an order of a fraction of µm.

During milling the mixture of copper and WC powder were disintegrated into spherical like nanoparticles (Fig. 2). It is seen in Fig. 2a that 2a disintegration was very effective and spherical like nanoparticles were obtained. Their size ranged from 5 to 45 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 Fig. 3 and Table 1.

Milling the powders in a planetary mill can result in the material contamination with the elements deposited in a container used or on the balls. The most frequently encountered contaminant is iron. Moreover, partial oxidation of the copper powders takes sometimes place. Analysis of the chemical composition in micro-areas was made (Figs. 3 and 4) confirming the presence of some amount of oxygen in the samples examined, which means that the copper oxides were not fully reduced in the process of powders sintering in a hydrogen atmosphere. On the other hand, significant contamination of the powders with iron was not confirmed (possibly its content was below the accuracy of the analysis method applied).

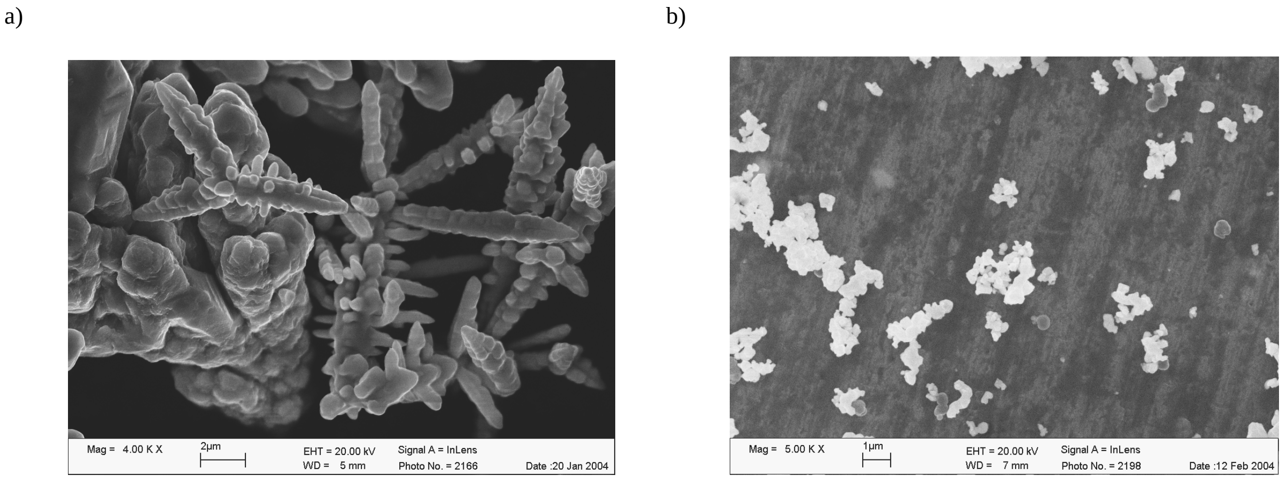

Fig. 1. The raw materials (SEM); a – dendritic copper powder, b – WC powder

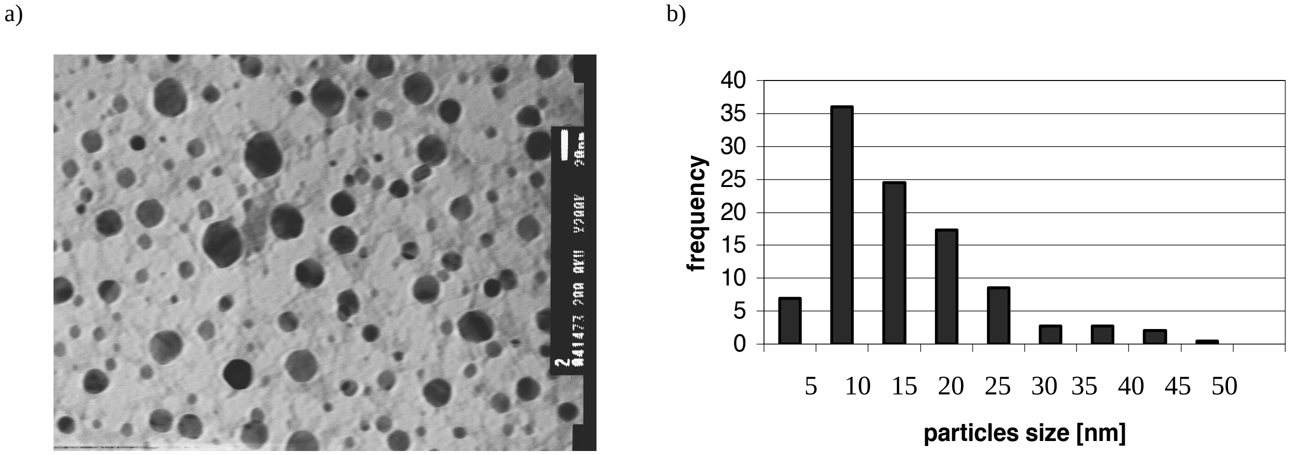

Fig. 2. The Cu-WC particles after disintegration in a planetary ball mill

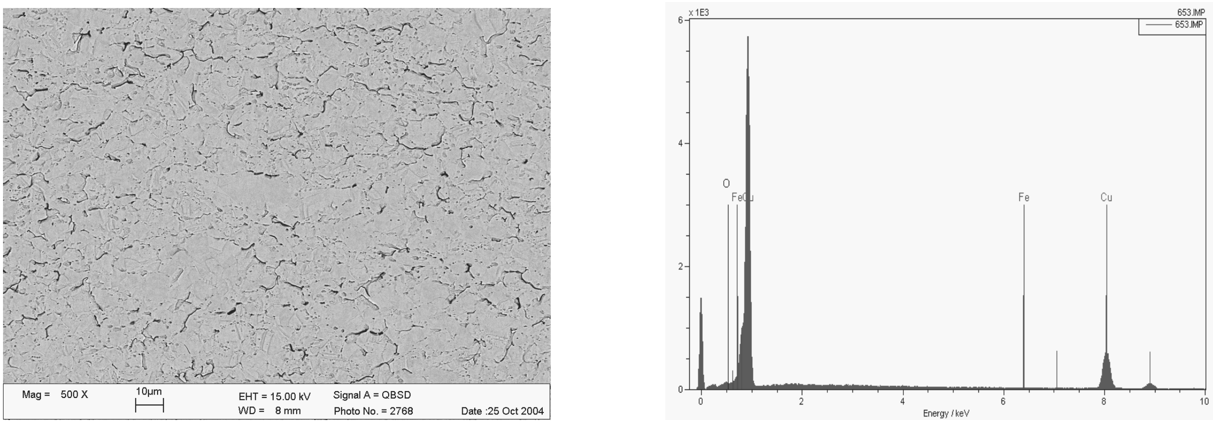

Fig. 3. Microstructure of a sintered copper sample together with energo-dispersive spectrum taken from theselected sample area

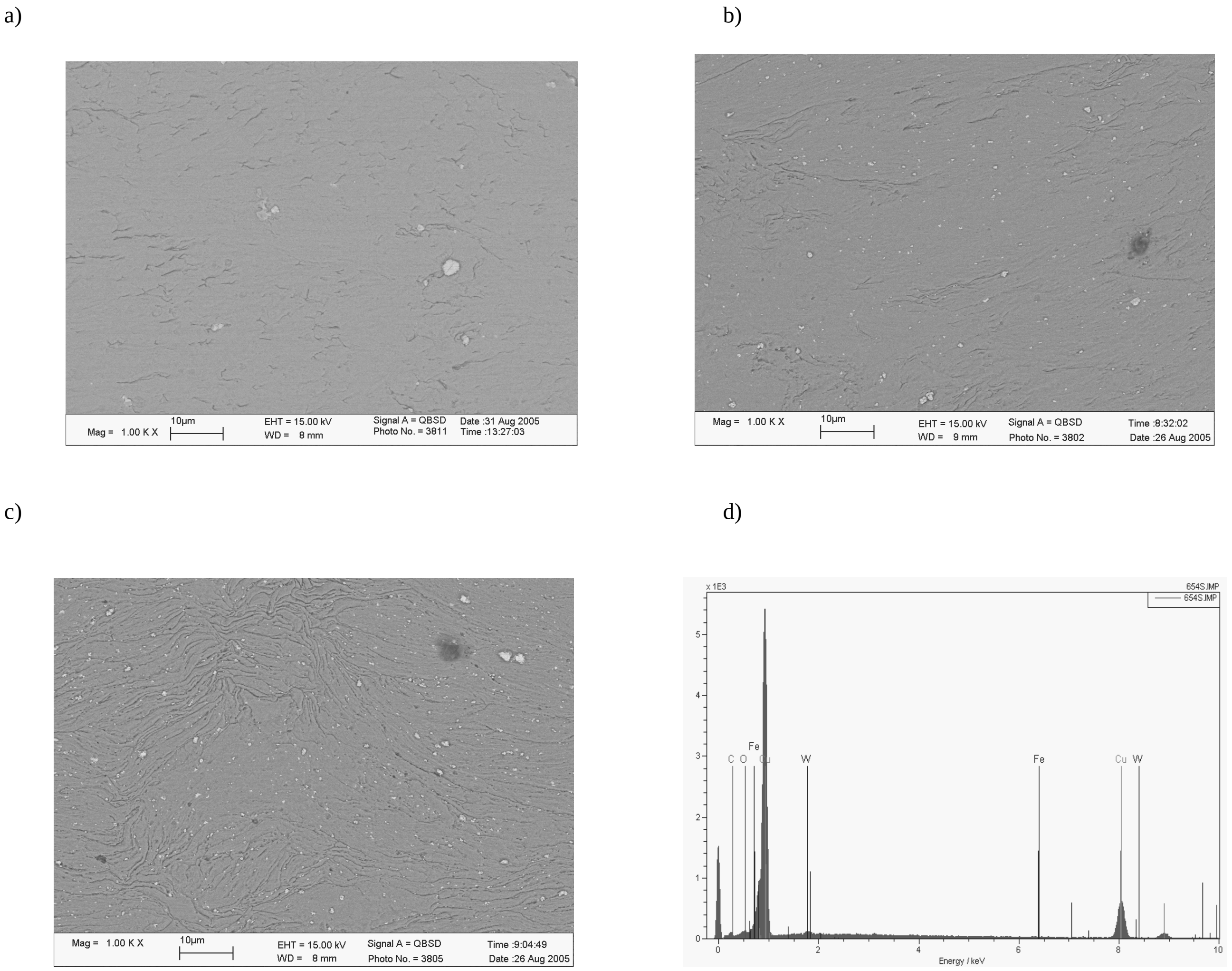

Fig. 4. Microstructures of the sintered samples; a) Cu– WC (0.5%), b) WC (1%), c) WC (1.5%), some observed deformation effects are due to the applied sizing process; d) energy dispersive spectrum– representative for the shown Cu-WC sample

Table 1.
Properties of the sintered materials

No	Composition	Hardness HV	Electrical conductivity [MS/m]	Density [g/cm^3]	Matrix average grain size [nm]	WC average grain size [nm]
1	Cu	55	49.5	7.768	72.15	-
2	Cu-0.5% WC	64.9	47.5	7.904	36.91	10.05
3	Cu-1% WC	70.3	39.3	7.834	60.55	14.09
4	Cu-1.5% WC	73.9	32.015	7.906	62.45	15.24
5	Cu-2% WC	77	30.56	7.619	-	-
6	Cu-3% WC	83	21.16	7.812	-	-

Hardness of the sintered samples (Table 1) increases with the increase a carbide phase content from 55 to 83 HV, which is, however, accompanied by significant decrease of electric conductivity. It should be expected that both mechanical properties and electrical conductivity might be improved by further density increase, which should be possible to accomplish through plastic working, e.g. hot extrusion.

Metallographic examination of the sintered samples by the scanning electron microscopy and chemical analysis performed in micro-areas proved high homogeneity of the carbide phase distribution within a copper matrix (Fig. 4). Although small amounts of a sub-micron particles of the WC phase can be observed (Figs 3a, 3b and 3c), the main fraction of this phase is nanometric in size, which has revealed only the TEM examination.

Results of the TEM examination have been shown in Figs 5-8. These results indicate that the applied parameters of sintering of copper powders without WC phase addition (570^{0}C and 1.5 hours) do not enable obtaining homogeneous nanostructure in polycrystalline material. In spite of the fact that homogeneous nanostructure is predominant over the most of the material volume (Fig. 5a), growth of the grains to the size of several hundred nanometres is observed in some areas (Fig. 5b).

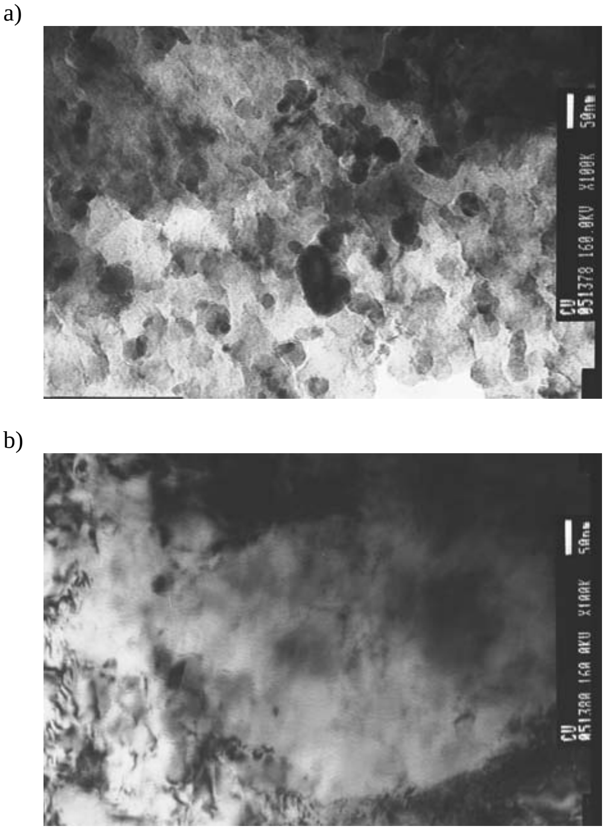

Fig. 5. Microstructure of a sintered Cu sample (TEM); a –area with nanometric grain sizes, b- area with sub-micron size of the grains

The applied sintering parameters were optimal for the Cu-WC powder mixture. After sintering, most of the grains were significantly below 100 nm in size (see Table 1) and they were highly homogeneous (Figs 6-8). The carbide phase was situated mainly on the grain boundaries and its average size ranged from 10 to 15 nm. This size of a dispersive phase and its arrangement is decisive for nanostructural stability of these materials.

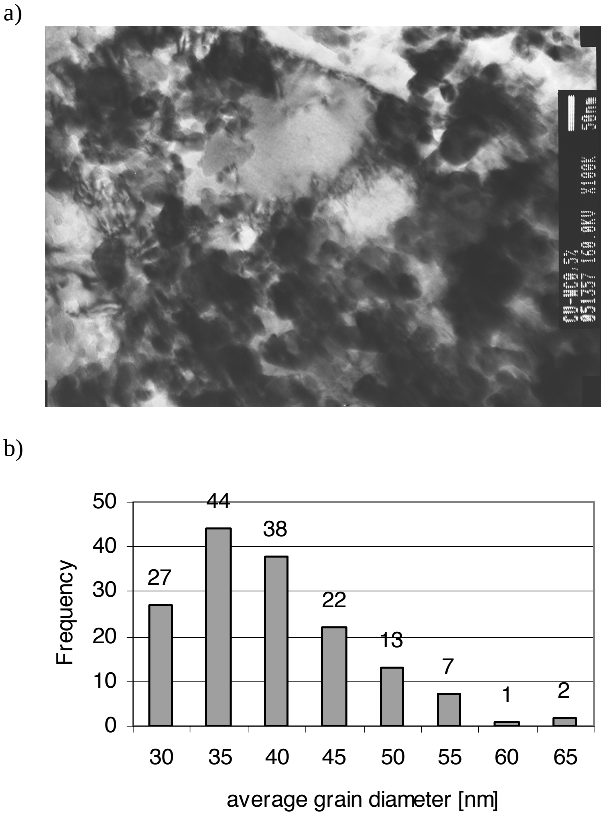

Fig. 6. Microstructure of a sintered Cu-WC(0.5%) sample (TEM); a– exemplary images of the extreme structures, b- grain size distribution

In order to assess mechanical properties and workability of the materials investigated, a cold compression test was performed. The results of this test are given in Table 2.

This table shows that with the increase of the WC phase content in a nanocrystalline matrix the yield strength YS0,2 also increases. It is worth noting that in the materials containing up to 1.5 % 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 a carbide phase (2 % and 3 %) a yield strength increase is accompanied by clear decrease in plastic properties. Besides, the materials become brittle and their strength becomes increasingly lower. Due to low plasticity it is difficult to additionally harden them by cold working. Therefore, the materials containing up to 1.5 % WC seem to be the most suitable for future applications and they were subject of further studies.

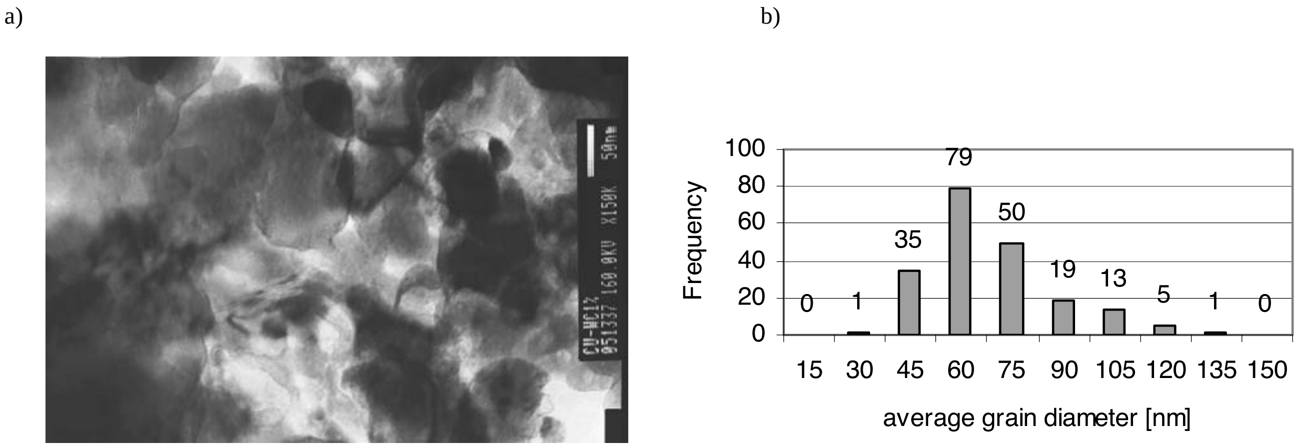

Fig. 7. Microstructure of a sintered sample Cu – WC (1%) TEM; a– exemplary images of the extreme structures, b- grain size distribution

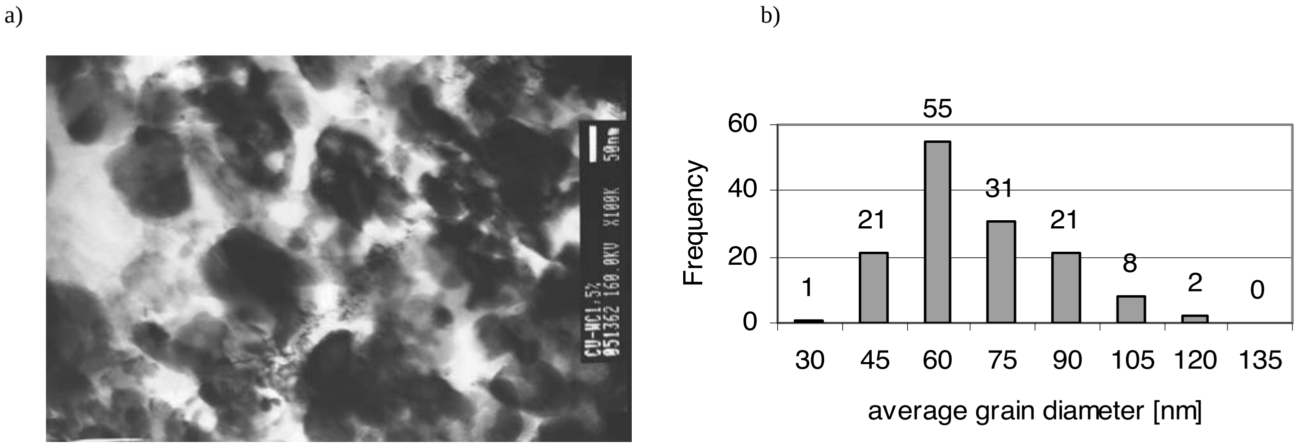

Fig. 8. Microstructure of a sintered Cu-WC (1.5%) sample (TEM); a– exemplary images of the extreme structures, b- grain size distribution

Table 2.
Compression test results

Sample	Composition	YS 0.2 [MPa]	Strength [MPa]	True strain	Hardness HV	Remarks
1	Cu	102.5	864	0.81	120	Test completed at a true strain =0.81
2	Cu-0.5% WC	165	1000	0.76	125	Test completed at a true strain =0.76
3	Cu-1% WC	205	1000	0.89	132	Test completed at true strain =0.81
4	Cu-1.5% WC	229	1000	0.82	134.5	Test completed at a true strain =0.81
5	Cu-2% WC	278	465	0.32	120	Brittle sample
6	Cu-3% WC	240	348	0.15	105	Brittle sample

Effectiveness of the WC phase in stabilising mechanical properties of the Cu-WC materials is illustrated in Fig. 8. As a stability criterion a change in their hardness after annealing at a temperature ranging from 550-700^{0}C for up to 8 hours has been assumed. The hardness changes after annealing for 1 hour are shown in Fig. 9a, and after 8 hours of annealing – in Fig. 9b

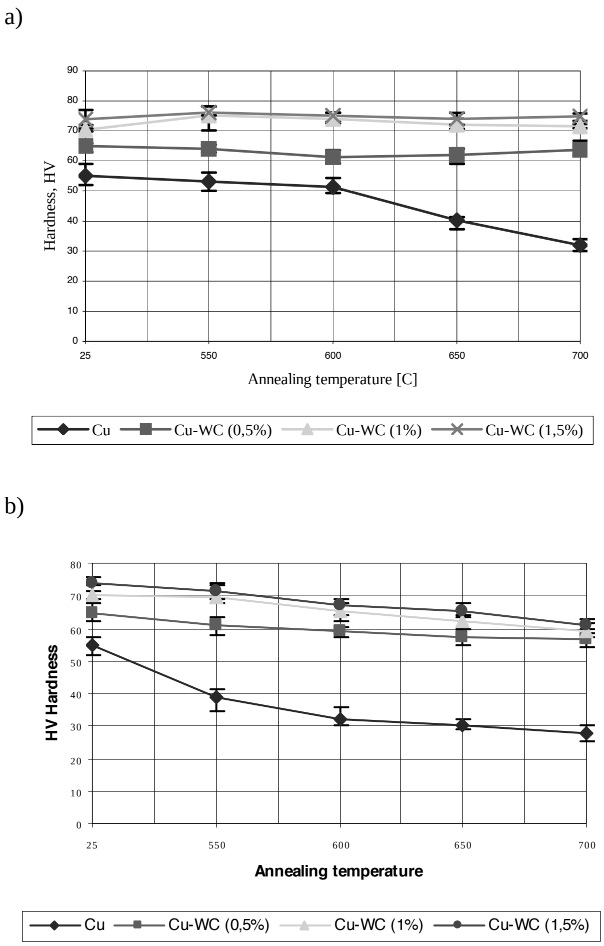

Fig. 9. Hardness changes of the nanocrystalline Cu-WC materials after annealing at the temperatures of 550, 600, 650 and 700^{0}C for: a) 1 hour., b) 8 hours

It is seen in Fig. 9a that hardness of copper non-containing a WC phase addition, annealed for up to 1 hour (which is a typical softening test), remains basically stable up to the temperature of 600^{0}C. With further increase of the annealing temperature hardness clearly starts to fall down to the level of 30 HV. Instead, hardness of the materials containing a hardening phase remains stable over the whole range of the annealing temperatures. After 8 hours of annealing, also these materials start to soften (Fig. 9b), although the softening process proceeds much slower than in the majority of other precipitation-hardened alloys. It was found that an addition of up to 1.5 wt % of WC improves mechanical properties of the material and increases softening temperature. It also stabilises the mechanical properties due to stable nanostructure of a copper matrix.

4. Conclusions

In this work microstructure and properties of the copper-based alloys dispersion-hardened with 0.5-3 wt % of tungsten carbide were investigated. The conclusions drawn from the obtained results are the following:

1. Nanocrystalline copper-based materials with an average grain sizes below 100 nm can be obtained by powder metallurgy techniques, including powders milling in planetary ball mills, compacting and sintering,
2. Mechanical properties of the sintered nanocrystalline pure copper are unstable at high temperatures. A clear decrease in hardness of this material is observed already after annealing at the temperature of 600^{o}C for 1 hour,
3. Mechanical properties of the nanocrystalline copper-based materials can be improved by means of a hardening phase particles of a nanometric size. In this work it appeared to be very effective to use tungsten carbide particles in an amount up to 1.5 wt %. The Cu-WC materials are characterised by higher hardness, yield stress and strength at the preserved high plasticity,
4. The nanostructures, precipitation-hardened with tungsten carbide particles, are more stable thus contributing to higher stability of the mechanical properties of the Cu-WC materials after annealing at elevated and high temperatures. The results of hardness measurements proved that these materials have good resistance to softening.

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