Journal of Achievements in Materials and Manufacturing Engineering

VOLUME 54
ISSUE 1
September
2012

Nanocrystalline copper based microcomposites

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Received 13.07.2012; published in revised form 01.09.2012

Materials

ABSTRACT

Purpose: The aim of this work was to investigate microstructure, mechanical properties and deformation behavior of copper microcomposites: Cu- Y_2O_3, Cu- ZrO_2 and Cu-WC produced by powder metallurgy techniques.
Design/methodology/approach: Tests were made with Cu-Y_2O_3, Cu-ZrO_2 and Cu-WC microcomposites containing up to 2% of a strengthening 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, additionally, measurements of HV hardness and electrical conductivity were made. Analysis of the initial nanocrystalline structure of these materials was made and its evolution during sintering and cold deformation was investigated.
Findings: It was found out that addition of up to 2 wt.% of a strengthening phase significantly improves mechanical properties of the material and increases its softening point. The obtained strengthening effect have been discussed based on the existing theories related to strengthening of nanocrystalline materials. The studies have shown importance of "flows" existing in the consolidated materials and sintered materials in pores or regions of poor powder particle connection which significantly deteriorate the mechanical properties of micro-composites produced by powder metallurgy.
Research limitations/implications: The powder metallurgy techniques make it possible to obtain copper-based bulk materials by means of input powder milling in a planetary ball mill, followed by compacting and sintering. Additional operations of hot extrusion are also often used. There is some danger, however, that during high-temperature processing or application of these materials at elevated or high temperatures this nanometric structure may become unstable.
Practical implications: A growing trend to use new copper based microcomposites is observed recently world-wide. Within this group of materials particular attention is put to those with nanometric grain size of a copper matrix, which show higher mechanical properties than microcrystalline copper.
Originality/value: The paper contributes to the knowledge of mechanical properties and the nanostructure stability of Cu-Y_2O_3, Cu-ZrO_2 and Cu-WC microcomposites. A controlled process of milling, compacting, sintering and cold deformation provides possibility to obtain nanocrystalline copper based materials with improved functional properties.
Keywords: Nanostructure; Dispersion hardening; Mechanical properties; Structure stability; Copper microcomposites

Reference to this paper should be given in the following way:
J.P. Stobrawa, Z.M. Rdzawski, W. Głuchowski, J. Domagała-Dubiel, Nanocrystalline copper based microcomposites, Journal of Achievements in Materials and Manufacturing Engineering 54/1 (2012) 49-57.

1. Introduction

Dispersion hardened materials are becoming more widely used in world technique in the applications where there is a need for specific properties, such as high strength and electrical conductivity, stable properties in elevated and high temperatures, resistance to variable mechanical and thermal load. It concerns copper-based materials, special alloys in iron, nickel and chromium matrix [1] or even precious metals [2].

There are various phases used worldwide to strengthen the copper matrix, and various methods to produce those materials. The main phases for matrix strengthening are oxide, carbide, metallic and intermetallic phases. From among the oxide phases the most commonly used are aluminum [3], zirconium [4] and silicon [5] oxides. Carbide phases are becoming more widely applied, and the most popular are tungsten [6,7], titanium [6] silicon [8,9] and zirconium [10] carbides.

The other strengthening materials covers usually a group of metals which form metallic systems of limited solubility in solid state with copper or metals, and metals of limited solubility in the solid state but forming intermetallic phases with copper. Examples of such strengthening phases include chromium [11,12], iron [13] and yttrium [14]. Also titanium boride is becoming popular [15].

Powder metallurgy is the most widely used method for production of dispersion hardened materials. That method can also be used, and recently is very popular, for production of materials with grains of nanometric size by milling of powders in high-speed planetary mills [16-19]. Also refinement of microstructure to nanometric size is possible using SPD technics [20-21].

The paper presents results of studies into dispersion strengthened materials in copper matrix of nanocrystalline grain size strengthened with particles of oxide phases Y_2O_3 and ZrO_2, and carbide phase WC.

2. Material and methodology

Materials in copper matrix of nanocrystalline grain size strengthened with particles of oxide phases Y_2O_3 and ZrO_2, and carbide phase WC in the amount of 0.5-2 wt.% were selected for the investigations into properties of dispersion strengthened materials. Nanocrystalline copper was used as a reference material.

It was decided that the samples of the dispersion strengthened materials will be produced by powder metallurgy methods with application of milling and synthesis of the initial powders and then by their compacting and sintering.

In the studied samples in a form of pellets of diameter 20 mm and height of 5 mm and in a form of rollers of diameter 10 mm and height of 30 mm were used.

Powder mixtures of electrolytic copper and strengthening phases were subjected to milling and synthesis in a planetary ball mill with 250 ml containers and 50 milling balls of diameter 10 mm.

The following process parameters were applied in the tests with the studied group of materials: rotational speed 250 rev./min, milling time up to 30 hours, atmosphere of argon and of methyl alcohol. The samples were sintered in temperature of 550-570°C (hydrogen atmosphere).

Tests of plastic forming of the sintered samples with application of hot and cold upset forging were planned in the final stage.

Studies into microstructure of the dispersion strengthened materials were conducted with application of Olympus optical microscope equipped with software for quantitative microstructure analysis, LEO 1525 scanning electron microscope and JEOL JEM 2000 FX transmission electron microscope.

Upset forging was carried out with Instron testing machine of pressure 10 T on the samples of diameter 10 mm and height 12 mm in ambient and high (400-550°C) temperatures. Hardness of the samples after sintering, straining and after softening tests was determined by Vickers technique. Changes in hardness of those materials during their annealing in the temperature range 550-700°C in the period of 1 hours were accepted as the stability criterion. Electrical conductivity was measured by Forster Sigmatest instrument.

3. Results and discussion

Morphology of the powders of copper and strengthening phases is presented in Fig. 1. Figure 1a shows particles of electrolytic copper powder. Their size along the main axes of a dendrite is in the range 10-20 µm, while the length of arms and branches changes from fractions of micrometer to 10 µm. Grains of strengthening phase powders (Fig. 1b-d) are more regular and their size ranges from fractions of micrometer to several micrometers.

The powders after mixing were comminuted in the planetary ball mill. Morphology of mixture particles with their size distributions is presented in Figures 2-4. The particles after milling usually have spherical shape. Only powders of Cu + Y_2O_3 mixture show significant difference from that shape. Particles of that mixture usually present polyhedron shapes. It should also be mentioned that in the mixture two particle fractions of different size were observed. Vast majority belonged to the fraction of monocrystal particles (Fig. 2a) of average grain size considerably lower than 100 nm. In the coarser fraction, in a form of polycrystal fine lamellae, the average grain size was about 150 nm (Fig. 2b). In other mixtures the average grain size ranged from about 20 (for Cu + WC) to about 50-60 nm for Cu +Y_2O_3.

High uniformity of distribution of strengthening phases in copper matrixes was observed in the metallographic studies of sintered samples by scanning electron microscope and in chemical analysis in microsections of the samples. Some small amount of submicron particles of strengthening phases can be observed, but strengthening phases are mostly composed of nanometric size particles, as seen in the results of studies performed with application of TEM only.

During milling of powders in a planetary mills there is a possibility of their contamination with elements from the container and milling balls, and iron is the most common impurity. There is also a possibility of partial oxidation of copper powders. Analysis of chemical composition conducted in microsections confirmed presence of oxygen in the examined samples, which means that copper oxides were not completely reduced during process of powder sintering in hydrogen atmosphere. Contamination of powders with iron, however, was not confirmed. It is possible that its content is too low to be determined by the applied method of analysis.

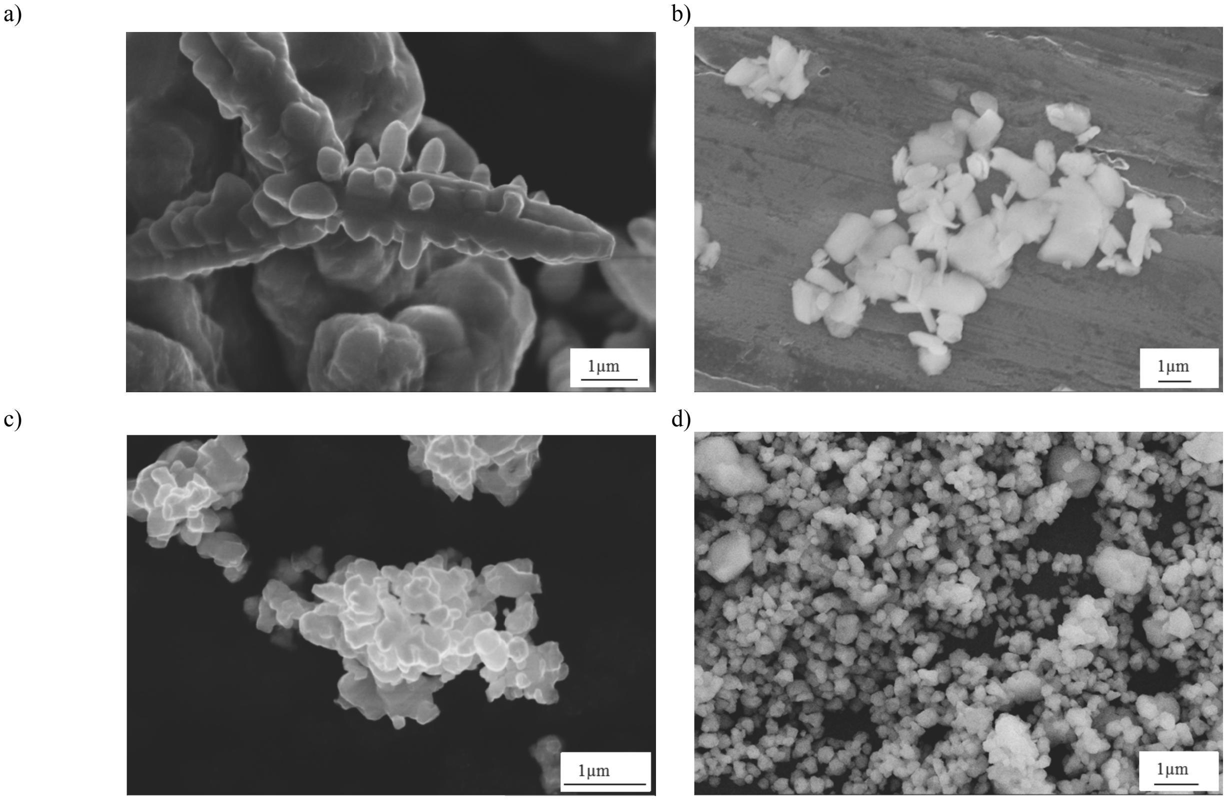

Fig. 1. Morphology of initial powders: a) electrolytic copper, b) yttrium oxide (Y_2O_3), c) tungsten carbide (WC), d) zirconium oxide (ZrO_2); SEM

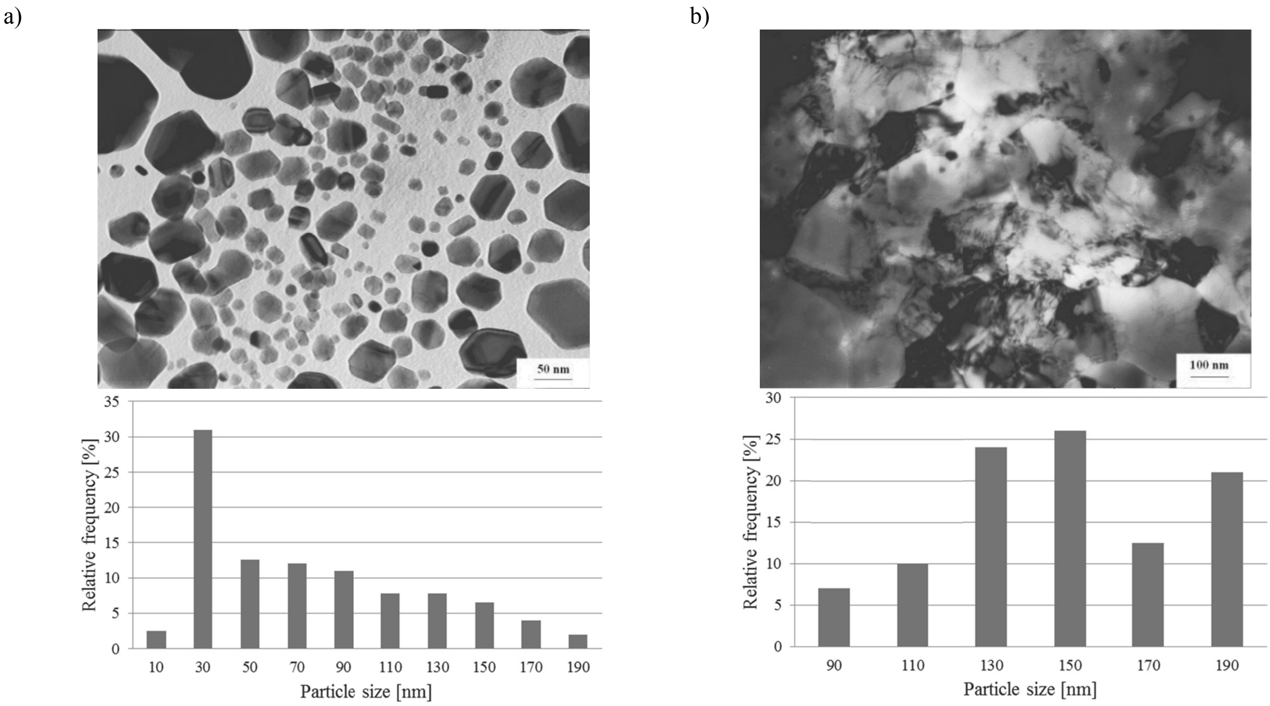

Fig. 2. Grains of copper and yttrium oxide after milling in planetary ball mill, a) monocrystal particles, b) polycrystal particles

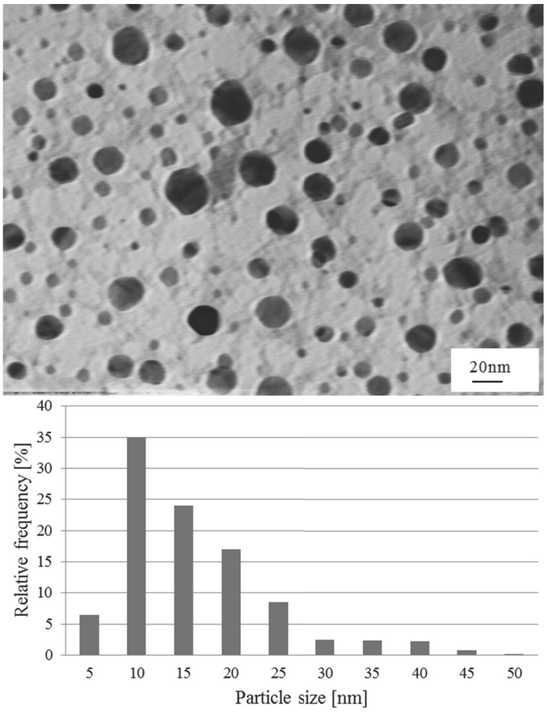

Fig. 3. Grains of copper and carbide WC phase after milling in planetary ball mill

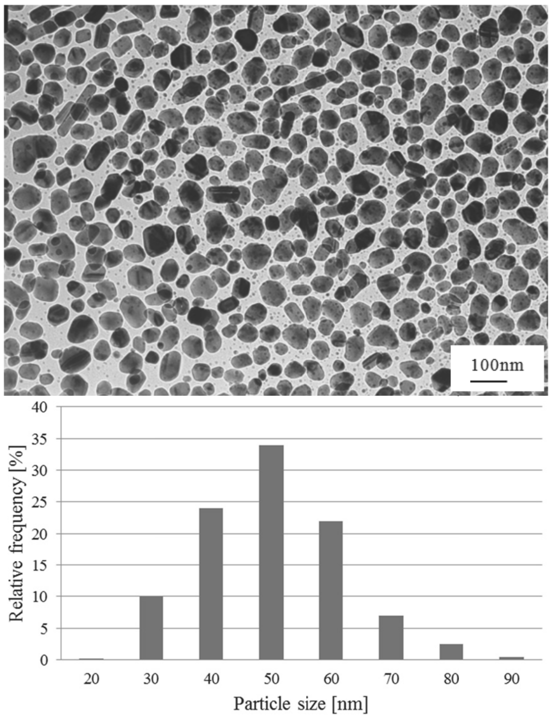

Fig. 4. Grains of copper and ZrO_2 phase after milling in planetary ball mill

Application of protecting atmospheres (acetone, argon) in the milling process significantly reduces possibilities for oxidation of powders of copper and non-oxide phases. Some oxides of copper or strengthening phases may form, however, on surface of powders during milling or storage and become reduced in relief annealing of powder mixture or during sintering in hydrogen atmosphere. In such situations, when temperature is high and annealing time is long, there is also a possibility for reduction of strengthening oxide phases, which is evidently disadvantageous. That is why analysis of the phases in the materials after sintering was additionally prepared. Microanalysis has shown that qualitative chemical composition of the particles is consistent with the chemical composition of the introduced phases. Quantitative analysis was not possible because of the size of those particles, therefore additional phase analysis of the examined materials was performed by X-ray diffraction. Results of the investigations confirmed that in the sintering no adverse phenomena occurred which might disqualify the material from further studies.

Basic functional properties of the sintered materials were determined. Results of studies into hardness, electrical conductivity and density are listed in Table 1.

Table 1.
Hardness, electrical conductivity and density of examined materials

No	Material	Sintered materials		
		HV	γ, MS/m	Density, g/cm^3
0	Cu	55	49	7.768
1	Cu-0.5%WC	64.9	39.295	7.904
2	Cu-1%WC	70.5	30.562	7.834
3	Cu-1.5%WC	73.9	32.015	7.906
4	Cu-2%WC	77	21.16	7.619
5	Cu-3%WC	83	20.61	7.812
6	Cu-1%Y_2O_3	72	32.17	7.533
7	Cu-1.5%Y_2O_3	76	34.15	7.46
8	Cu-2%Y_2O_3	81	23.845	7.027
9	Cu-1% ZrO_2	64	49.5	7.74
10	Cu-1.5% ZrO_2	72	49	7.72
11	Cu-2% ZrO_2	74.5	45.9	7.71

Copper samples after sintering show hardness at the level of 55 HV and electrical conductivity of about 49 MS/m. All the dispersion strengthened materials have higher hardness, i.e. 62-87HV (depending on the type and content of strengthening phase). In the Cu-Y_2O_3 materials with increase of Y_2O_3 content from 1 to 2% the electrical conductivity decreases from 32 to about 24 MS/m, while in the Cu-WC materials with increase of WC content from 0.5% to 3% it decreases from 39 to about 20 MS/m. Considering the optimization of hardness and electrical conductivity the Cu-ZrO_2 materials provide the best results. Their electrical conductivity is at the level of 46-48 MS/m.

The relatively low level of electrical conductivity is also strongly influenced by low, seldom exceeding 90% of theoretical, density of sintered samples. Low density results from agglomeration of nanocrystalline particles. It is difficult to break the agglomerates during compacting and sintering. Formation of voids among them leads to porosity and low density (Table 1).

Compression tests were conducted to determine mechanical properties of the produced materials and their applicability for further plastic working. In the cold compression test both proof stress and elongation of the examined materials were determined. The results are presented in Table 2. It has to be noted that because of high plasticity of majority of those materials the compression tests were stopped after reaching close to critical conditions of the testing machine. Therefore A_c values for those materials are not precise but approximate only. For the same reasons the compression strength is given for brittle materials only. The Table shows also hardness of the samples deformed in the compression test.

Copper samples which are produced by powder metallurgy methods can be easily deformed in the test of cold upset forging. The proof stress slightly exceeds 100 MPa and elongation -55%. The advantageous plastic properties are also observed in Cu-WC (up to 1.5% WC), Cu-Y_2O_3 (up to 1% Y_2O_3) Cu-ZrO_2 (up to 2% ZrO_2) materials, and their proof (0.2%) stress is also higher by about 60-100%. Materials of higher strengthening phase content (above 2%) are brittle and cannot be treated by cold plastic working.

After application of the strain with 50% reduction, density in the range 97-98% of theoretical density and hardness increase to 115-150HV were reached. It should be emphasized that no electrical conductivity decrease was observed since the expected drop with reduction increase is compensated by electrical conductivity rise resulting from reduced porosity.

Figures 5-9 show results of studies into microstructure of the strained copper samples and dispersion strengthened Cu-WC, Cu-Y_2O_3, Cu-ZrO_2 materials. The results explain the obtained properties and behavior of examined materials in compression test.

In Fig. 5 strain microstructure of nanocrystalline copper sample is presented. A combined mechanism of plastic strain can be clearly observed. Beside dislocation mechanism also significant contribution into the strain is coming from mechanism of flow in nanocrystalline grain boundaries and in the boundaries of globular grains formed in the result of interactions between nanocrystalline grains. Significant contribution into the strain is also brought by flow along the voids resulting from relatively high porosity and along the surface of movement of globular grains or by higher mass of the sample material during formation of samples or their sizing after sintering.

Majority of the materials with low content of strengthening phase are deformed in a similar way to the nanocrystalline copper.

a) b)

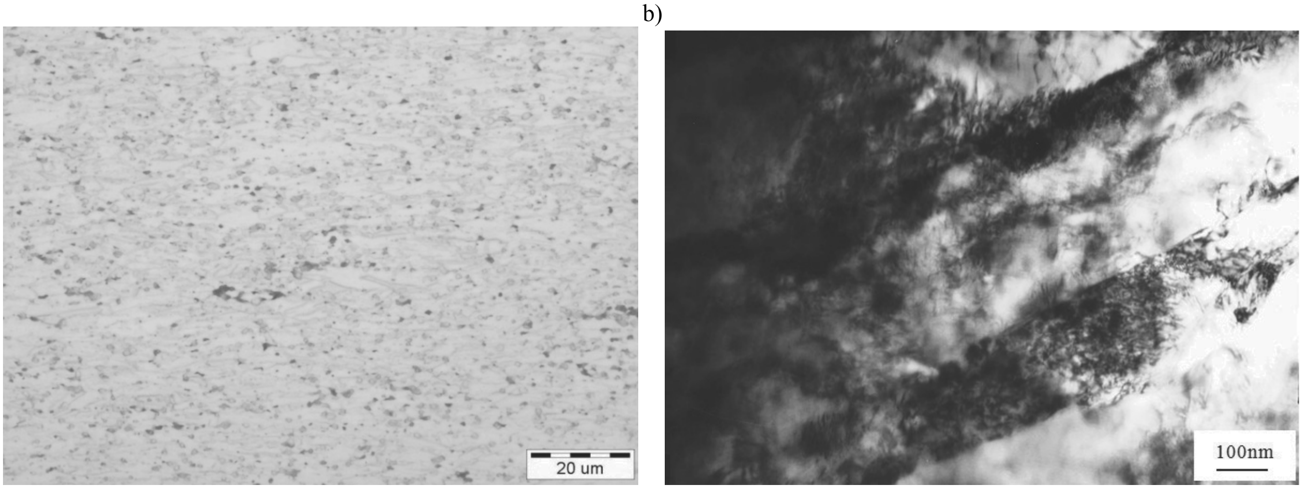

Fig. 5. Microstructure of strained Cu sample, a) light microscopy, b) TEM

Table 2.
Compression test results

No	Material	$R_{0.2}$, MPa	Rc, MPa	A_c, %	Hardness HV
0	Cu	102.5	-	-55.7	120
1	Cu-0.5%WC	165	-	-53	125
2	Cu-1%WC	205	-	-59	132
3	Cu-1.5%WC	229	-	-58	134.5
4	Cu-2%WC	278	465	-28	120
5	Cu-3%WC	240	348	-12.8	105
6	Cu-1%Y_2O_3	189.5	-	-48.3	126
7	Cu-2%Y_2O_3	189.1	411	-20	130
8	Cu-3%Y_2O_3	-	-	-	134
9	Cu-1%ZrO_2	180	-	-49.7	136
10	Cu-1.5%ZrO_2	180		-51	137
11	Cu-2%ZrO_2	190	-	-48	141

It concerns Cu-WC, Cu-Y_2O_3, Cu-ZrO_2 materials which contain up to about 2 wt.% of strengthening phase. Some microstructures after cold deformation of those samples are presented in Figs. 6 and 7 (WC - 1 and 1.5 wt.%), Fig. 8 (1 wt.% of Y_2O_3), Fig. 9 (2 wt.% of ZrO_2).

In the study also tests of compression in high temperature (in the range 400-550°C) were conducted.

The basic functional properties of the hot strained materials are presented in Table 3. The Table shows that in majority of the examined materials hot plastic working results in density increase and in improvement of electrical conductivity. It also brings a possibility to reach higher hardness than in sintered materials. Of special importance is the fact that also materials of higher content of strengthening phase can be formed in the process of controlled heat treatment and plastic working, even those of high brittleness after sintering.

Stability of nanocrystalline structure in the examined materials becomes significantly reduced in hot straining processes. During compression (especially above 450^{o}C) dynamic recrystallization takes place (Fig. 10) which results in the grain growth.

Figures 11-13 present results of studies into effectiveness of strengthening phases as stabilizers of mechanical properties of materials in copper matrix of the initial Cu, Cu-Y_2O_3, Cu-WC, Cu-ZrO_2 nanostructure, respectively. Changes in the material hardness during annealing in temperature range 550-700°C for 1 hour were considered as the stability criterion. For comparison a similar test was performed with nanocrystalline copper produced by powder metallurgy methods in the same conditions. The presented diagram (Fig. 11) shows that hardness of copper without strengthening phase is relatively stable up to the temperature of 600^{o}C. At higher annealing temperature a significant drop to the level of 30 HV is observed.

a) b)

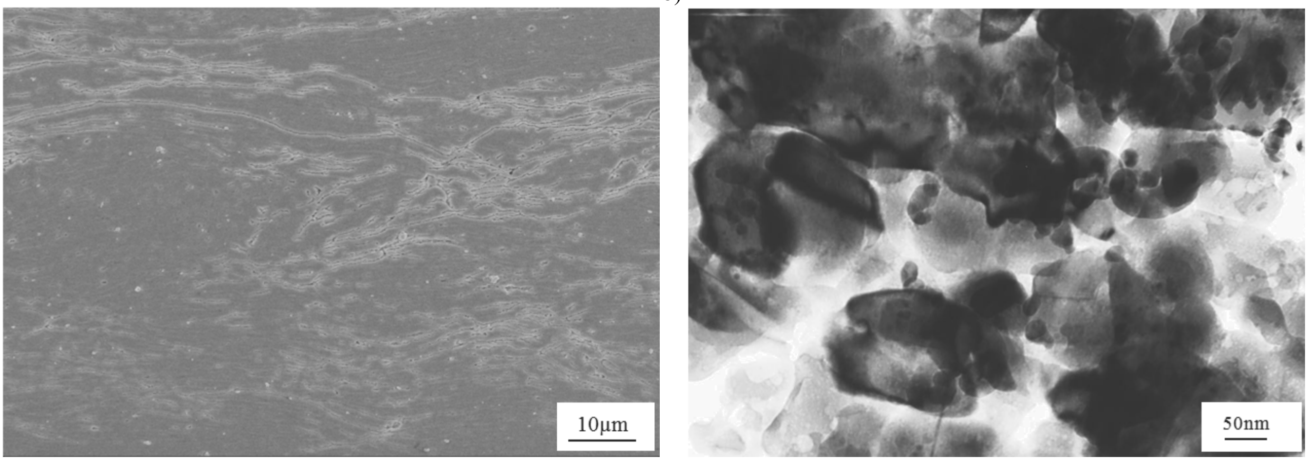

Fig. 6. Structure of strained Cu – 1% WC sample, a) SEM, b) TEM

a) b)

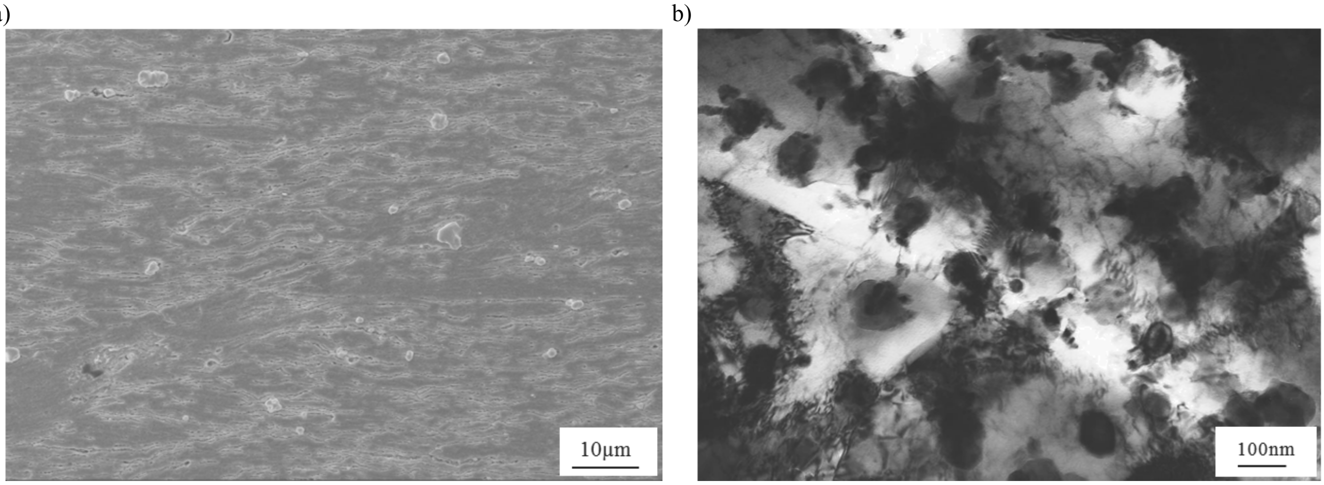

Fig. 7. Structure of strained Cu – 1.5% WC sample, a) SEM, b) TEM

a) b)

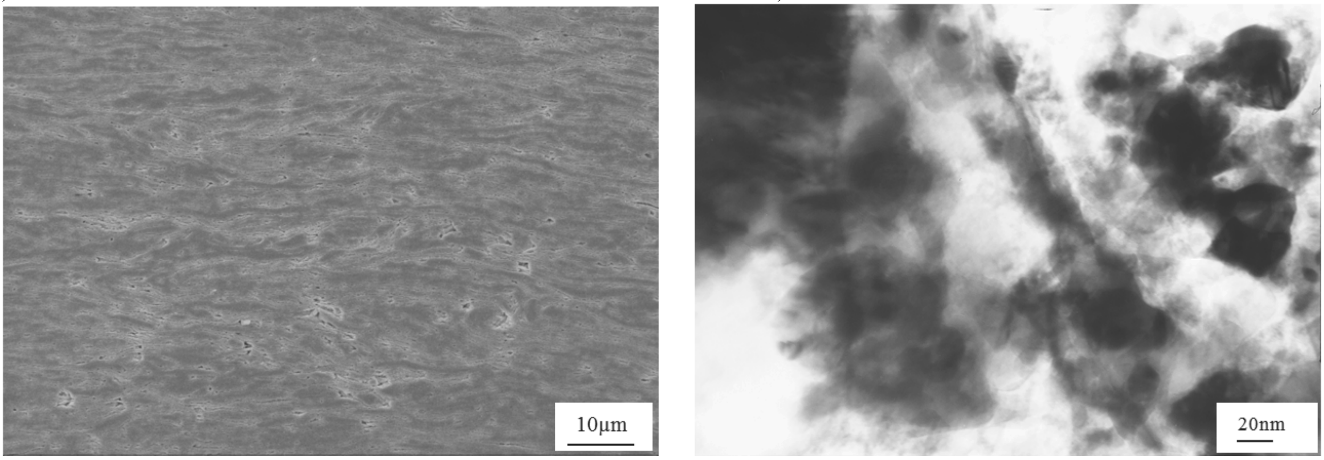

Fig. 8. Structure of strained Cu – 1% Y_2O_3 sample, a) SEM, b) TEM

a) b)

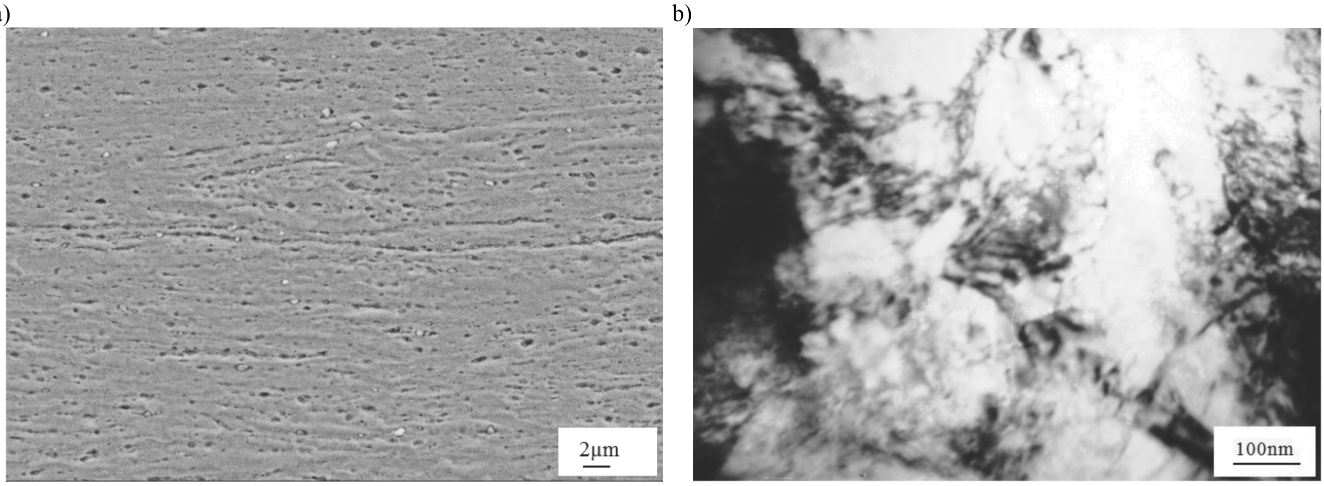

Fig. 9. Structure of strained Cu – 2%ZrO_2 sample, a) SEM, b) TEM

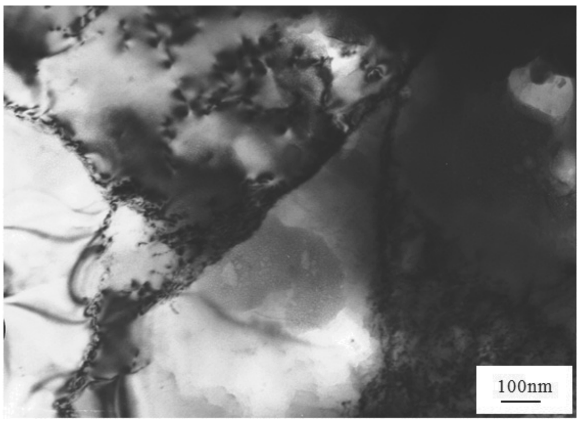

Fig. 10. Microstructure of Cu - WC (1%) sample hot strained in temperature 500°C

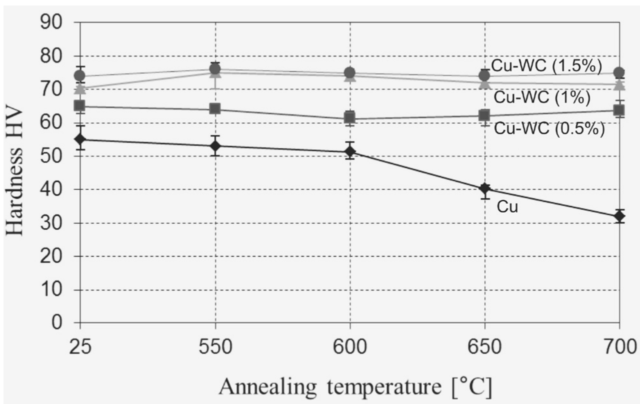

Fig. 11. Changes in nanocrystalline Cu-WC material hardness after annealing in temperature range 550-700°C for 1 hour

Table 3.
Basic functional properties of the examined microcomposites after hot straining

Material	Density, g/cm^3	Hardness HV	Electrical conductivity, MS/m
Cu-1%WC	8.77	20°C – 132	37.1
		400°C – 116.5	44.3
		500°C – 79.1	45.5
		550°C – 81.6	42.3
Cu-1.5%WC	8.79	20°C – 134.5	36.5
		400°C – 114.9	43.5
		500°C – 98.3	46.05
		550°C – 91.2	44
Cu-2%WC	8.72	20°C – 120	35.8
		400°C – 115.3	41
		550°C – 95	42
		600°C – 85	42.5
Cu-1%Y_2O_3	8.77	20°C – 114	32.17
		450°C – 110.3	44.8
		500°C – 104.1	41.5
		550°C – 61.2	42.7
Cu-2%Y_2O_3	8.79	20°C – 118	38.8
		450°C – 112.9	38.7
		500°C – 108.1	39.5
		550°C – 62.8	40.2
Cu-3%Y_2O_3	8.72	20°C – 116	35.5
		450°C – 114.4	34.7
		500°C – 109.8	34.8
		550°C – 78.3	37.5
Cu-1.5%ZrO_2	8.63	20°C – 137.2	45.2
		450°C – 89.5	50.0
		500°C – 70.2	48.5
		550°C – 50	42.0
Cu-2%ZrO_2	8.615	20°C – 141.8	40.8
		500°C – 65.8	45.8
		550°C – 50.1	46

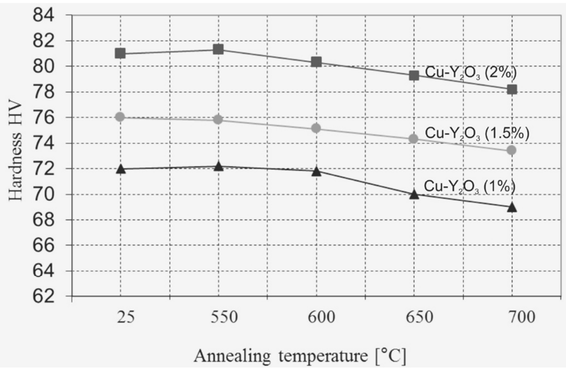

Fig. 12. Changes in nanocrystalline Cu-Y_2O_3 material hardness after annealing in temperature range 550-700°C for 1 hour

The drop results from recrystallization process. Hardness of dispersion strengthened materials remains stable in the whole range of annealing temperature and no significant changes were observed in their structure.

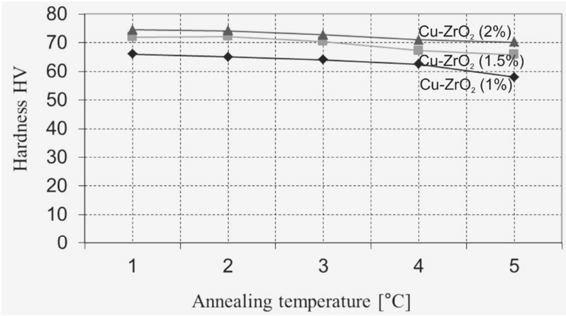

Fig. 13. Changes in nanocrystalline Cu-ZrO_2 material hardness after annealing in temperature range 550-700°C for 1 hour

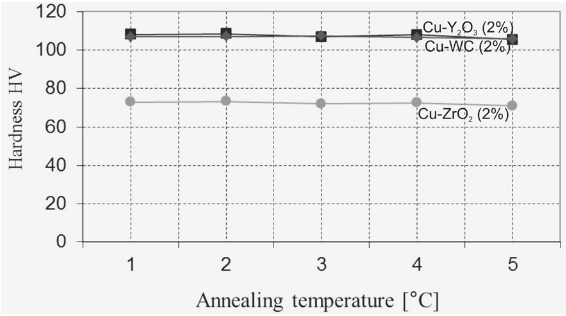

Fig. 14. Changes in hardness of dispersion strengthened materials of sub-microcrystalline grain size annealed in temperature range 550-700°C for 1 hour

Also materials preliminary subjected to hot plastic working show good microstructure stability and, consequently, also hardness. Fig. 14 shows an example of hardness changes with temperature of annealing in materials which contain 2% of strengthening phases and which were strained in temperature of 550°C. The changes show high stability of the submicron matrix grains produced in the result of the dynamic recystallization.

4. Summary

Application of milling of powders in a planetary ball mill under the developed process conditions provides possibility to produce a mixture of nanocrystalline Cu-Y_2O_3, Cu-ZrO_2 and Cu-WC powders.

The developed parameters for sintering of those mixtures (temperature 550-570°C, time - 1 hour) ensure that the nanometric structure (average grain size considerably below 100 nm) will remain unchanged in the sinters. That stability of grain size is also maintained in a long-term annealing in the temperature range 600-650°C.

The sintered materials show relatively low density which usually does not exceed 90% of the theoretical density. In the result both hardness and electrical conductivity of those materials is limited. Together with the influence of agglomeration of nano-particles and partial change of strain mechanism it has an effect on the value of proof stress in the compression test, which is significantly lower than the one expected from theoretical studies.

Cold and hot strain significantly improves density of sintered materials (from about 90% to the values close to the theoretical density (97-98%)) and their electrical conductivity. It also increases hardness of the examined materials. That effect, however, is clearly limited in the materials of higher strengthening phase content (above 2%), which also show high brittleness.

Stability of nanocrystalline structure of the examined materials becomes significantly reduced in a hot strain process. Dynamic recrystallization results in growth of the initial nano-grains.

Production of matrix grains in the range 300-500 nm in the process of controlled heat treatment and plastic working is an evident advantage. Such a microstructure (together with influence of the higher - close to theoretical - density) ensures higher hardness and electrical conductivity than in the sintered materials. It is characteristic that by application of heat treatment and plastic working there is also a possibility to form materials which showed high brittleness after sintering (characterized by high strengthening phase content).

In the group of the developed materials especially interesting are: Cu-WC, Cu-Y_2O_3, Cu-ZrO_2, but the optimum content of the strengthening phase in the materials for further hot and cold plastic working should not exceed 2 wt %. In the materials meant exclusively for hot plastic working the content can be higher (up to 3%).

The materials combine advantageous mechanical properties with high electrical conductivity and microstructure stability in elevated and high temperatures. Comparative studies of functional properties of those materials with properties of precipitation hardened alloys show their advantage in applications for components operating in high temperature and in variable conditions of current, thermal or mechanical load. Such components can be used as electrodes or electrode terminals for resistance welding, etc.

Acknowledgements

This work was supported by the State Committee for Scientific Research under the projects No PBZ-KBN-096/T08/2003 and KBN-1003/T08/2004/27.

References

[1] A. Czyrska-Filemonowicz, B. Dubiel, Mechanically alloyed, ferritic oxide disperssion strengthened alloys: structure and properties, Journal of Materials Processing Technology 64 (1997) 53-64.

[2] Z. Rdzawski, High - temperature structural stability of new platinum alloys used in the glass industry, Proceedings AMT'2001, Materials Engineering 5 (2001) 765-767 (in Polish).

[3] D.Y. Ying, D.L. Zhang, Processing of Cu-Al_2O_3 metal matrix nanocomposite materials by using high energy ball milling, Materials Science and Engineering A 286/1 (2000) 152-156.

[4] J. Cadek, K. Kucharowa, Novel interpretation of High temperature creep in an ODS Cu-ZrO_2 Alloy, Kovove Materials 40 (2002) 133-145.

[5] U. Lagerpusch, V. Mohles, D. Baither, B. Anczukowski, E. Membach, Double strengthening of copper by dissolved gold-atoms and by incoherent SiO_2- particles: how do the two strengthening contributions superimpose?, Acta Materialia 48 (2000) 3647-3656.

[6] A. Zuniga, R. Palma, A. Sepulveda, T. Lobel and L. Nunez, Microstructure and mechanical behavior of Cu-based composites reinforced with WC and TiC particles, prepared by spray forming, Proceedings of the 2nd International Latin American conference on Powder Technology, Iguacu, 1999.

[7] Y.V. Baikalova, O.I. Lomovsky, Solid state of synthesis of tungsten carbide in an inert copper matrix, Journal of Alloys and Compounds 297/1-2 (2000) 87-91.

[8] Y. Zhan, G. Zhang, Friction and wear behavior of copper matrix composites reinforced with SiC and graphite particles, Tribology Letters 17/1 (2007) 91-98.

[9] K.M. Shu, G.C. Tu, The microstructure and the thermal expansion characteristics of Cu/SiC_p composities, Materials Science and Engineering 349/1-2 (2003) 236-247.

[10] M. Lopez, J.A. Jimenez, D. Corredor, Precipitation strengthened high strength-conductivity copper alloys containing ZrC ceramics, Composites A 38 (2007) 272-279.

[11] B.R. Juan, G.C. Jorge, M.Z.V. DePaul, Fabrication and hot extrusion of mechanically alloying Cu-15wt%Cr alloy, Advanced Powder Technology 293-3 (1999) 470-477.

[12] K. L. Lee, Effect of oxidation on the creep behavior of copper-chromium in situ composite, Composites Part A: Applied Science and Manufacturing 34/12 (2003) 1135-1271.

[13] R. Subramanian, S. Ramakrishnan, P. Shankar, Role of disclination and nanocrystalline state in the formation of quasicrystalline phases on mechanical alloying of Cu-Fe powders, Journal of Materials Science and Technology 16/5 (2000) 499-503.

[14] L.K. Tan, Y. Li, S.C. Ng, L. Lu, Structures, properties and responses to heat treatment of Cu-Y alloys prepared by mechanical alloying, Journal of Alloys and Compounds 278/1-2 (1998) 201-208.

[15] J.P. Tu, N.Y. Wang, Y.Z. Yang, W.X. Qi, F. Liu, X.B. Zhang, H.M. Lu, M.S. Liu, Preparation and properties of TiB_2 nanoparticle reinforced copper matrix composites by in situ processing, Materials Letters 52 (2002) 448-452.

[16] C.C. Koch, Top-down synthesis of nanostructured materials: mechanical and thermal processing methods, Reviews On Advanced Materials Science 5 (2003) 91-99.

[17] J.P. Stobrawa, Z.M. Rdzawski, Characterisation of nano-structured copper - WC materials, Journal of Achievements in Materials and Manufacturing Engineering 32/2 (2009) 171-178.

[18] J.P. Stobrawa, Z.M. Rdzawski, Dispersion - strengthened nanocrystalline copper, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 35-42.

[19] J.P. Stobrawa, Z.M. Rdzawski, W.J. Głuchowski, Micro-structure and properties of nanocrystalline copper - yttria microcomposites, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 83-86.

[20] J.P. Stobrawa, Z.M. Rdzawski, W. Głuchowski, W. Malec, Microstructure evolution in CRCS processed strips of CuCr0,6 alloy, Journal of Achievements in Materials and Manufacturing Engineering 38/2 (2010) 195-202.

[21] J. Stobrawa, Z. Rdzawski, W. Głuchowski, W. Malec, Ultrafine grained strips of CuCr0.6 alloy prepared by CRCS method, Journal of Achievements in Materials and Manufacturing Engineering 33/2 (2009) 166-172.