

The new approach of the production technique of discontinuous Cu-C composite

Nov pristop v proizvodni tehniki diskontinurnega Cu-C kompozita

Rebeka Rudolf^{1,2}, Ivan Anžel¹

¹University of Maribor, Faculty of Mechanical Engineering / Slovenia

²Zlatarna Celje d.d., Celje / Slovenia

Abstract: The samples of the Cu-C composite were produced by two different techniques: (i) the sintering of powders, and (ii) the internal carbonisation of rapidly solidified pure copper. The aim of the present research was to produce a discontinuous Cu-C composite with the submicron dispersion of graphite particles.

The results of our microstructural investigation show that the use of the mechanical alloying and sintering of consolidated powders is an inappropriate way to achieve a submicron dispersion of the graphite particles. On the other hand, the combination of rapid solidification and internal carbonisation was found to be an efficient technique to obtain the requested microstructure.

Key words: Cu-C composite; sintering; internal carbonisation; microstructure

Povzetek: Vzorci Cu-C kompozita so bili izdelani z dvema različnima tehnikama: (i) s sintranjem prahu in (ii) z notranjo karbonizacijo hitro strjenega čistega prahu. Namen raziskovalnega dela je bil izdelati diskontinuiran Cu-C kompozit s pod-mikrometrsko disperzijo grafitnih delcev. Rezultati mikrostrukturnih preiskav kažejo, da uporaba mehanskega legiranja ter sintranja konsolidiranih prahov ni učinkovita metoda za doseg pod-mikrometrске disperzije grafitnih delcev. Po drugi strani pa se je kombinacija hitrega strjevanja in notranje karbonizacije pokazala kot učinkovita tehnika za doseg želenе mikrostrukture.

Ključne besede: Cu-C kompozit; sintranje; notranja oksidacija; mikrostruktura

1. Introduction

Copper is one of the most suitable engineering materials for thermal and electrical application. Like any other metal it softens at higher temperature, so the strengthening is one of the ways to overcome this problem. The copper matrix has been successfully strengthened with graphite reinforcements - particles and discontinuous or continuous fibre. The system Cu/C shows good thermal, electrical and stress properties in comparison to other Cu-based metal matrix composites [1], on the other hand the Cu-C phase system is characterised by highly restricted mutual solubility of elements in solid state (α_{Cu} with about 0.02 at.% solubility of C and graphite with no reported solubility of Cu) [2]. Therefore the main problems in developing of Cu-C composite are the extremely weak interfacial bonding matrix-fibre and the attainment of a high volume percentage of finely dispersed, incoherent graphite particles of submicron size. Our research focuses

on the achievement of the discontinuous Cu-C composite with the submicron dispersion of graphite particles.

The Cu-C composite reinforced with C-particles can be produced by different techniques. In this paper two were presented: (i) sintering of powders, and (ii) internal carbonisation of rapidly solidified pure copper [3]. The sintering of Cu and C powders consists of the mechanical alloying and the annealing of the consolidated powders, while the combination of the rapid solidification (RS) and the internal carbonisation (IC) represents a new way in the conventional route production of the Cu-C composite. The rapid solidification serves as a process where the numerous defects in the microstructure were created, while the internal carbonisation enables the C-atoms segregate on these defects [4]. The increasing of C-concentration on these positions consequently produces the supersaturation and the thermodynamic conditions for the formation of C-clusters, which in the further stage form the C-particles.

2. Experimental procedure

2.1. Synthesis of sintered Cu-C composite

The high purity copper powder (99.99%) with the particle size 140 μm , and graphite powder with three different sizes of particles were separately mixed in an arthritic mixer for 1 hour. Figure 1 shows the typical shape of the initial Cu in C particles. Each mixture was subsequently cold pressed in a uniaxially press at 210 MPa. Obtained were greenbodies of about 99% of the bulk density having cylindrical shape with 70 mm in diameter

and 3 mm in height. The compacted tablets were than annealed in a furnace at 1300 K and vacuum 10^{-2} mbar for 3 hours.

The described technology was used in preparing the following Cu-C specimens:

- Composite A with 5 vol.% of spherical graphite (2r= 1 μm , 99,9995% purity),
- Composite B with 5 vol.% of spherical graphite (2r= 2-15 μm , 99,9995% purity),
- Composite C with 5 vol.% of nano-scaled graphite (2r= 0.3 μm , 99,6% purity)

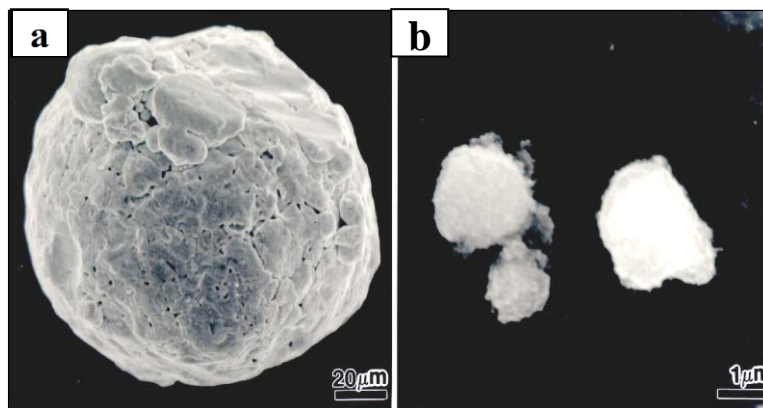


Figure 1. a) Cu particle, b) spherical graphite particles

In the first step the microstructures of cold pressed (CP) and the sintered specimens were examined separately. In the second step the graphite volume fraction and also the porosity measurements of all specimens were performed: (i) in samples with the ideal geometry by calculation, and (ii) in samples with the irregular shape with the measurements of real density with pyknometer.

2.2. Synthesis of Cu-C composite with combination of RS/IC

The rapid solidification process of pure Cu (99.99%) was performed under an Ar atmosphere using a quartz crucible 48 mm in inner diameter and nozzle with an orifice diameter of 1.5 mm. The melt was ejected by Argon overpressure of 0.02-0.03 MPa onto the surface of a copper-beryllium wheel rotating at the speed of about 21 m/s. Continuous ribbons 3 to 5 mm in width and 60 to 80 μm in thickness were produced. The microstructure of RS- α_{Cu} ribbons consists of a zone with columnar α_{Cu} grains only a few μm in size, extending from the wheel surface up to the free surface of the ribbon and is shown in Figure 2.

The experimental specimens for IC were prepared from pieces of RS- α_{Cu} and nano-scaled powders of amorphous carbon. Short pieces of RS- α_{Cu} were packed in a powder of amorphous carbon, isostatically pressed into 3 cm long

tablets and enclosed in a quartz ampoule. The heat treatments (HT) were carried out in a tube furnace at temperature of 1273 K, for various periods of time.

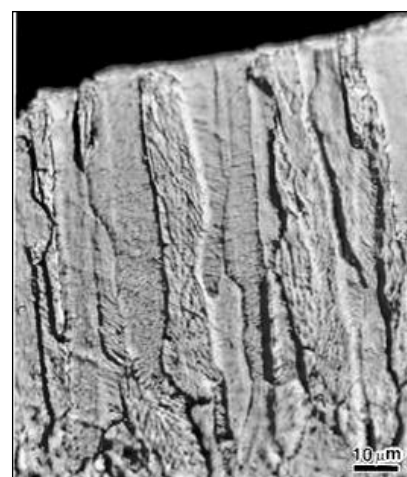


Figure 2. Microstructure of RS- α_{Cu} matrix

Microstructural characterisation of sintered and heat-treated RS samples was carried out by optical microscopy (OM), scanning electron microscopy (SEM-Jeol JSM 840 A) as well as EDX microanalysis (Link Analytical AN 1000) and transmission electron microscopy (TEM). In

addition Auger Electron Spectroscopy (AES-Microlab 310 equipped with SEM and X-ray photoelectron Spectrometer -XPS) was used to determine the elemental composition of precipitated particles in the RS- α_{Cu} matrix. The surfaces of particles were cleaned and etched with Ar^+ ions ($E= 2keV$, $\rho= 12 \mu Acm^{-2}$, $\Theta= 47^\circ$) to remove surface contaminants and to obtain compositional depth profiles of particles.

The sintered and the heat-treated RS samples were etched in $FeCl_3-H_2O-HCl-C_2H_5OH$ solution, while the thin foils of heat-treated RS ribbons were prepared by electro-polishing in a solution CrO_3 and CH_3COOH .

3. The results and discussion

3.1. Analysis of sintered Cu-C composite

EDX - analysis of cold pressed and sintered microstructure revealed the dark field inside grains consisting of fine graphite particles and the dark field on the grain boundaries presenting partially the pores and partially the great graphite agglomerates. The CP microstructure of samples A and B shows bimodal

distribution of the graphite particles, which average size in the Cu-grains is roughly $0.5-0.7 \mu m$ and on the grain boundaries about $13-14 \mu m$ (Fig. 3a, 3b). During the mechanical mixing of the composite C the high degree of nano-scaled graphite agglomeration was observed, consequently in the CP microstructure only the large pores and the graphite agglomerates along the grain boundaries are identified (Fig. 3c). The average size of these agglomerates is about $18 \mu m$. The results of graphite volume fraction in the CP samples show that the fractions in all samples are slightly above $\sim 3.5\%$, which is less than the theoretical value (5 %).

The results of porosity measurement further show that the CP composites A and B have practically equal porosity ($\sim 0.5 vol. \%$), while the composite C has $6\times$ higher value of porosity. It was also found that the volume fraction of porosity in the sintered A and B composites is higher than in the CP samples ($\sim 1.8\%$) and that the sintered composite C has an equal degree of porosity after sintering in comparison with the CP state.

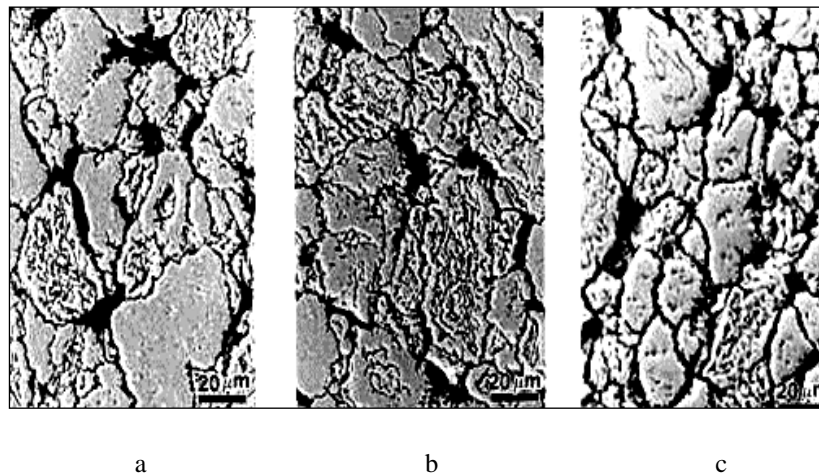


Figure 3. Microstructure of A, B and C composites chemical etched with $FeCl_3-H_2O-HCl-C_2H_5OH$ solution

The depth etching of cross and longitudinal section of A and B composites revealed that the smaller C-particles are mainly oblong and of bar shape (Figure 4a in 4b). The stereometric analysis of graphite volume fraction by classical etched microstructure was based on assumption that the smaller C-particles are spherical; consequently the calculated values of graphite volume fraction were smaller than theoretical ($\sim 1.5\%$). Considering the real bar shape on the depth-etched microstructure the deviation of the quantitative determinate graphite volume fraction was minimised to 0.7% . The determinate values are a slightly greater than the theoretical value which is the result of a stronger Cu-matrix solving in the surrounding of C-particles by the depth etching.

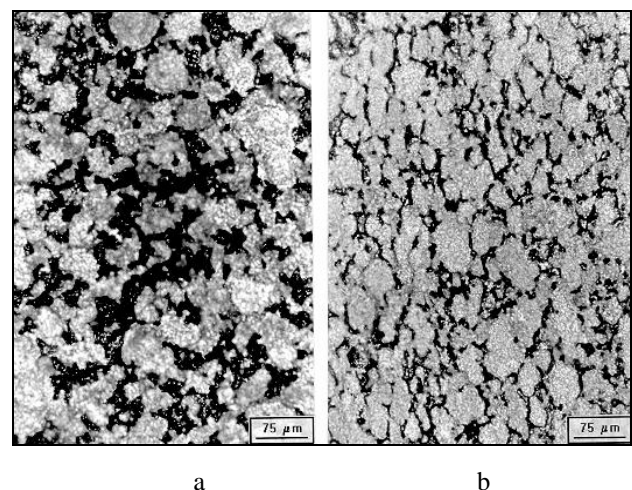


Figure 4. Depth-etched microstructure of composite A: **a)** cross and **b)** longitudinal section

Based on the results of microstructural characterisation as well as on the results of quantitative microstructure analysis the following microstructural features and characteristic changes occurring during mechanical mixing, cold pressing and sintering been identified:

- By mechanical mixing of powder an intensive agglomeration of C-particles occurred, whose tendency was inversely proportional to the initial size of graphite particles;

- The degree of agglomeration determines a distribution of graphite on the volume of matrix. The greater initial size of the C-particles (lower degree of agglomeration) increases the fraction of the uniform distribution of the C-particles, while at higher degree of agglomeration the priority of C-particles distributed along the boundary increases;

- During cold pressing the microstructural evolution depends on two mechanisms, which consequently influence the bimodal distribution of graphite in the cold pressed samples. Graphite agglomerates were spread along the boundary, while by the dispersed C-particles imprinted in the surface of Cu-particles the sliding of C-layers took place. Consequently, the spherical morphology of graphite changes to bar morphology;

- The presence of oxygen in the phase of sintering of the Cu-C composite caused an internal oxidation of graphite resulting in the increased porosity fraction.

After each phase of sintering it was also found that in this manner the required fine submicron dispersion of graphite particles in the Cu-matrix could not be obtained.

3.3. Analysis of internally carbonised RS Cu-ribbons

Metallographic examination of the RS matrices of the heat-treated experimental samples after various time of HT revealed the microstructure consisting of α_{Cu} grains and very fine submicron particles homogeneously distributed through the volume of the matrix (Fig. 5).

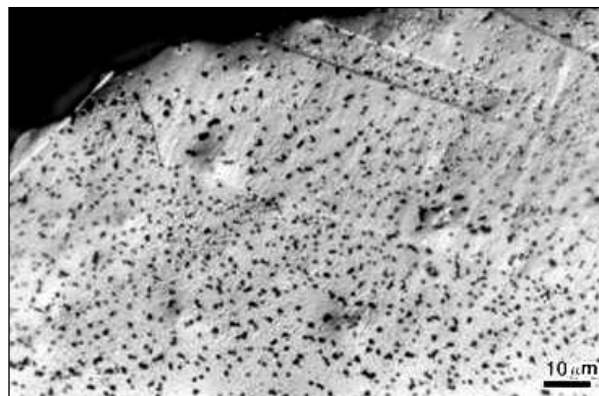
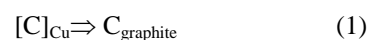


Figure 5. Micrographs of RS- matrix after HT at 1273 K for 9 min

It was found that the volume fraction of precipitated particles depends on the temperature and time of HT. The higher degree of HT temperature and its duration causes the higher volume fraction of particles. The particles precipitate simultaneously throughout the entire volume of α_{Cu} matrix and no precipitation front appeared in the microstructure during the experiment. During the internal carbonisation C-atoms start with dissolution into the copper lattice, continue with diffusion in the matrix interior and concentrate in some places producing great super-saturations of carbon. These places are most probably numerous defects in the crystal lattice of the RS- α_{Cu} matrix and at these positions was obtained enough high activity of carbon atoms needed for the formation of C-clusters, which in the further stage form the C-particles.

In the "normal" internal oxidation processes the solubility product of compound at reaction front has to be exceed and the critical super-saturation for homogeneous precipitation is attained. Consequently fine particles of compounds start to precipitate from the solid solution. In our case, we cannot be deal with the solubility product because we do not have an alloy but the pure metal. So the critical supersaturation is needed for the formation of critical C-clusters, which in the further stage overgrow into the C-particles. On the basis of this theory and thermodynamic data [2] the following reaction of dissolved C on numerous defects in the crystal lattice of the RS- α_{Cu} matrix was expected:



The results of the EDX analyses with the X-mapping confirm that the precipitated particles contain carbon corresponding to the distribution of elements in the region of the precipitated particles in the RS- α_{Cu} matrix as shown in Fig. 6, which confirms that these particles might be graphite particles.

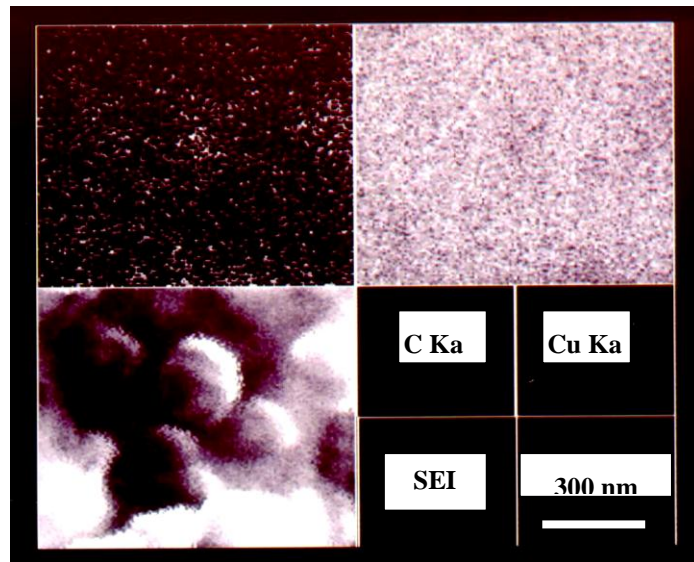


Figure 6. Distribution of elements in the region of precipitated particles in RS- α_{Cu} matrix

TEM examination and diffraction figure of the precipitated particles shown in the Fig.7 also revealed that

the particles are pure polycrystalline graphite with the average size about 0.5 μm .

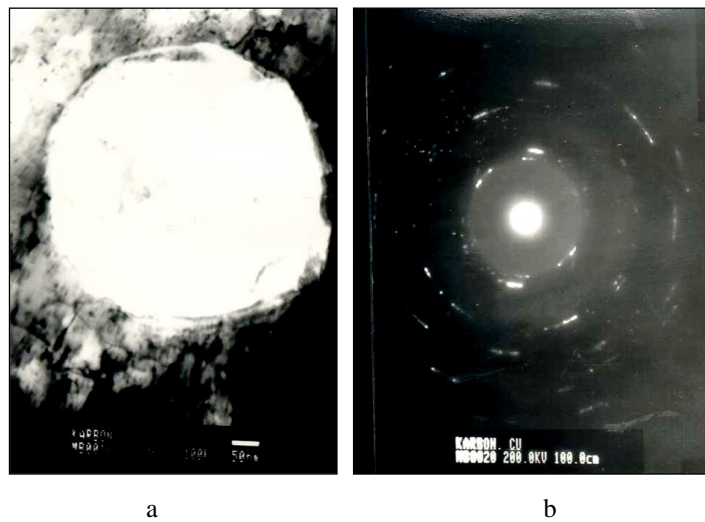


Figure 7. a) TEM image of polycrystalline graphite, b) diffraction figure of precipitated particles

Additionally, the energy position and shape of an Auger peak in the direct energy spectrum (EN(E) versus the electron kinetic energy) as well as in the differentiated

form (EdN(E)/dE- for display and peak identification) clearly show, that the particles consist of pure graphite (curve P1 and P2 in Figure 8).

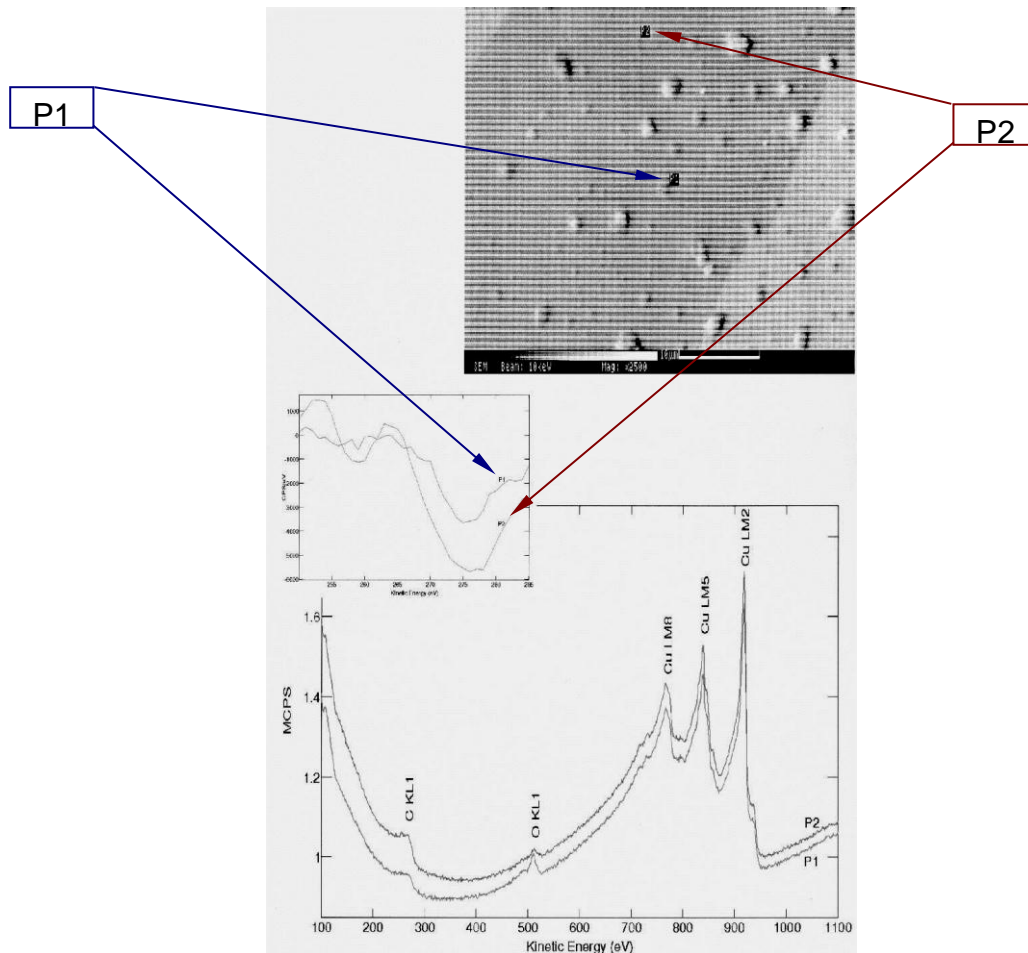


Figure 8. The Auger spectra from the precipitated particles in the RS- α_{Cu} matrix

Based on these arguments we can conclude that the process of particles formation in the RS- α_{Cu} matrix during internal carbonisation consists of next stages:

- in the first stage the carbon atoms dissolve at the α_{Cu}/C interface into the lattice of α_{Cu} matrix and diffuse in their interior. While the critical concentration of carbon needed for graphite formation of clusters is higher than the maximum solubility of carbon in copper is no reaction in the RS- α_{Cu} matrix and the carbon concentration increases in the entire volume of the matrix up to the solubility limit. At numerous defects in the crystal lattice the carbon atoms are attracted and produce at these positions great supersaturations;
- in the second stage, when the critical supersaturation for graphite formation is attained, fine particles of graphite start to precipitate from the copper matrix. The particles precipitate simultaneously throughout the entire volume of RS- α_{Cu} matrix, no precipitation front appears in the microstructure. These arguments confirm that the graphite precipitation primarily runs on the point defects (void clusters, voids, ..) and that the degree of supersaturation depends on the type of these

defects and their position. The simultaneous precipitated C-particles are namely of different size.

4. Conclusions

On the basis of the received results and analyses the following conclusions can be summarised:

1. The combination of rapid solidification and internal carbonisation makes the fabrication of discontinuous Cu-C composite with submicron size of graphite particles possible.
2. The experiments confirmed the hypothesis, that during the internal carbonisation the C-atoms segregate on the defects in the rapidly solidified microstructure. The increasing of C-concentration on these positions consequently produces the supersaturation and the thermodynamic conditions for the formation of C-clusters, which in the further stage form the C-particles.
3. The volume fraction and size of the precipitated graphite particles are dependent on the initial rapidly solidified microstructure, on the temperature and the time of the internal carbonisation.

4. Precipitation process of C-particles is run without precipitation of carbonisation front with a simultaneous precipitation of C-particles throughout the entire volume of α_{Cu} - matrix. The C-concentration in the matrix reaches the maximum solubility, while the C-supersaturation is achieved on the defects in the crystal lattice.
5. The fabrication of the discontinuous Cu-C composite with the use of mechanical alloying and sintering was demonstrated as inappropriate for the achievement of submicron dispersion of graphite particles.
6. During the mechanical mixing of powder an intensive agglomeration of C-particles occurred. The tendency was inversely proportional to the initial size of graphite particles. The degree of agglomeration determines a distribution of graphite on the volume of matrix. The greater initial size of the C-particles (lower degree of agglomeration) increases the fraction of the uniform distribution of the C-particles, while at higher degree of agglomeration the priority of C-particles distributed along the boundary increases.
7. During the cold pressing the microstructural evolution depends on two mechanisms, which consequently influence the bimodal distribution of graphite in the cold pressed samples. Graphite agglomerates are spread along the boundary, while in the dispersed C-particles imprinted in the surface of Cu-particles the sliding of C-layers took place. Consequently, the spherical morphology of graphite changes to bar morphology.
8. The presence of oxygen in the phase of sintering of the Cu-C composite caused an internal oxidation of graphite resulting in the increased porosity fraction.

References

1. Dofman S., Fuks D.: " Formation and relative stability of interstitial solid solution at interfaces in metal matrix composites", *Materials & Design* Volume18, 1997, p. 4-6.
2. Brandes E.A., Brook G.B. (eds.): "Smithell's Metals Reference Handbook", Butterworth-Heinemann Ltd, London, 1992.
3. Anzel I., R. Rudolf, A. Krizman, A.C. Kneissl: " Microstructural changes during internal carburisation of Cu-Al alloy", *Praktischen Metallographie*, 2002, p. 401-413.
4. RUDOLF, Rebeka, GILIĆ, M., ROMČEVIĆ, Maja J., ANŽEL, Ivan. Optical properties of plastically deformed copper : amorphous state with residual nanocrystals. *Optoelectron. Adv. Mater. Rapid Commun. (Print)*. [Print ed.], Sep. 2011, vol. 5, no. 9, str. 932-935.

