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Electrical conductivity and hardness of Cu-graphite composite after ECAP

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Abstract

Hot isostatic pressing (HIP) prepared Cu-graphite composite at 6 vol.% graphite was equal-channel angular pressing (ECAP) processed in following way: 4 × B_C. After that, the microstructure, hardness and electrical conductivity of ECAP processed composite were investigated and compared with the properties of as-HIPed composite. Better hardness due to smaller grain size of copper matrix and certain changes of graphite phase shape and spatial distribution were observed for ECAP processed sample. The electrical conductivity was observed unchanged by ECAP processing which is consistent with the behaviour of pure copper after ECAP processing.

K e y w o r d s: metal matrix composites, powder processing, ECAP, hardness, electrical conductivity

1. Introduction

Cu-alloy/graphite composites or lead/tin copper alloys are widely used in sliding bearings and brushes applications [1, 2]. In the case of low voltage and high current densities for sliding parts of welding machines, it is required to employ materials with a very high specific electrical conductivity, good thermal conductivity, thermal stability, hardness and low friction coefficient. These conditions are fulfilled by copper-graphite (Cu-graphite) composite material [3–6]. It can be prepared by various methods, such as infiltration, sintering, cold pressing, hot pressing or hot isostatic pressing (HIP-ing) [3, 7–9]. Recently the wear and friction coefficient of Cu-graphite composites made by HIP process were investigated [10–12]. It is confirmed that the better homogeneity of graphite phase spatial distribution leads to lower friction coefficient for the composite at constant volume fraction of graphite and can be mostly realised as follows: The first way is to use fine graphite powder. The second way is to use a copper coating on graphite particles to avoid graphite powder clustering.

The grain size, shape and spatial distribution of materials can be altered by ECAP process [13–16]. ECAP is usually used for producing ultrafine-grained (UFG) structures. During ECAP deformation, the sample transverse section is unchanged, thus permitting an infinite number of pressings or passes (in practice from 4 to 8). Therefore, it was proposed to test the ECAP technology on HIP-ed Cu graphite composite, and then the ECAP process influence on the micro hardness of Cu-graphite composites was investigated [17].

The main aim of this work is to study how the ECAP process affects HIP-ed Cu-graphite composite microstructure and physical and mechanical properties and to compare the results with ECAP processed UFG copper properties and structural changes.

2. Material and methods

Cu-graphite composite material at 6 vol.% graphite was prepared by HIP-ing of mixture of copper (particle size $< 70\,\mu m$, average particle size $22\,\mu m$,

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Table 1. Image analysis of graphite clusters at Fig. 2. Here ⊥ is the cross-sectional area perpendicular and ∥ area parallel to ECAP direction

Sample	Number of clusters (–)	Average size (μm)	Perimeter (μm)
HIP-ed	705	5.14	128
ECAP-ed ⊥	1041	4.49	113
ECAP-ed ∥	994	4.49	110

purity 99.9 %) and graphite (average particle size 16 μm, purity 99.9 %) powders. The copper powder was electrolytic Cu powder of dendritic shape (manufacturer Kovohuty a.s., Krompachy, Slovak Republic), while graphite was of flake shape (grade CR5, Grafit a.s., Netolice, Czech Republic). The starting powders were wet mixed (ethanol was used as solvent) in Turbula shaker and dried afterwards at 150 °C for 2 h. Then the mixture was cold compacted to a cylinder at 200 MPa, which was put into a steel tube, evacuated and sealed. The sample was put into hot isostatic pressing equipment and was HIP-ed at 900 °C for 1 h under the pressure of 100 MPa under argon atmosphere.

From the HIP-ed sample, the precursor of geometry $11.8 \times 11.8 \times 80\,\mathrm{mm}^3$ was machined and subjected to four passes by route B_C to study the effect of ECAP processing technology on resulting composite microstructure. Route B_C denotes a rotation of 90° around pressing axis between each pressing. It is known that route B_C is experimentally an optimum processing route for the grain refinement and for attaining a homogeneous microstructure [13]. The ECAP die with 90° angle of channel intersection, sharp die corners $\psi = 0°$ and channels cross-section of $12 \times 12\,\mathrm{mm}^2$ was utilised. The graphite lubricant was applied onto the dies surface prior pressing. The composite sample prior each turn was heated to 400 °C for 15 min and then ECAP processed at 400 °C with back-pressure of 75 MPa using average load of 28 kN and average ram speed of $1\,\mathrm{mm\,s}^{-1}$.

The density of sample was calculated from known geometry and air weight. ECAP processed sample was cut parallel and perpendicular to ECAP direction. Samples were then polished, etched (Kalling's etching for 10 s) and the microstructure was observed using light microscopy (Olympus GX51) and SEM electron microscopy (JEOL JSM-7600F with EDS, WDS and EBSD detectors). Image J software was used for image analysis of the obtained microstructures.

The hardness HV30 of the samples was measured using standard equipment at load of 294 N for 10 s. The hardness of HIP prepared pure copper sample was also measured for comparison (an identical copper powder was used).

The electrical conductivity of the composite samples was measured by four probe DC method [18] at 296 K. The composite samples with the length of 22 mm (HIP) and 25 mm (ECAP) and the cross section of $4 \times 10\,\mathrm{mm}^2$ were used for the measurement. One of the voltage electrodes was moved with the step of 0.5 mm against the fixed position of the second one. The measurement in 40 different positions was performed for each sample in order to evaluate the electrical conductivity and to check the macroscopic homogeneity of the sample.

3. Results and discussion

The density of HIP composite sample was 8.55 $\mathrm{g\,cm}^{-3}$. The sample after ECAP process had a density of 8.50 $\mathrm{g\,cm}^{-3}$. Sample after HIP-ing was fully dense without observable pores. Therefore this difference can be attributed to density scatter inside of large HIP billet (ø 50 mm × 200 mm), from which the sample of geometry $11.8 \times 11.8 \times 80\,\mathrm{mm}^3$ was machined.

It was confirmed that the ECAP process changes the microstructure of the investigated composite – the technology affects the graphite phase size and morphology and also the grain size of copper matrix.

Primarily, during ECAP process the shear deformation can change the volume of graphite clusters by dividing them into two or more clusters of smaller size. Indeed, the graphite clusters in copper matrix after ECAP process became smaller as their average diameter decreased from 5.14 to 4.49 μm (Table 1) according to performed image analysis. Also the decrease of spatial distribution of graphite clusters was observed as indicated the higher number of observed graphite clusters after ECAP process at the same cross sectional area of the investigated samples (Fig. 2). Almost similar values of number of clusters, average size and perimeter for cross sections parallel and perpendicular to ECAP direction indicated good homogeneity of the ECAP processed sample.

The morphology of graphite clusters was also changed during ECAP process. This was observed by image analysis of micrographs in Fig. 1: For HIP-ed sample the orientation of graphite clusters is purely 45° and 90° with maximal roundness values of 0.65 and 1. Roundness is the measure of how closely the shape of an object approaches that of a circle. For ECAP processed sample the orientation of graphite clusters for both directions (⊥, ∥) was slightly

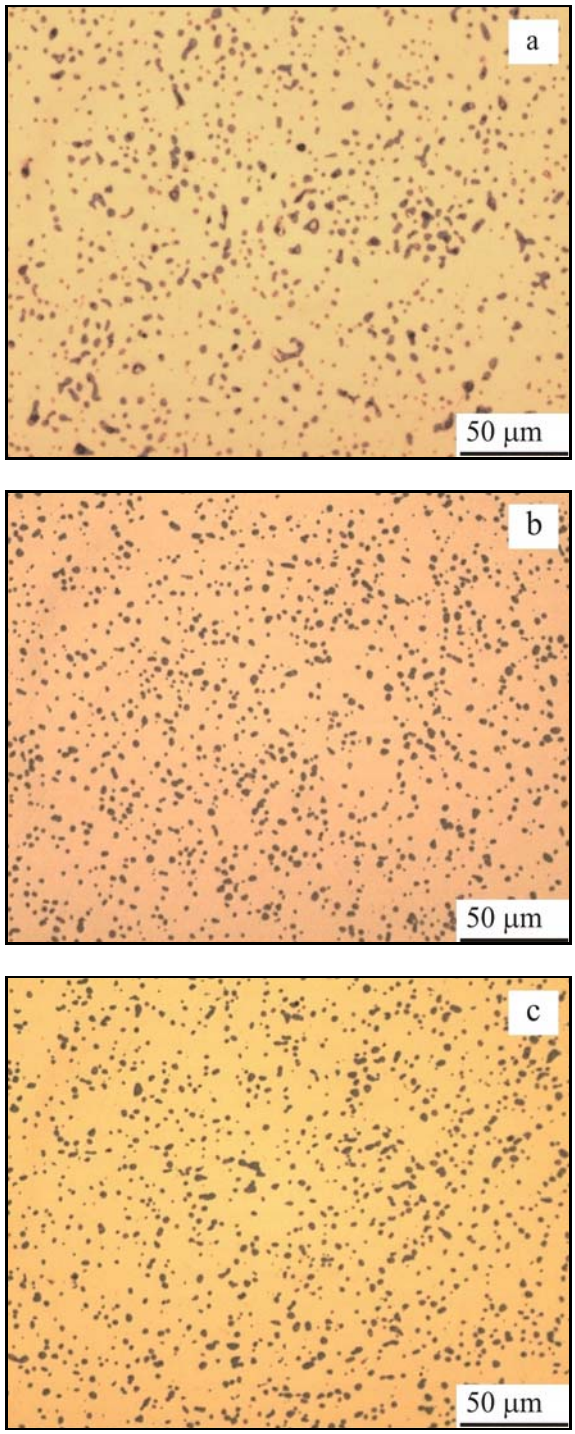

Fig. 1. Cross sections of (a) as received composite sample and composite sample (b) perpendicular and (c) parallel to ECAP direction.

scattered around 45° and 90° but the maximal roundness values changed significantly to 0.48, 0.67, 0.82 and 1 for perpendicular, and maximum roundness values of 0.49, 0.61, 0.68, 0.74 and 1 for parallel to ECAP direction. The shift of roundness values after ECAP process to more elliptical cluster shape is evident. The

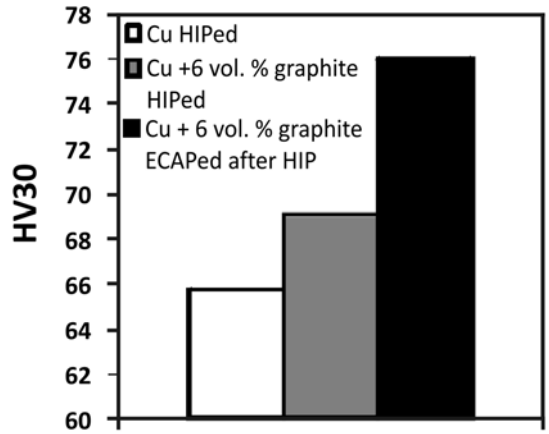

Fig. 2. Hardness HV30 of HIP-ed Cu and Cu-graphite samples and ECAP processed HIP-ed Cu-graphite sample.

ECAP process also decreased the shape complexity of graphite clusters as smaller perimeter values after 4 B_C passes indicate.

The Vickers hardness results of the investigated samples are shown on Fig. 2. They were also compared with hardness of HIP-ed Cu sample prepared from identical Cu powder at the same processing HIP conditions. It is evident that admixing of small amount of graphite particles with higher strength and modulus into the ductile copper matrix increased the hardness of the resulting composite. The hardness of ECAP processed composite material increased further significantly. It can be explained in analogy with UFG copper – smaller copper grain size in composite is affecting the composite hardness. Indeed, it was found, using EBSD observations, that the average size of copper grains in composite decreased from 6.8 ± 1.4 µm prior to 2.1 ± 0.8 µm after ECAP process (Figs. 3, 4). The observed decrease of copper grain size is smaller in comparison with pure copper, where ultra fine grains of nanometre size can be usually prepared by ECAP. This is probably governed by graphite clusters within copper matrix. Graphite particles act against the grain size refinements of copper as they are there as an obstacle diminishing interaction of shearing plane with crystal structure and the deformation texture of f.c.c. copper.

After converting HV values to SI units (HV values multiplied by 9.807 to obtain MPa) we have used Tabor standard work [19] to express the yield stress σ_Y of the investigated composite material. For non-strain-hardening materials, the Vickers hardness number HV is approximately related to the constant yield stress by following equation:

$$HV = 3\sigma_Y. \quad (1)$$

Thus experimental data points for copper grain

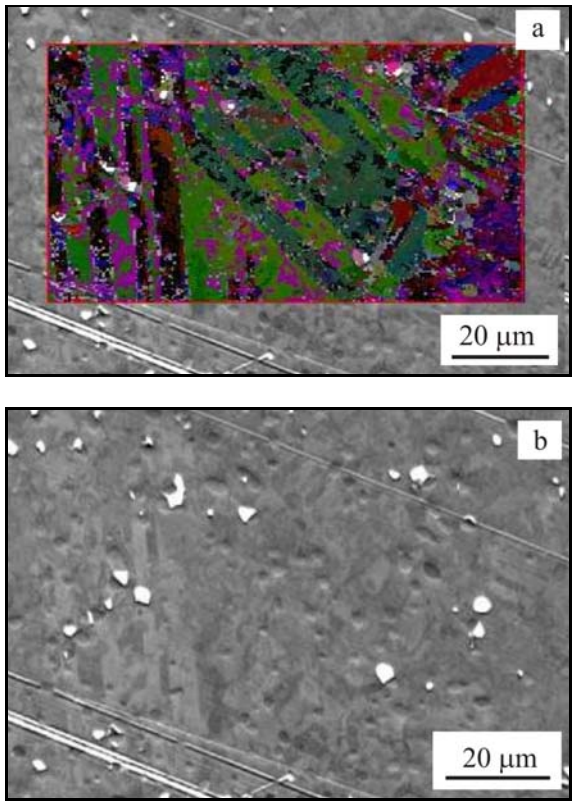

Fig. 3. HIP-ed sample: (a) Cu grains size and orientation (EBSD), (b) original SEM image.

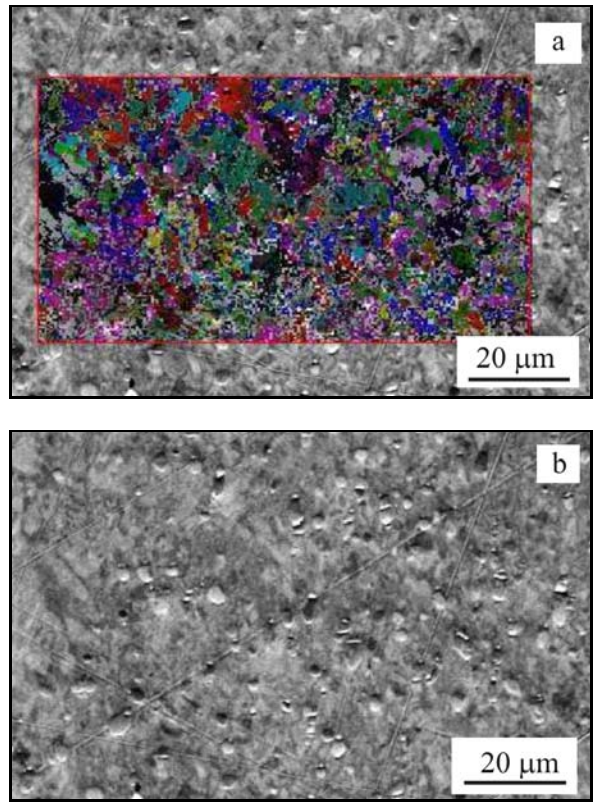

Fig. 4. ECAP-ed sample: (a) Cu grains size and orientation (EBSD), (b) original SEM image.

size d in the investigated composite materials can be used in the well-known Hall-Petch relationship

$$\sigma_{\mathrm{Y}} = \sigma_0 + kd^{-1/2} \tag{2}$$

to estimate Hall-Petch coefficient k and intrinsic stress for dislocation movement σ_0 after ECAP process. The obtained value of Hall-Petch coefficient $k = 0.074\,\mathrm{MPa\,mm^{1/2}}$ is lower and falls outside of literature value defined range 0.104–0.25 $\mathrm{MPa\,mm^{1/2}}$ [20] for pure copper. However, in this case we have a composite system. It is evident that the specimen is not pure metal, there are the impurities as graphite particles in copper matrix and as it is not oxygen free copper there are some oxides present also at copper-copper and mainly at copper-graphite grain boundaries. These may act as effective barriers to dislocation movement thus influencing significantly the Hall-Petch dependence for Cu-graphite samples. Due to this also the obtained value of intrinsic stress $\sigma_0 = 198\,\mathrm{MPa}$ is higher than usual values of intrinsic stress for copper 36 MPa [20].

Measurement of the electrical conductivity of composites confirmed that the measured samples were homogeneous on the all length of measured range of the moving electrode. The original HIP-ed Cu-graphite sample possesses electrical conductivity of $5.01 \pm 0.03 \times 10^7\ \mathrm{S\,m^{-1}}$. The observed value is in very good consistency with previously measured electrical conductivity data [4] in the range of 0–40 vol.% graphite in Cu-graphite composites. For example, electrical conductivity of HIP-ed pure Cu sample is $5.88 \pm 0.04 \times 10^7\ \mathrm{S\,m^{-1}}$ [4]. It is evident that addition of 6 vol.% of graphite decreases the electrical conductivity of final composite when compared to pure HIP-ed copper. The sample after ECAP process has slightly smaller value of electrical conductivity $4.98 \times 10^7\ \mathrm{S\,m^{-1}}$, but the difference is only minimal.

As was stated in the work of Hellming et al. [21], the overall favourable assessment of the effect of ECAP on the mechanical and physical properties of copper is also based on the fact that ECAP does not lead to any significant deterioration of electrical conductivity of copper. It can be concluded that in this work it was also confirmed for Cu-graphite composites with 6 vol.% graphite.

The reason for this is following: The overall conductivity is a function of the conductivity of copper grains and graphite clusters and existing interfaces between them. The dominant part is the conductivity of copper grains itself and the area of grain boundaries between copper grains for the investigated composite. Due to simple mechanical bonding between cop-

per and graphite it can be expected that electrons will preferably move within copper grains. The conductivity of copper-copper grain boundaries can be identified with the electron reflectivity [22]. Differences in electron reflectivity correspond to differences of grain size distribution functions, as this influences the matching between boundaries of neighbouring grains. Our observation of grain size changes indicates that the changes are not as enhanced as it is in the case of pure copper [21].

4. Conclusions

HIP prepared Cu-graphite composite with 6 vol.% graphite was ECAP processed in $4 \times B_C$. The microstructure, hardness, electrical conductivity and wear properties of ECAP processed composite were investigated and compared with the properties of as-HIPed composite. It can be concluded that qualitatively the observed microstructure and properties changes are similar to the behaviour of UFG copper prepared by ECAP process. Quantitatively, the results are influenced by the graphite phase within copper matrix.

The following changes due to ECAP processing were observed:

– the graphite clusters become smaller: an average diameter decreases from 5.14 to 4.49 μm and the clusters distance also decreases as is indicated by increasing number of graphite cluster;

– anisotropy of graphite cluster increases slightly due to elongation of clusters (smaller roundness);

– graphite clusters after ECAP are less complex shaped (smaller average perimeter);

– average size of copper grain decreases from 6.8 ± 1.4 μm prior to 2.1 ± 0.8 μm after ECAP processing (EBSD observations on SEM);

– the hardness of composite increases from 69.1 HV30 prior to 76.0 HV30 after ECAP;

– the observed Hall-Petch coefficient k is 0.074 MPa mm$^{1/2}$ and corresponding intrinsic stress σ_0 is 198 MPa for the investigated Cu-graphite composite;

– electrical conductivity of the Cu-graphite sample after ECAP process has almost the same value 5×10^7 S m^{-1} as original HIP sample. It can be concluded that electrical conductivity of Cu-graphite composite is not affected by ECAP process up to 4th pass and has similar behaviour as pure copper behaviour under ECAP process.

It can be concluded that ECAP processed composite has homogeneous structure, smaller graphite cluster size and spatial distribution, the less complex morphology of graphite clusters, smaller grain size of copper matrix, increased hardness and almost the same electrical conductivity. Qualitatively, the property changes of copper matrix composite at 6 vol.% graphite due to ECAP process behave similarly as property changes of pure copper due to ECAP process.

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