21 YEARS OF BALKAN TRIBOLOGICAL ASSOCIATION

ROMANIAN TRIBOLOGY ASSOCIATION

UNIVERSITY PETROLEUM-GAS OF PLOIESTI, ROMANIA

BALKANTRIB'14

8th INTERNATIONAL CONFERENCE ON TRIBOLOGY, 30thOct.-1stNov.2014, SINAIA, ROMANIA

Friction and wear properties of copper-based composites reinforced with micro- and nano-sized Al_2O_3 particles

Aleksandar VENCL[1)*], Viseslava RAJKOVIC[2)], Fatima ZIVIC[3)]

[1)] Tribology Laboratory, Faculty of Mechanical Engineering, University of Belgrade, Serbia
[2)] Department of Materials Science, Institute of Nuclear Sciences “Vinca”, University of Belgrade, Serbia
[3)] Tribology Center, Faculty of Engineering, University of Kragujevac, Serbia
[*]Corresponding author: avencl@mas.bg.ac.rs

Abstract: *Copper-based composites with hard particles are widely applied in electrical sliding contacts such as those in railway overhead current collection system, lead frame in large scale integrated-circuit, welding electrodes, transfer switches and electrical contact material. Powder metallurgy is the most applicable technology way of producing the copper-based composites, especially when the matrix material is reinforced with second phase particles. Two copper-based composites reinforced with micro-sized Al_2O_3 particles (app. 750 nm in size) and nano-sized Al_2O_3 particles (less than 100 nm in size), and produced by powder metallurgy technology, were compared with a Cu-Cr-Zr alloy produced by casting technique. The tribological tests were carried-out on ball-on-disc nanotribometer, under the high-load (1 N), low-speed (8 mm/s) dry sliding condition. The addition of micro-sized Al_2O_3 particles did not showed so beneficiary effect, since this composite had the lowest hardness and wear resistance, and at the same time, the highest coefficient of friction. On the other hand the addition of nano-sized Al_2O_3 particles increased considerably hardness of composite and improved the wear resistance to a significant extent, and also reduces the coefficient of friction.*

Keywords: *copper-based composites, Al_2O_3 particles, dry sliding, friction, wear.*

1. Introduction

Copper and copper alloys constitute one of the major groups of commercial metals. They are well-known materials that are widely used in industrial applications mainly because of their excellent electrical and thermal conductivities, outstanding resistance to corrosion, ease of fabrication, and good strength and fatigue resistance [1]. Copper can be strengthened by alloying it with other elements or by incorporating fine particles of a second phase in its matrix. The second phase can be a metal or an inter-metallic compound precipitated from a solid solution by an aging treatment, or it can be non-metallic particles, such as a stable oxide, added to or formed within the copper matrix. The effectiveness of these oxide particles as strengtheners depends upon particle size (finer is better), particle distribution (well dispersed is better), particle density (more per unit volume is better), and particle spacing (closer is better) [2].

There are several ways to incorporate the oxide particles in a copper matrix. Conventional melting and casting techniques do not work well because wide differences in the densities of copper and the oxide phase lead to segregation in the melt. The most common methods to produce Cu-Al_2O_3 composites involve powder metallurgy (PM) technology. These methods range from simple mechanical mixing of the constituents to complex methods, such as internal oxidation. Internal oxidation is regarded as the most suitable method for preparing these kinds of composites because it is capable of producing high-quality products on an industrial scale [3]. Internal oxidation produces a superior product because it develops the finest oxide particle size, smallest interparticle spacing, and most uniformly spaced particles required for optimum properties [2].

There are very few tribological experiments conducted on copper-based composites reinforced with Al_2O_3 micro- and nano-sized particles, and most of them did not explain tribological tests in detail. Nevertheless, all of them report that addition of Al_2O_3 particles decrease the wear rate of the copper matrix, and usually wear rate decreases as the Al_2O_3 content in the composites increases. Zhou et al. [4] investigated fretting wear resistance of Cu-Al_2O_3 composites prepared by PM technology (powders were prepared by coprecipitation method). The amount of Al_2O_3 nano-particles was varied from 1 to 5 wt.%, with the majority of particles of about 60 nm in diameter. Fretting wear results showed that wear volume of the composites is always lower than that of copper, and the lowest wear volume is achieved with addition of 2 wt.% Al_2O_3. The wear mechanism of copper was adhesion. For composites with up to 1 wt. % of Al_2O_3 adhesive wear associated with oxidation wear was the dominant type of wear, and for composites with the higher amount of Al_2O_3 abrasive wear associated with delamination is noticed. Soleimanpour et al. [5] used similar amount of Al_2O_3 (from 0.7 to 5.5 wt.%) to produce Cu-Al_2O_3 composites by internal oxidation of cast alloys. Particles sizes in most cases were below 1 µm. Their results also confirm beneficial effect of Al_2O_3 particles presence on the wear resistance of composites. This effect was more pronounced with higher content of Al_2O_3 particles. The dominant type of wear, for lower content of Al_2O_3 particles, was oxidative wear (at the beginning) and delamination wear (at the end of tests). For higher content of Al_2O_3 particles, mainly adhesive wear with plastic flow of the surface layers was noticed.

In our study the tribological tests were carried-out under the dry sliding condition on ball-on-disc tribometer, for three copper-based materials. Two copper-based composites, containing Al_2O_3 micro- and nano-sized particles and produced by PM technology (one by mechanical alloying and another by internal oxidation), were compared with copper-based alloy Cu-0.4Cr-0.08Zr, produced by casting.

2. Experimental details

2.1. Materials

Three different copper-based materials, obtained by different processing techniques, were tested in this study. The first was copper-based composite containing Al_2O_3 micro-sized particles and produced by PM technology (preceded by mechanical alloying), referred to as Cu-micro Al_2O_3. Starting components were copper powder and 5 wt.% Al_2O_3 particles. This mixture was mechanically milled and compacted. The second material was composite containing Al_2O_3 nano-sized particles and produced by PM technology (proceeded by mechanical alloying and internal oxidation), referred to as Cu-nano Al_2O_3. Starting component was prealloyed copper powder containing 2.5 wt.% Al. This powder was subjected to internal oxidation, i.e. during milling, aluminium being less noble than copper, dissolved in the copper matrix, oxidizes first reacting with oxygen from the air and forms nano-sized Al_2O_3 particles (app. 4.7 wt.%). Average particles sizes were 750 nm (in Cu-micro Al_2O_3C) and less than 100 nm (in Cu-nano Al_2O_3).

The third material, used for the purpose of comparison, was copper-based alloy Cu-0.4Cr-0.08Zr (referred to as Cu-Cr-Zr) produced by casting, followed by heat treatment. Designation and basic properties of tested materials are shown in Table 1. Detailed processing parameters for all materials and other properties are given elsewhere [6].

Table 1 Designations and basic properties of samples

Designation	Processing method	Chemical composition	Microhardness HV_{50}	Surface roughness R_a, µm
Cu-micro Al_2O_3	PM – mechanical alloying	Cu-5Al_2O_3	129	0.29
Cu-nano Al_2O_3	PM – mechanical alloying and internal oxidation	Cu-4.7Al_2O_3	224	0.21
Cu-Cr-Zr	Casting	Cu-0.4Cr-0.08Zr	177	0.08

Microstructure of the Cu-micro Al_2O_3 composite is shown in back-scattered electron (BSE) mode (Fig. 1a). Dark globules in the structure are micro-sized Al_2O_3 particles with approximate diameter of 750 nm. The SEM analysis (Fig. 1b) illustrates the presence of aluminium and oxygen in these particles implying their chemical composition.

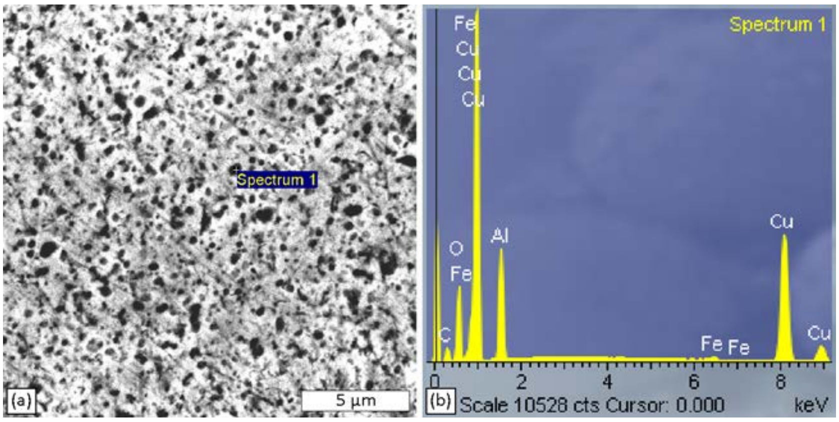

Figure 1 Microstructure and SEM analysis of Cu-micro Al_2O_3 composite: (a) BSE image and (b) EDS spectrum of a particle

Figure 2a shows the microstructure of Cu-nano Al_2O_3 composite. Globular uniformly distributed nano-sized Al_2O_3 particles, with diameter less than 100 nm, could be seen. SEM analysis (Fig. 2b) detected the presence of aluminium and oxygen in these small particles suggesting that the chemical composition of these particles corresponds to Al_2O_3. Small amount of iron probably originates from the milling steel balls. It should be noted that in the case of EDS analysis the diameter of electron beam was 1 µm, which was considerably larger than the diameter of Al_2O_3 particles. It means that the electron beam was not focused only to the particle, but also encompassed the surrounding copper matrix. The distribution of nano-sized Al_2O_3 particles in this composite was favourable in comparison with Cu-micro Al2O3 composite, and the grains size was restricted to a lower value due to the nano-sized particles pinning effect on grain growth [6].

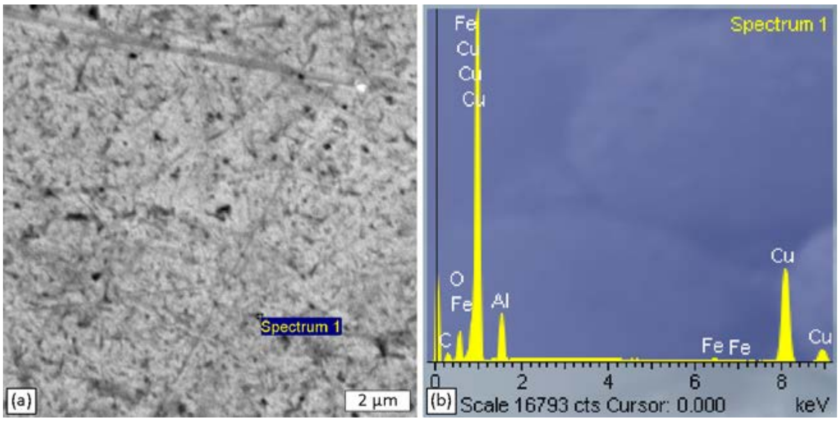

Figure 2 Microstructure and SEM analysis of Cu-nano Al_2O_3 composite: (a) BSE image and (b) EDS spectrum of a particle

2.2. Tribological testing

Tribological tests were performed on the nanotribometer with ball-on-disc configuration (rotation sliding mode), in accordance with ASTM G99. Static body (counter-body) was a steel ball made of 100 Cr6 martensitic bearing steel with 1.5 mm in diameter. Moving body was flat circular disc made of the tested materials. A schematic diagram of nanotribometer is presented in Figure 4. Sliding speed was constant (8 mm/s), as well as, normal load (1 N). The value of the initial contact pressure was around 1.4 GPa (Fig. 3a). Test was done without lubrications (dry sliding conditions), and in ambient air (temperature of 25 °C). Sliding distance of 30 m was the same in all tests. Before and after the testing, both the ball and the disc were degreased and cleaned with isopropyl alcohol.

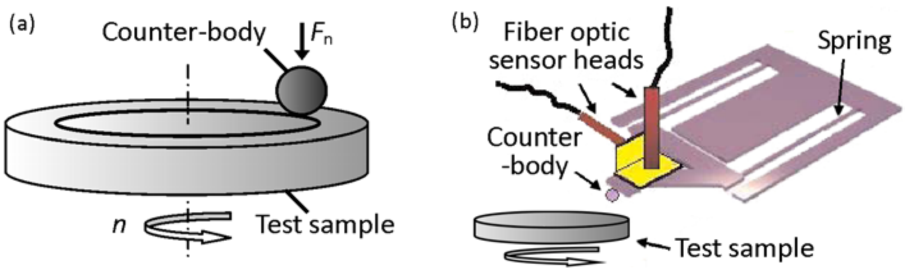

Figure 3 Schematic diagram of ball-on-disk nanotribometer: (a) contact conditions and (b) rotation sliding module

The coefficients of friction were continuously recorded, and those at the steady-state sliding were given in this article. Sampling rate for coefficient of friction measurements was 20 Hz. Wear volumes of the discs (test samples) were quantitatively assessed for each test, after a total sliding distance of 30 m, by measuring the wear tracks width with optical microscope (OM). It was assumed that the cross-sectional area of the wear track is represented by a flat segment of a sphere.

Penetration depth (PD) to which steel ball penetrates the flat surface of the flat disc during sliding, thus determining depth of the wear track on the flat sample, was also continuously recorded. Used nanotribometer is equipped with optical displacement sensor (fiber optic sensors) for measuring deflection of the cantilever (Fig. 3b), with high sensitivity. Light emitted from the sensor tip is reflected from the reflective areas attached to the spring (yellow rectangles in Fig. 3b), received by the sensor and converted into electrical signal. The signal is related to the distance between the sensor tip and a reflective area on the cantilever. Due to a nature of fiber optic sensors, besides measuring forces, it is also used to measure distance between the cantilever tip (tip of the steel ball) and flat surface of the sample (disc samples), which represents penetration depth value. Sampling rate was the same as for coefficient of friction measurements, i.e. 20 Hz.

After testing, the morphologies of the worn surfaces were investigated by using scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) was used to analyze the composition of the worn surface. Wear of the counter-body (Cr6 steel ball) was also monitored with OM.

3. Results and discussion

3.1. Coefficient of friction, penetration depth and wear factor

The repeatability of the results was poor so, for some materials, more than three replicate measurements were necessary.

The examples of, continuously recorded, coefficient of friction diagrams were presented in Fig. 4. Fluctuation of the coefficient of friction values (deviation from the average value) was present from the beginning to the end of tests, and it was characteristic for all tested materials. This suggests that stick-slip phenomenon occurs. It happens since the sliding speed was low and the normal load was high (causing high adhesion between samples and counter-body). The coefficient of friction for Cu-nano Al_2O_3 composite was more or less constant during the tests (Fig. 4b). For other two materials (Cu-micro Al_2O_3 composite and Cu-Cr-Zr alloy) a similar change in coefficient of friction was noticed: a rise right after the start of the test followed by a steady-state (Figs. 4a and c). Comparing to Cu-nano Al_2O_3 composite the stick-slip phenomenon was more pronounced at these two materials (especially for Cu-micro Al_2O_3 composite), which is in correlation with the observed wear mechanism (see Section 3.2).

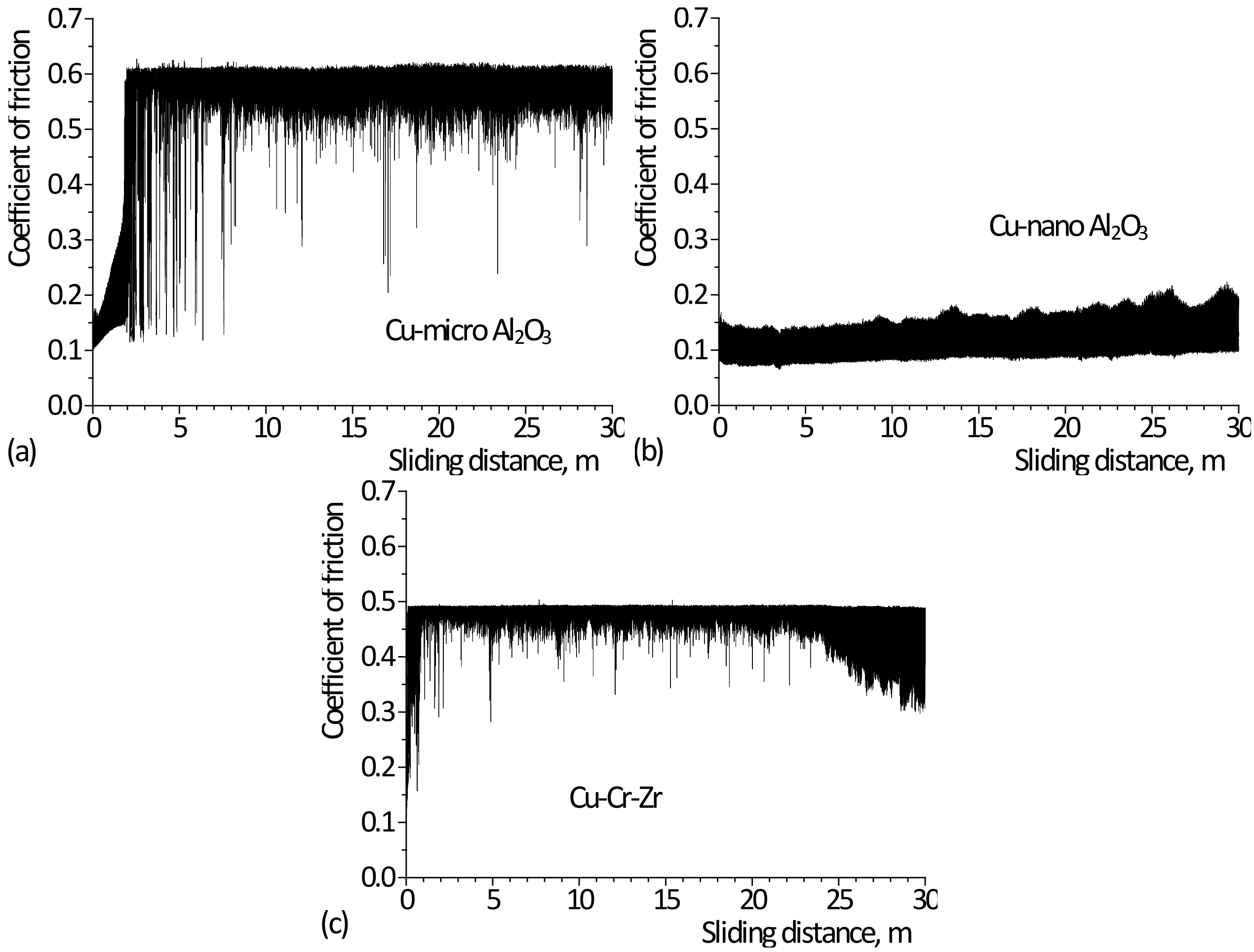

Figure 4 Examples of the coefficient of friction diagrams: (a) Cu-micro Al_2O_3 composite, (b) Cu-nano Al_2O_3 composite and (c) Cu-Cr-Zr alloy; Sampling rate 20 Hz

Fluctuation of the penetration depth values during the tests was noticed for all materials as well, with some examples presented in Fig. 5. In addition, in most of the cases, recorded values were unstable (Fig. 5a) and/or show negative trend (Fig. 5b) so, the penetration depth could not be taken as a representative value and could not be used for the wear calculation. Looking at the SEM images of worn surfaces (Figs. 7-9) it is clear that accumulation of material during the tests causes these shapes of penetration depth diagrams.

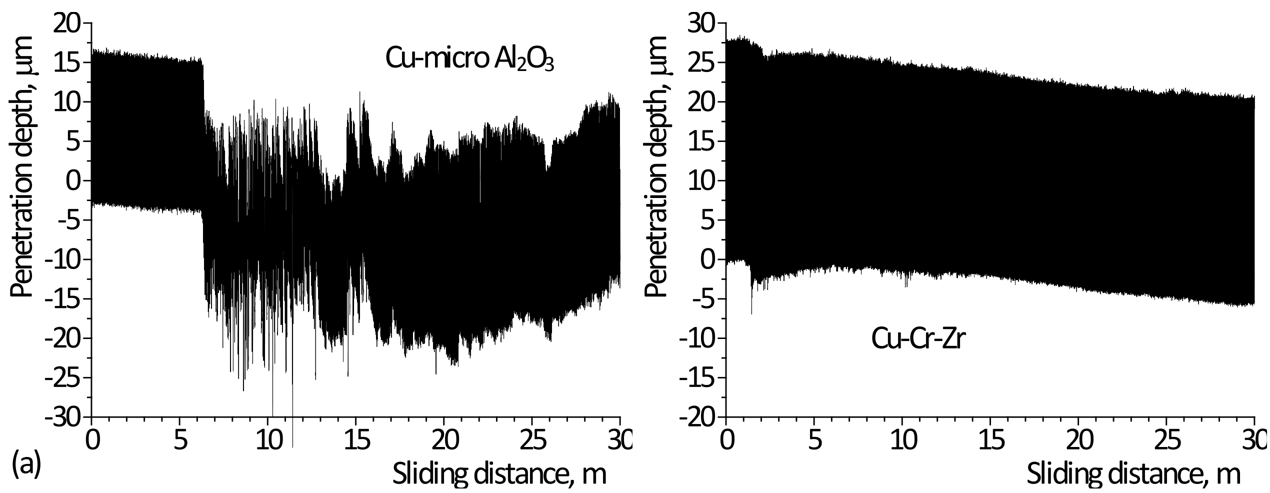

Figure 5 Examples of the penetration depth diagrams: (a) Cu-micro Al_2O_3 composite and (b) Cu-Cr-Zr alloy; Sampling rate 20 Hz

The averaged values of the coefficient of friction and wear factor (specific wear rate) for tested materials are presented in Fig. 6. Obtained values of the steady-state coefficient of friction corresponds to dry sliding conditions, and are in correlation with the hardness values (see Table 1), i.e. the material with highest hardness (Cu-nano Al_2O_3 composite) showed the lowest coefficient of friction, whereas the softest material (Cu-micro Al_2O_3 composite) displayed the highest coefficient of friction.

The coefficients of friction of Cu-micro Al_2O_3 composite and Cu-Cr-Zr alloy in contact with steel ball were around 0.5, which is similar with the values obtained by some other researches [4], under similar sliding speed and load. For high-load, low-speed conditions coefficient of friction of copper could be even higher (around 1) [7,8], but in our case the roughness of Cu-Cr-Zr alloy was very low (see Table 1), and it is well-known that the roughness influence is more pronounced in the low-speed range. Coefficient of friction for sliding pair: Cu-nano Al_2O_3 composite – steel ball, was more than 3 times lower in comparison with other two sliding pairs, which is connected with the fact that in this case the adhesion between sliding pair was less pronounced (see Section 3.2).

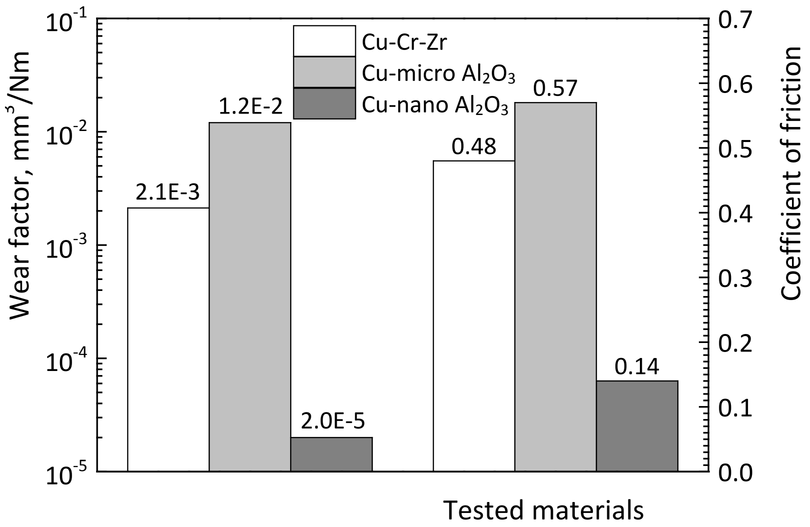

Figure 6 Wear factor and averaged coefficient of friction values of tested materials at the end of tests

Obtained values of the wear factors are in correlation with the hardness values (see Table 1), and also with coefficient of friction values of the tested materials. Wear factor values in Fig. 6 are presented in the logarithmic scale since the differences between the materials were very high (more than two and a half order of magnitude). Generally the wear factor (specific wear rate) values of all tested materials, and especially Cu-micro Al_2O_3 composite and Cu-Cr-Zr alloy, are higher than it is reported in the literature.

Zhou et al. [4] in ball-on-plate fretting wear tests (counter-body: steel ball; normal load: 0.1 to 1 N; sliding speed: avg. 12 mm/s) for Cu composite with 2 wt.% nano Al_2O_3 particles (60 nm in diameter) obtained wear factor of app. 1.9×10^{-6} mm^3/Nm. Soleimanpour et al. [5] in pin-on-disc linear sliding tests (counter-body: steel disc; normal load: 1 to 2 MPa; sliding speed: 0.5 m/s) for Cu composite with 5.5 wt.% nano Al_2O_3 particles (below 100 nm in diameter) obtained wear factor of app. 1×10^{-5} mm^3/Nm. Zhang et al. [8] in ball-on-plate fretting wear tests (counter-body: WC-Co ball; normal load: 1 to 11 N; sliding speed: 0.01 mm/s) for annealed coarse-grained Cu obtained wear factor of app. 1.1×10^{-5} mm^3/Nm.

Wear factors obtained in our study were higher than expected due to the several reasons: contact geometry, combination of high-load and low-speed, surface roughness, counter-body material, etc. In addition, the wear factor values in our study were calculated from total wear volume (not from steady-state wear volume, since the wear was measured only at the end of tests). All these reasons could be perceived and explained by the analysis of the wear mechanism through SEM images and EDS results.

3.2. Wear mechanism

Wear mechanism shows that in the case of Cu-nano Al_2O_3 composite dominant types of wear were delamination and light abrasion (Fig. 7), while the other two materials endured severe adhesive wear (Figs. 8 and 9). The Cu-nano Al_2O_3 composite worn surface shows presence of the adhesive wear also (8a), but it was much less pronounced than in other two materials (Figs. 8a and 9a). This suggests that this material is less ductile than the other two, and that its shear strength is enhanced. As a support for the “less ductile” claim is the presence of delamination and light micro-abrasive wear (8b). The Cu-nano Al_2O_3 composite showed the lowest wear and coefficient of friction values. In addition, the lowest wear of the counter-body (steel ball) occurred when it was in the contact with this composite (Fig. 10).

The reinforcing Al_2O_3 particles in this composite were very fine (most of the Al_2O_3 particles formed in the copper matrix, after internal oxidation, had less than 100 nm in diameter). These small particles prevent the extensive deformation of the matrix, which has positive effect on the wear and friction values. The weight fraction of reinforcing Al_2O_3 particles was similar in both composites: 4.7 wt.% in Cu-nano Al_2O_3 composite and 5 wt. % in Cu-micro Al_2O_3 composite, but the size of these particles was very different (less than 100 nm and approximately 750 nm, respectively). This enables better distribution of the nano-sized particles, i.e. nano-sized particles was app. 7.5 times smaller, so if the amount is almost the same, the distances between particles need to be shorter (app. 7.5 times).

The Cu-micro Al_2O_3 composite endures severe adhesive wear, and plastic flow on the surface of the material could be noticed (Fig. 8a). This corresponds to the hardness value (see Table 1) which is the lowest for this material (lower hardness usually means lower shear strength). Worn material is accumulated over the wear track (most obvious is in the middle of Fig. 8a). This accumulated worn material caused fluctuation of the penetration depth value during the tests (see Fig. 5a). The micro-sized Al_2O_3 particles in this composite were unable to prevent plastic flow of the material, i.e. these particles were detected in worn adhesive plates (Fig. 8b). This is confirmed with EDS analysis (Figs. 8c and d) which shows that micro-sized Al_2O_3 particles were presented in the accumulated worn-out material. The EDS analysis reveals presence of aluminium, oxygen and the small concentration of iron probably originating from the counter-body steel ball. The fact is that some of the particles remain in composite, while others were detached from it (three-body micro-abrasion) or were just protruded to the surface (two-body micro-abrasion). This also caused wear of the counter-body (steel ball), which was the highest when it was in the contact with Cu-micro Al_2O_3 composite.

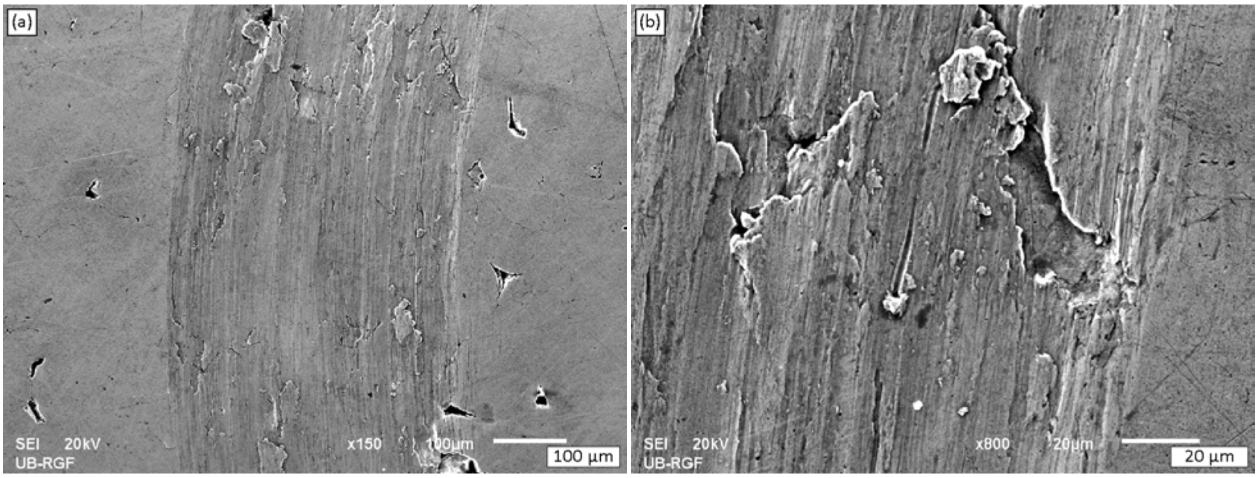

Figure 7 SEM images of Cu-nano Al_2O_3 composite worn surface: (a) entire wear track width and (b) detail

It is well-known that the wear resistance of composites is very dependant on reinforcement size (dimensions) and working conditions. A general rule is that the wear increases with the increase of the particle size for high-load, low-speed conditions, whereas for low-load, high-speed conditions the effect is opposite [9]. In our study, the loads were high (initial Hertz pressure was around 1.4 GPa) and the speed was very low (8 mm/s). In this situation the coarser particles increase the wear. This is followed with very high wear factor (order of 10^{-2}), which for adhesive wear in unlubricated conditions should be from 10^{-7} to 10^{-2} [10].

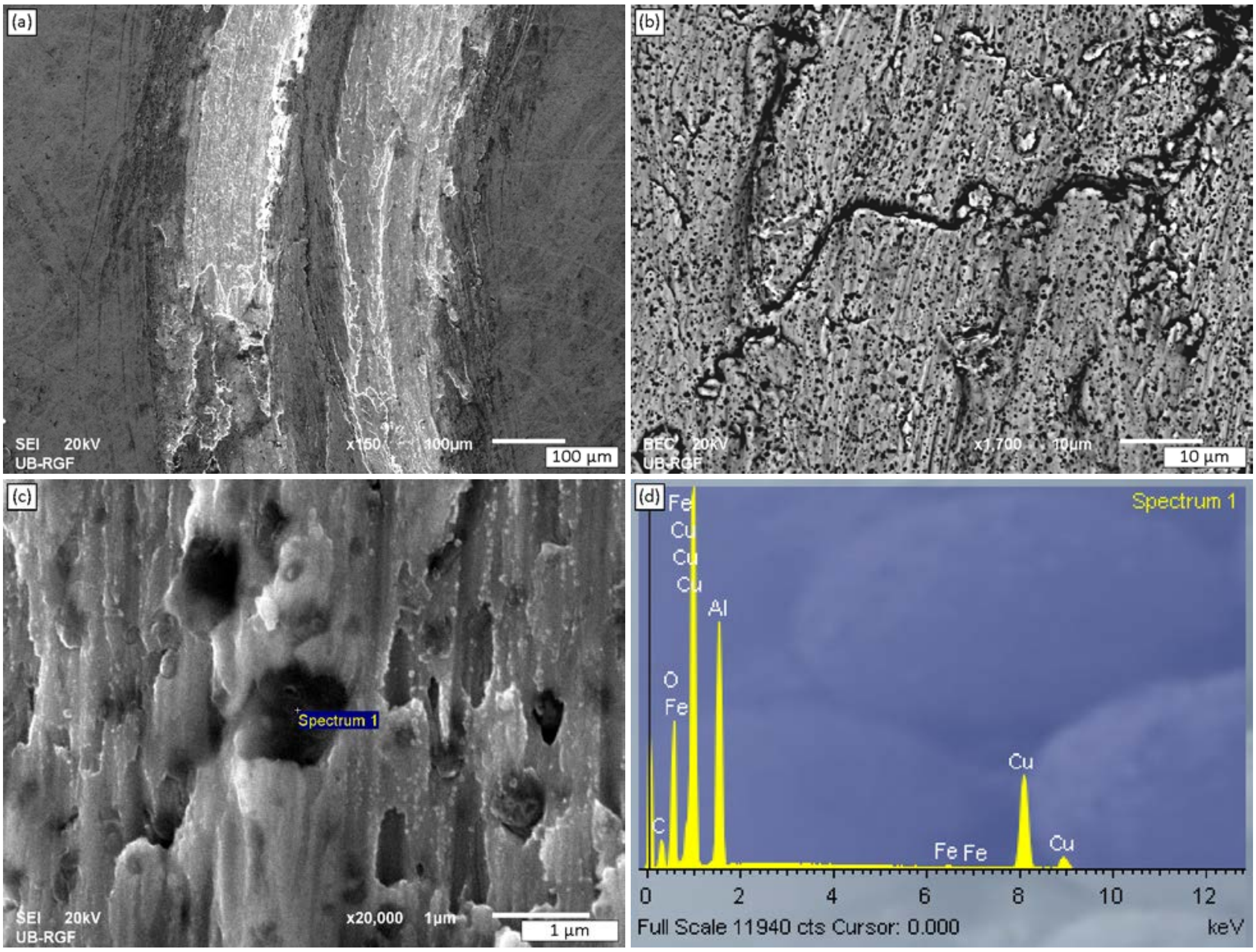

Figure 8 SEM images and EDS analysis of Cu-micro Al_2O_3 composite worn surface: (a) entire wear track width, (b) detail in BSE mode, (c) Al_2O_3 particles in the worn material and (d) EDS spectrum of a Al_2O_3 particle

Worn surfaces of Cu-Cr-Zr alloy (Fig. 9a) showed similar appearance as Cu-micro Al_2O_3 composite, i.e. severe adhesive wear, and plastic flow of the material is noticed. This material did not have hard reinforcing particles and flow of the material was more even (accumulation of the material was all over the wear track), Fig. 9b.

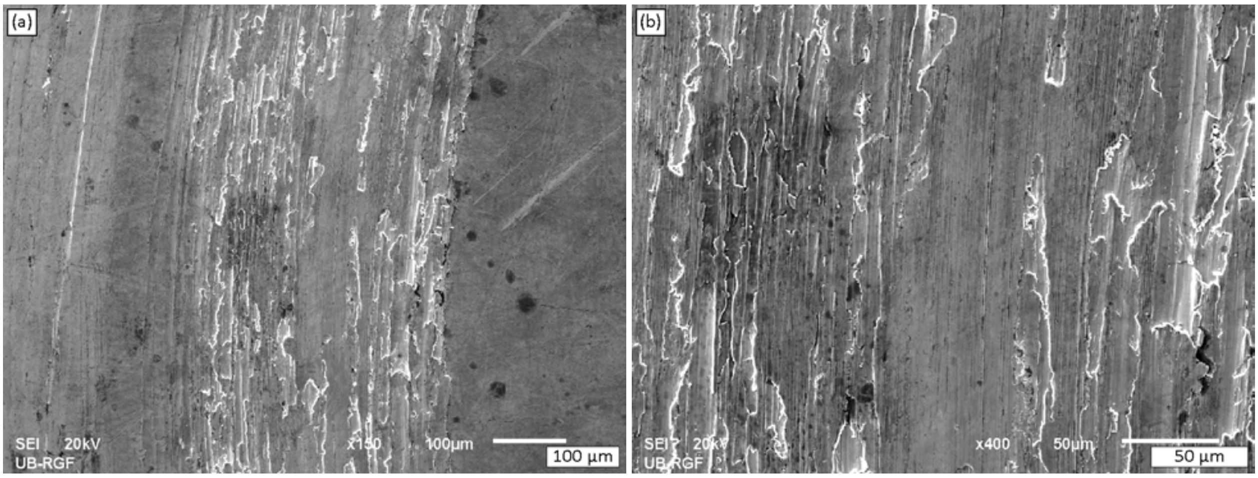

Figure 9 SEM images of Cu-Cr-Zr alloy worn surface: (a) entire wear track width and (b) detail

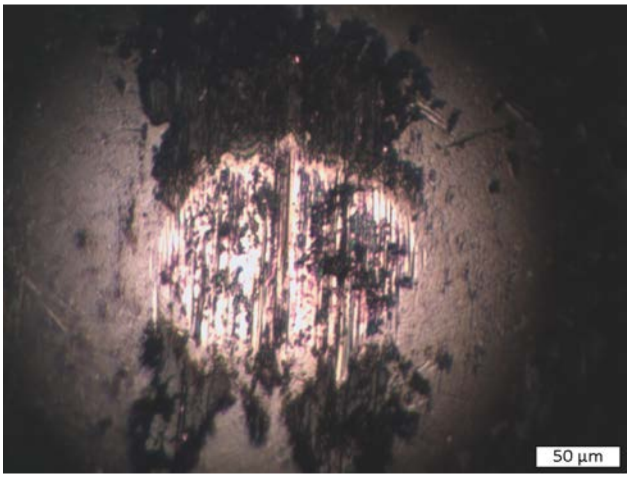

Figure 10 OM image of the Cr6 steel ball worn surface in contact with Cu-nano Al_2O_3 composite

4. Conclusion

Three copper-based materials obtained by different processing techniques were studied in dry sliding condition under the high-load and low-speed. Two copper-based materials were composites, containing Al_2O_3 micro- and nano-sized particles and produced by PM technology (one by mechanical alloying and another by mechanical alloying and internal oxidation). Third material was copper-based alloy Cu-0.4Cr-0.08Zr, produced by casting.

According to the tribological results it is obvious that the addition of nano-sized Al_2O_3 particles considerably increases hardness of Cu-nano Al_2O_3 composite and improves the wear resistance to a significant extent, and also reduces the coefficient of friction. Favourable distribution of nano-sized Al_2O_3 particles combined with its pinning effect on grain growth reduced the deformation of matrix during the sliding process. Reduced deformation of the material together with high hardness of nano-sized Al_2O_3 particles ensured wear resistance of this material, which was much higher (more than two order of magnitude) than the wear resistance of other two materials.

Composite containing micro Al_2O_3 particles and Cu-0.4Cr-0.08Zr alloy exhibits severe adhesive wear with plastic flow of the material on the surface. Testing conditions for these two materials were too severe, and that is why their wear factors have high values.

In case of Cu-micro Al_2O_3 composite, although in general Al_2O_3 particles have a reinforcing role, it seams that they did not reduce the wear. On contrary, some of these particles were detached and act as a third body increasing wear, or were protruded to the surface increasing the wear of the counter-body. The wear of this material, as well as the wear of the counter-body in contact with this material, were the highest of all examined materials. The lowest wear resistance of Cu-micro Al_2O_3 composite could be explained by the particle size and their mutual distance. Present in the same quantity, larger Al_2O_3 particles compared to smaller are at a greater distance from one another, so that they provide lower resistance to wear.

Acknowledgement

This work has been performed as a part of activities within the projects OI 172005, TR 34028 and TR 35021. These projects are supported by the Republic of Serbia, Ministry of Education, Science and Technological Development, whose financial help is gratefully acknowledged.

References

[1] Tyler D.E., Black W.T.: Introduction to Copper and Copper Alloys, in: *ASM Handbook Volume 2, Properties and Selection: Nonferrous Alloys and Special-Purpose Materials*, ASM International, Metals Park, (1990), 216-240.

[2] *Glidop® (SCM Product Literature, 1994)*, SCM Metals Products, Research Triangle Park, (1994).
[3] Liu R., Song K., Jia S., Xu X., Gao J., Guo X.: Morphology and frictional characteristics under electrical currents of Al_2O_3/Cu composites prepared by internal oxidation, Chinese Journal of Aeronautics, 21 (2008) 3, 281-288.
[4] Zhou G., Ding H., Zhang Y., Hui D., Liu A.: Fretting behavior of nano-Al_2O_3 reinforced copper-matrix composites prepared by coprecipitation, Metalurgija – Journal of Metallurgy MJoM, 15 (2009) 3, 169-179.
[5] Soleimanpour A.M., Abachi P., Purazrang K.: Wear behaviour of *in situ* Cu-Al_2O_3 composites produced by internal oxidation of as cast alloys, Tribology – Materials, Surfaces & Interfaces, 3 (2009) 3, 125-131.
[6] Vencl A., Rajkovic V., Zivic F., Mitrović S., Cvijović-Alagić I., Jovanovic M.T.: The effect of processing techniques on microstructural and tribological properties of copper-based alloys, Applied Surface Science, 280 (2013), 646-654.
[7] Emge A., Karthikeyan S., Kim H.J., Rigney D.A.: The effect of sliding velocity on the tribological behavior of copper, Wear, 263 (2007) 1-6, 614-618.
[8] Zhang Y.S., Wang K., Han Z., Liu G.: Dry sliding wear behavior of copper with nano-scaled twins, Wear, 262 (2007) 11-12, 1463-1470.
[9] Vencl A.: Tribology of the Al-Si alloy based MMCs and their application in automotive industry, in: Magagnin L. (Ed.): *Engineered Metal Matrix Composites: Forming Methods, Material Properties and Industrial Applications*, Nova Science Publishers, Inc., New York, (2012), 127-166.
[10] Kato K., Adachi K.: Wear Mechanisms, in: B. Bhushan (Ed.): *Modern Tribology Handbook, Volume One, Principles of Tribology*, CRC Press, Boca Raton, (2001), ch. 7.