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Tribological Characteristics of Copper Based Composites with Al_2O_3 Particles at Various Temperatures

Abstract: Two copper based composites: an experimental Cu-Al_2O_3 and commercial GlidCop AL-60 grade (with 1.1 wt.% Al_2O_3) with grains size approximately 1–2 µm were treated by Equal Channel Angular Pressure (ECAP) technique in order to induce severe plastic deformation and to reduce the grain size by about an order of magnitude. Microstructure of the as-received and ECAPed states of both systems were observed. Hardness of the experimental materials was measured by instrumented indentation. Tribological properties were studied by pin-on-disk technique in dry sliding against a steel ball at a various temperatures from room temperature up to 873 K. For all systems the coefficient of friction and specific wear rates were evaluated. Worn surfaces were studied by scanning electron microscopy and level of oxidation was measured using EDX spectrometry. It was found that between 473 K and 673 K the coefficient of friction decreased significantly. At lower temperatures the finer grained systems were more wear resistant than the as-received ones. The wear rate of all systems decreased down to zero at 673 K due to formation of hard oxide rich layers. Damage mechanisms were identified and their relationship with structural characteristics was inferred.

Keywords: ECAP, Cu-Al_2O_3, GlidCop, nanocomposites, sliding wear, tribology

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1 Introduction

Copper is a traditional and very versatile material used widely in many industrial applications mainly for its excellent electrical and thermal conductivity. In order to increase its generally low hardness and more importantly low yield and tensile strength a variety of Cu alloys has been developed. However, they tend to exhibit a rather large decrease in both electrical and heat conductivity and low long term stability at elevated temperatures. In most cases also conventional melting and casting techniques do not work very well, because large differences in densities of copper and incorporated oxides lead to their segregation. Here, powder metallurgy can provide a solution in dispersing particles in the prepared material and achieve appropriate characteristics [1]. Another way how such desirable properties can be achieved is creating very fine, submicron-grained microstructures [2]. Such microstructures can be prepared by inducing severe plastic deformation [3]. This can be conveniently done by technique of the Equal Channel Angular Pressing (ECAP) which by multiple pressings of material through the die creates very fine grained nanostructure [4]. The materials prepared in this way are suitable for demanding parts of machines frequently exposed to intense friction and wear, such as washers, bearing liners, etc, where properties such as high strength and ductility, fatigue strength, wear resistance, etc., are required.

Aim of this work was to investigate the effect of refining of microstructure by ECAP process on tribological behavior and wear of various Cu-Al_2O_3 micro and nanocomposites at room and elevated temperatures.

2 Materials and experimental procedures

Two initial materials were used. The first one was a copper based composite produced as an experimental PM system by reaction milling and mechanical alloying. In this case Cu powder with the calculated addition of Al was homogenized by attrition in oxidizing atmosphere. The distribution of the obtained CuO was uniform. A subsequent treatment at 1023 K induced the reaction of CuO with the added Al powder, and led to the formation of Al_2O_3 particles. The

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remaining CuO was reduced by attrition in a mixture of $H_2 + H_2O$ (rate 1:100). The powder was compacted by cold pressing and hot extrusion at 1023 K–1073 K. In this way a micro-grained material with 2.7 wt% Al_2O_3 nanoparticles was prepared.

The second material was a particular grade of a commercial composite Glidcop AL-60 grade [5], with 1.1 wt.% Al_2O_3, produced by SCM Metal Products, Ltd. Glidcop is an industrial material and one of the leading candidates for practical applications. It is a metal matrix composite alloy (MMC) prepared by mixing copper primarily with aluminum oxide ceramic particles. The addition of small amounts of aluminum oxide has minuscule effects on the performance of the copper at room temperature (such as a small decrease in thermal and electrical conductivity), but greatly increases the copper's resistance to thermal softening and enhances high temperature strength [5]. The addition of aluminium oxide also increases resistance to radiation damage. As such, the alloy has found use in applications where high thermal or electrical conductivity is required while also maintaining strength at elevated temperatures or radiation levels.

Both initial materials were then transformed by the ECAP method in order to induce severe plastic deformation and to achieve very fine grained microstructures, and in such way to turn them into nanocomposite systems. The as-received samples were pressed in two passes through two right angled (90°) channels of a special die [6].

The notification of the experimental materials is explained in Table 1.

Microstructures were studied using TEM thin foils, in order to reliably identify matrix and dispersed phases.

Hardness and elastic modulus was measured using the depth sensing indentation (DSI) also called instrumented indentation technique. The measurements were carried out on a nano-indentation tester TTX-NHT by CSM Instruments. Berkovich pyramid diamond tip was used in sinus mode loading of 5 Hz frequency and 5 mN load amplitude. Loads up to 100 mN were applied. The resulting load-penetration (P-h) curves were evaluated according to the analysis of Oliver and Pharr [7] and values of hardness and elastic modulus as functions of depth as well as elastic and plastic deformation energies were calculated. Up to 20 indentations were performed and the obtained data were statistically evaluated.

Table 1: Experimental materials

Material	Designation	Matrix grain size
Micro-Cu-Al_2O_3	micro-Cu	1–2 μm
Nano-Cu-Al_2O_3	nano-Cu	100–200 nm
Glidcop AL-60	Glidcop	1–1.5 μm
Glidcop after ECAP	ECAP Glid	100–220 nm

Wear testing was performed on a High Temperature Tribometer THT, by CSM Instruments, using ball-on-disk technique. The sample was fixed on a turntable with adjustable rotational speed. The tangential force exerted on the holder was measured and from that the coefficient of friction (COF) was calculated and recorded as function of distance/time/laps. The vertical position of the holder was measured in order to monitor the displacement due to material removed by wear. As friction partners steel balls (chromium steel 100Cr6 with hardness 62 HRC) with 6 mm diameter were used. The loading of 1 N was applied using a dead weight system. The nominal wear track radius was 2 mm, the sliding speed was set to 5 cm/s and the overall sliding distance was 100 m. Testing was done on air (humidity 40% ± 5%), in dry conditions at temperatures 293 K, 473 K, 673 K, and 873 K. The heating was provided by an integrated furnace which reached the target temperature in the sample chamber in about 30 minutes and then during another 30 minutes it was allowed for the temperature to homogenize and stabilize. After the tests, both tribological partners (the steel ball and the sample) were observed using light microscopy. The depth and shape of the wear tracks were measured by a stylus profilometer (Mitutoyo SJ-201) on three or more places, the average trough cross section area was calculated and subsequently the volume of the removed material was estimated. The specific wear rates (W) were then expressed according to ISO 20808 [8] as the volume loss (V) per distance (L) and applied load (F_p):

$$W = \frac{V}{L.F_p}\left[\frac{mm^3}{m.N}\right], \tag{1}$$

and compared for both material systems.

3 Results and discussion

Microstucture studies were performed earlier and their results were reported in detail elsewhere [9, 10]. The TEM observations showed that in the as-received Glidcop there was less than 1% of residual porosity present, which was subsequently significantly reduced by the ECAP process. The matrix grains in Glidcop had elongated shape while in micro-Cu they were more equiaxed. In both materials in their as-received states the matrix grains had micrometric mean size, 1–2 μm in micro-Cu and 1–1.5 μm in Glidcop,

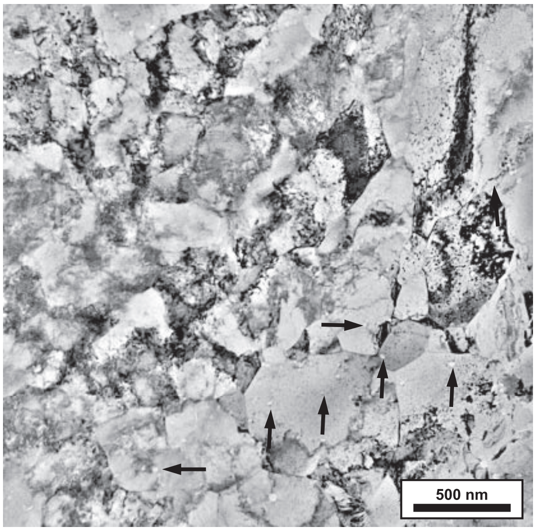

Fig. 1: TEM micrograph of Glidcop after ECAP. Arrows point to several of intragranular Al_2O_3 particles. Their typical size was ~10 nm. The size of Cu grains was 100–220 nm.

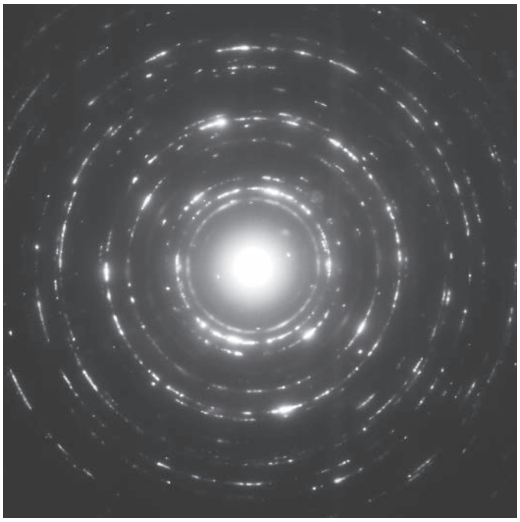

Fig. 2: Electron diffractogram of the Cu matrix and Al_2O_3 particles from Fig. 1.

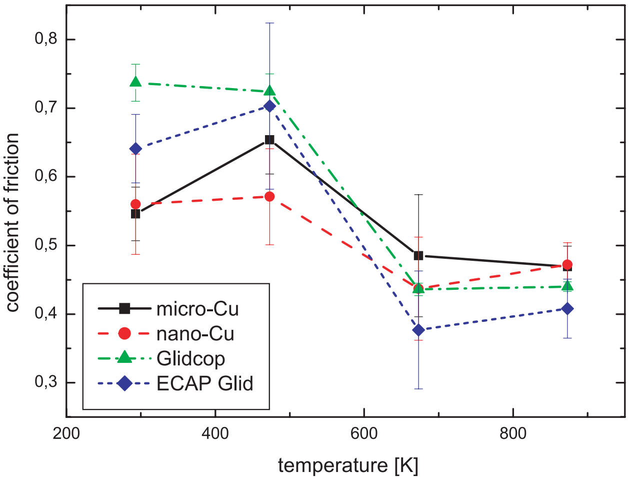

Fig. 3: Coefficient of friction of all experimental materials as function of temperature.

respectively. After ECAP it decreased down to hundreds of nanometers, approximately 100–220 nm (Table 1). Fig. 1 shows a TEM micrograph of Glidcop after ECAP illustrating grain sizes. Electron diffraction confirmed presence of Al_2O_3 particles (small bright particles in Fig. 1 – arrows).

The friction behavior of all four states was in terms of coefficient of friction (COF) generally quite similar. In the beginning there was a short run-up phase (2 up to 20 meters of sliding distance) where the contact surfaces were setting up.

Fig. 3 shows the coefficient of friction for all experimental materials as function of temperature. One can see that the friction starts higher at room temperature and at 200 °C (approx 0.7 in both cases). The COF of both Glidcop based composites is higher than those for the micro- and nano-Cu which are close to the results in literature [11, 12] where values 0.5–0.6, i.e. the values typical for steel-copper dry friction contact were reported. In both types the ECAPed states then had slightly lower COF than the coarser as-received ones. With increase of temperature the coefficient of friction for all materials dramatically decreased, down to 0.45–0.5 for micro-Cu and nano-Cu and even more for Glidcop, to 0.42 for the as-received Glidcop and to 0.38 for the ECAP Glidcop. Then, with further increase of temperature it remained the same. Generally, the ECAPed materials had slightly lower coefficient of friction than corresponding as-received ones, albeit the scatter was quite high.

After finishing the testing the wear tracks were observed and measured by optical microscopy and profilometry, in order to quantify the wear resistance.

Fig. 4 shows the comparison of specific wear rates of all materials at the experimental temperature range. At room temperature the two Glidcop materials are less wear resistant than micro and nano-Cu. One can also observe that the materials after ECAP were more resistant than the corresponding as-received systems.

Lower friction and higher wear resistance is connected to the increase in hardness caused by refining of microstructure, in other words by increase in volume fraction of grain boundaries. The nano-hardness measurements showed that ECAP of micro-Cu lead to increase of hardness from 2.278 ± 0.202 GPa (micro-Cu) to 2.689 ± 0.193 GPa (nano-Cu). In Glidcop based systems the hardness grew from 2.638 ± 0.090 GPa (Glidcop) up to 2.690 ± 0.157 GPa (ECAP Glid).

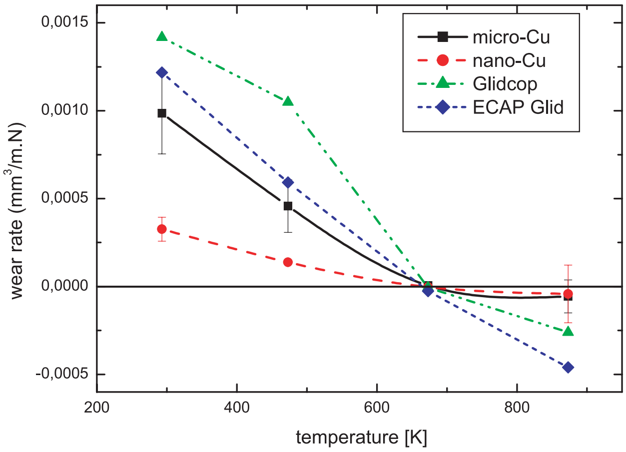

Fig. 4: Temperature variance of wear rates.

With increasing test temperature wear resistance increases (the wear rate decreases) which is in agreement with results reported for pure copper with submicro- and nanocrystalline microstructures [13]. The decrease of wear rate around 673 K even crosses the zero line and becomes negative, which means that the surface of the materials effectively stopped to lose material, and conversely, it was the material from the tribological counterpart (the steel ball) which started to stick to the surface of the tested specimen in the form of iron oxides. The scanning electron microscopy of the wear tracks reveals this change of wear mechanism. Fig. 5 shows Glidcop as a typical example to illustrate described behaviour, which is essentially the same in all four materials. Similarly, typical track profiles measured by profilometry are illustrated in Fig. 6.

Based on these observations one can conclude that regarding the mechanisms of wear damage, at room temperature multicycle plastic deformation leading to cracking and debris formation is dominant. Qualitatively, there are only little differences in wear mechanisms of as-received and ECAP-ed materials. However, the higher density of grain boundaries lead to higher hardness in ECAP-ed materials which consequently resulted in their better wear resistance.

At elevated temperatures oxidation of both the wearing copper material as well of the steel ball in friction pair is playing the main role. As follows from the worn surfaces, on the wear tracks the sticking (soiling) with formed oxides are evident and as a result instead of volumetric wear the coefficient of wear was negative – the material was added to the surface. It is in accordance with studies carried out by Stott and others, showing that oxides would reduce or eliminate completely metal-metal contact, thereby providing protection against wear damage [14, 15]. The damage is confined mostly within the oxide layers and thus the deformation in the bulk underneath the contact area is very limited. Furthermore, it is also supported by other studies, which showed that at testing in air at elevated temperatures, i.e. in an oxidizing environment, the wear behavior of copper-based materials with high level of oxidation depends on the rate of oxidation and on thickness, morphology, adherence, and toughness of the oxide layer that forms on the surface of the material during the oxidation process [16–18].

Comparison of the experimental materials shows more intensive oxidation of the ECAPed materials at higher temperatures in comparison with the as-received ones, and more oxidation in Glidcop based materials than for the other two samples. For instance, while for tests performed at 473 K the EDX measurement found about 8 at.% oxygen at the surface in all samples, for the materials tested at 873 K as much as 40 to 50 at.% oxygen were found (Fig. 7). The higher level of oxidation in the ECAPed samples is connected to the finer grains and higher density

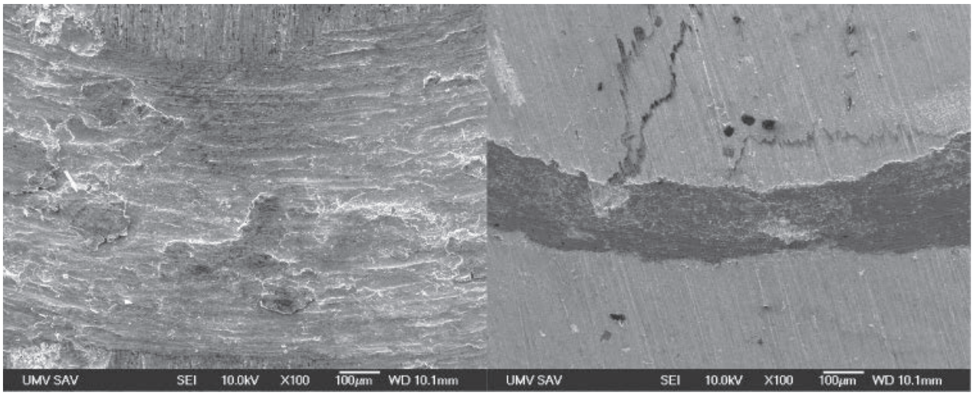

Fig. 5: An example illustrating the change of wear behaviour with temperature: Wear tracks on surface of Glidcop made at room temperature (left), and at 673 K (right).

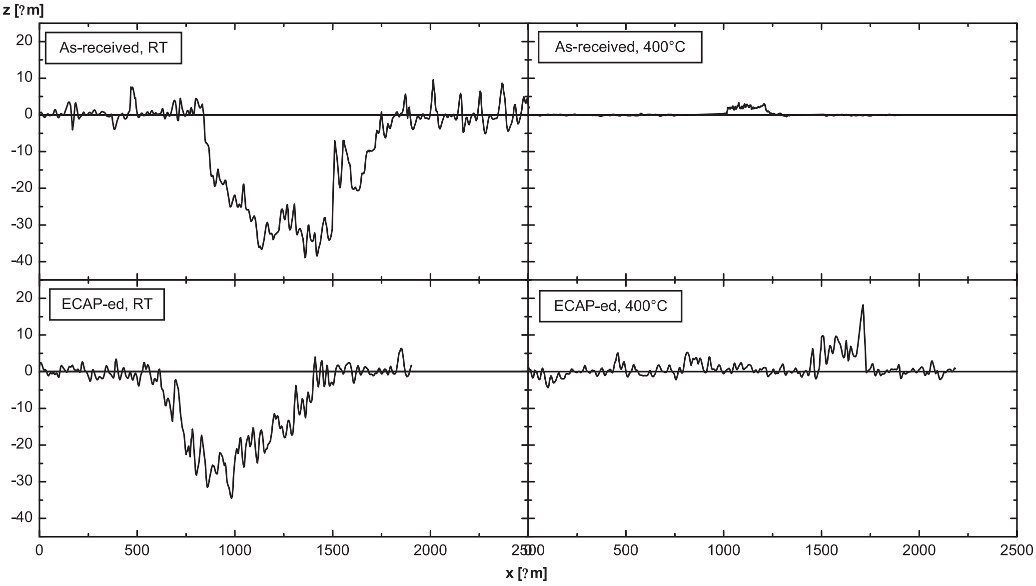

Fig. 6: Typical profiles of wear tracks in Glidcop based materials formed by testing at room temperature and 673 K.

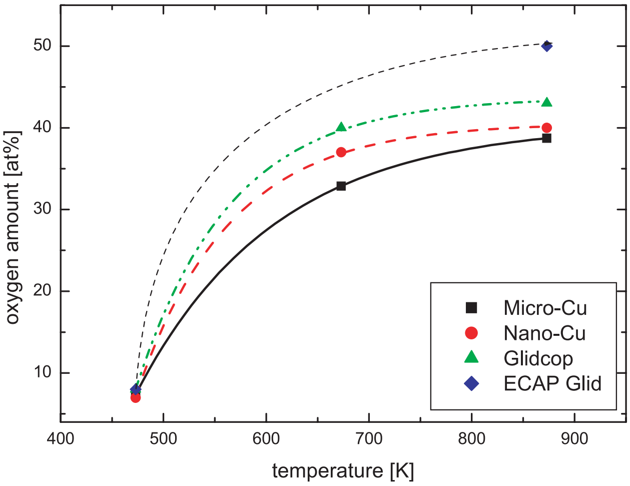

Fig. 7: Concentration of oxygen (in atomic %) on the surfaces of the four materials tested at various elevated temperatures.

of the grain boundaries. Nevertheless, similar oxidation tendency in all materials suggest that the oxidation is governed by volume processes rather than by the grain boundary diffusion.

The most probable cause of higher oxidation of Glidcop when compared to micro-Cu is its residual porosity (approximately 1% in the as-received material). Even after ECAP, which was done at room temperature, this porosity is not completely eliminated and a small fraction of micropores remains in the microstructure.

Wear of the spherical steel pin was also observed and evaluated but here only little changes were seen.

4 Conclusions

The results of the experiments allow to conclude the following:

- Coefficient of friction in all materials decreased at 673 K. The friction of Glidcop based materials was higher than that in Micro-Cu based ones. Materials treated by ECAP (severely reduced grain size) had lower COF than their respective as-received ones.
- At lower temperatures the nano-grained materials were more wear resistant than the micro-grained ones which showed beneficial effect of severe refinement of microstructure. With increasing temperature the wear rates decreased and at and above 673 K they reached zero. This is caused mostly by formation of hard oxide layer on the surfaces of experimental materials.
- Oxidation of all materials follows the parabolic law and while the nanograined materials had slightly more oxygen, very similar overall oxidation profiles suggests that the oxidation is dominated by volume diffusion.

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