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DYNAMICS OF Pb EMERGENCE TO THE SURFACE IN SELF-LUBRICATING COMPOSITE MATERIALS AT ELEVATED OPERATING TEMPERATURES

Petya TABAKOVA[1], Anna PETROVA[1,*], Snezhana ATANASOVA[1], Hristo KOLEV[2], Feyzim HODJAOGLU[3], Reni ANDREEVA[3], Ivan ZAHARIEV[3], Georgi AVDEEV[3], Korneli GRIGOROV[1,*]

*Corresponding author: ani@phys.bas.bg

Abstract: *Friction and wear of machine parts is a major problem in the automotive and aerospace industries. The choice of material with high mechanical and good tribological properties determines the trends in modern materials science. Self-lubricating composite antifriction materials (SCAM) with Cu-matrix reinforced with particles with lubrication properties are of great concern. The main objective is to trace the Pb dynamics to the film surface as the operating temperature increase to 800 °C. As the temperature arise, surface and subsurface layers of lubricants are formed, meanwhile the coefficient of friction drop significantly. X-Ray Photoelectron Spectroscopy (XPS) was used to determine the surface element concentration and provide information about their chemical state. X-ray diffraction (XRD) coupled with fluorescent analyses (XRF) was used to analyse the phase composition and structure of the samples. Additionally, we provide Glow Discharge Optical Spectroscopy in order to prove the element dynamic through the surface in work conditions. The latter is very important, because new elements and oxides are formed which improve the tribology in situ.*

Keywords: *Self-lubricating materials, friction.*

1. INTRODUCTION

The practical problem that will be considered in this article is to ensure such an interaction at the friction point during relative movement of the adjacent surfaces, in which there is no macroscopic damage to the rubbing surfaces and the wear remains minimal. Researchers have been studied these complex phenomena for years, probably from the time when the simplest mechanisms were created. The results achieved in this direction, no matter how significant they are, still do not correspond to the efforts made. This is mainly due to the fact that with the development, improvement and creation of new machines and mechanisms, the requirements for the materials of the rubbing surfaces are constantly increasing. Dry friction is a phenomenon that occurs in contact in the absence of lubricant and contamination between the surfaces of the contacting bodies. Dry friction occurs in contact joints in aerospace and aviation equipment, machines in the food, textile, and chemical industries, where lubricants are unsuitable for safety and security reasons [1].

In general, the copper-based materials, used as sliding pairs, have poor tribological properties which ends-up on high wear and consequently in high expenses. That's why, from a long data, these materials are the subject of intensive research to low their friction and temperature during operation. In that way, the name solid

self-lubricants arise. By adding some quantities of alloying elements (less than 10 - 20 weight %), the tribological properties of the base material undergoes a tremendous change and then those materials are furtherly referred as composites [2].

The composite materials are prepared by casting. At melting temperature of 1150 °C, the additives are introduced into the Cu-matrix in the following order: Mn, Pb, P and Ce [3]. Then, this is followed by cooling to room temperature. Their application area is vast; they can be used manufacturing of machine parts operating in sliding contacts such as bearings, inserts, bushings and hinges, as well as under considerable loads in frictional units of machines and mechanisms [4].

It is found that at high-temperature conditions, which take place normally at dry friction when engines run out of oil, the addition of Cu-Pb-xSn immersive alloy, leads the lead floats to the surface where form netty-shape SPP's (Second Phase Particles) [5]. The latter phenomenon decreases the friction, almost in one order, downing the temperature and the wear.

The combination of the copper matrix and solid lubricant additives creates a composite material with enhanced tribological properties (friction and wear). The distribution of the alloying elements within the copper matrix is crucial for optimal performance [6].

As a rule, introducing a small quantity of Ce into the Cu - matrix increases the wear resistance of the material by 1.5 to 2.0 times and reduces friction coefficient (FC) by 1.3 – 1.4 times when operating in extreme conditions, such as high pressure, vacuum environment and etc. [4, 6].

It has been established that materials (with additive Mn, P and Pb), at a load above 10 MPa, intensive wear is observed, leading to destruction and losses of the material's working capacity [7]. Mn forms a solid solution with Cu, which increases the strength of the matrix up to a certain concentration without reducing the plasticity. Phosphorus forms a Cu_3P-solid phase [8]. This phase, play a role as a network [9], which is located along the grain boundary and increases the wear resistance of the material. Pb, in the form of separate spherical conglomerates, plays the role of a natural solid lubricant [10].

Normally, Ce with Pb form a hard-melting solid compounds CePb and Ce_2Pb. In such way they increase the mechanical and tribological characteristics of the self-lubricating material. Further, a heterogeneous structure with a lower FC is formed.

The results of friction and wear tests show as low as FC $\mu = 0.11$ and low wear $J = 30$ μg/m, which is explained by the strengthening of the composite by presence of the hard-melting compounds CePb and Ce_2Pb, which are located inside the grains of the volume. The positive influence of Ce is maintained up to of 1.5 wt. %. Increasing it concentration above this level cause an increase in the FC. Thus, adding of Ce lead to a significant improvement of the antifriction characteristics [3, 11].

2. EXPERIMENTAL

The studied material has been obtained by powder metallurgy (hot pressing). We have studied two copper-based samples, on is pure copper - sample 1 and sample 2 is copper alloy with additives. It contains Copper, Phosphorus, Tin and Lead. The microstructure is made up of solid solutions of tin and partially of phosphorus in copper. The remaining part of phosphorus forms a copper phosphide phase, which, in the form of a broken network, is located around the grains of the solid solutions. The presence of this network increases the wear resistance of the material. Alloying with tin improves the mechanical and antifriction properties. The copper phosphide phase strengthens and reduces the plastic deformation of the composite under dry friction conditions in vacuum [6, 8]. The constituent components have differentiated

functions. Copper and its alloys form a supporting part (matrix).

The investigated composite alloy has been produced by copper casting of 1150°C in atmosphere. Thus, the additives were added immediately after removing the melt from the oven in the following order: first is added the Mn, then Pb, followed by the P and Ce. The melt is mixed until homogenisation.

Ex-situ X-ray photoelectron spectroscopy (XPS) analysis of samples 1 and 2 were conducted using an ESCALAB MkII electron spectrometer equipped with a twin-anode MgKα/AlKα non-monochromatic X-ray source. The instrumental resolution was approximately 1eV. The obtained data were analysed using SpecsLab2 CasaXPS software (Casa Software Ltd). Spectral processing included subtraction of X-ray satellites and Shirley-type background correction [12]. Peak positions and areas were evaluated using symmetrical Gaussian-Lorentzian curve fitting. The relative concentrations of different chemical species were determined by normalizing peak areas to their photoionization cross-sections, calculated by Scofield [13].

The chemical composition, phase identification and quantification were analysed with X-Ray Fluorescent Analyses (XRF). The equipment of the X-ray fluorescence analysis includes a Zetium XRF spectrometer with a mapping module from the manufacturer Malvern-PANalytical.

The crystalline structure was revealed by XRD in θ-2θ configuration with step size [°2θ] = 0.02 and scan step = 1 [s] with a Philips PW1050 diffractometer from 10 to 90° using a Cu-cathode λ = 1.54060 [Å].

The hardness and coefficient of friction of the samples were measured using Tribometer UMT-2 by Bruker Inc. (Billerica, MA, USA) an AISI 52100 steel ball with a radius of 5 mm as a counter body. The tests were conducted on a dry surface and included two parts. The first sequence consisted of a reciprocating linear movement of 4 mm length with a load ramp from 0 to 10 N measured for 1 h. The second implied a constant normal load of 10 N for 4 h. Thus, FC assumes the tangential force to the normal force given by the equipment.

3. RESULTS AND DISCUSSION

The main technological principle in the creation of self-lubricating materials is the achievement of optimal parameters: low friction and high load capacity with reduction the formation of seizures in the contact during operation. Thus, addition of lead is very essential for improving the antifriction performance at heavy loads [10]. The lead and its form as oxide phases usually form conglomerates and does not interacts with the copper matrix.

The oxidation state and the surface atomic concentrations of the elements in samples 1 and 2 were investigated. Two points of each sample were examined - pristine surface and the scratched one. The scratched process was carried out in vacuum with SiC (P2000) sandpaper to remove the very top layer without breaking chemical bonds.

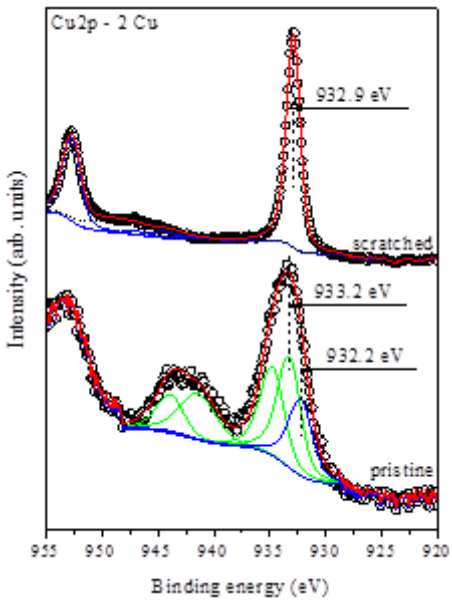


Figure 1. High-resolution XP spectra of Cu2p core level of pristine and scratched surfaces of sample 1. Open circles - experimental data, red curve - fitting, coloured thick lines represent different constituents - oxidation states.

Sample 1 (pure Cu)

Fig. 1 displays the high-resolution Cu2p spectra of the pristine and scratched surfaces of sample 1. The pristine surface (lower spectrum) indicates an enrichment of Cu^{2+} ions, as evidenced by a peak at 933.2 eV, accompanied by a pronounced shake-up satellite in the 937-948 eV range. This signature is comparable to that observed by Yoshida et al. In XPS studies of 2-mercaptobenzothiazole metal complexes [14]. The presence of nitrogen and sulphur traces suggests that the Cu^{2+} species may be part of a complex.

The blue-marked peak (Fig. 1) at 932.2 eV, with a low-intensity satellite in the 940-950 eV range, is indicative for Cu^{1+} oxidation state [15]. Following the same scratching procedure as used for sample 1, the Cu2p spectrum of the scratched sample 1 (Fig. 1) exhibits a significant shift. The main Cu2p peak is now at 932.8 eV, with a low-intensity satellite in the 940-950 eV range, confirming the presence of Cu^{1+} ions (39.49 at. %).

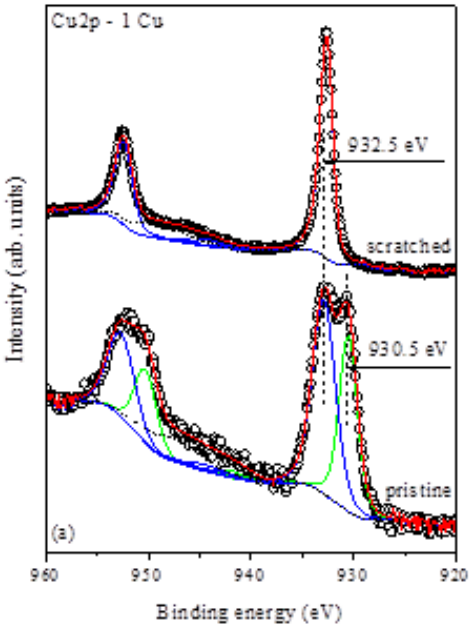
The shift of 0.7 eV suggests the removal of Cu_2O species formed due to oxidation upon air exposure. The uncovered surface consists of a C-H-N-O complex bound to the copper substrate, consistent with previous findings [16].

Table 1. Surface atomic concentrations and BE after fitting of C1s, O1s, and Cu2p core levels and oxidation states of sample 1, and C1s, O1s, Pb4f and Cu2p spectra and their oxidation states for sample 2.

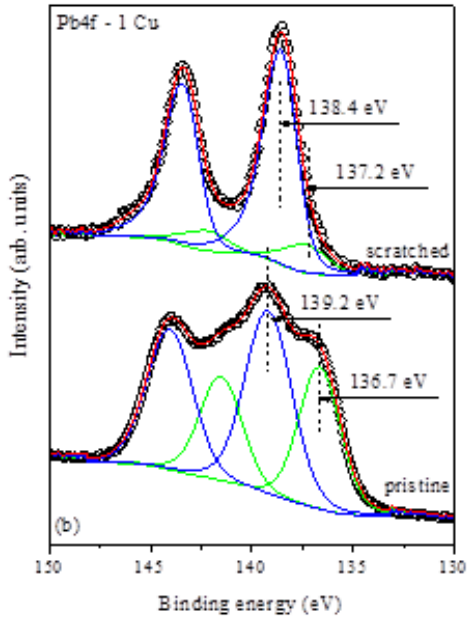
Sample 1 (pristine)									
	C 1s				**O 1s**	**-**		**Cu2p**	
[at. %]	70.50				21.71	-		7.52	
[at. %]	15.45	41.74	13.31		21.71	-		1.61	5.91
BE [eV]	283.7	285.0	287.7		530.0 531.8 533.0	-		932.2	933.2
Sample 1 (scratched)									
[at. %]	41.25				19.25	-		39.49	
[at. %]	-	22.64	15.58	3.03	19.25	-		39.49	-
BE [eV]	-	285.0	285.8	288.4	530.9 532.1 534.3	-		932.9	-
Ox. state	-	C-C H-C	C-O	C=O H-C=O		-		Cu^{1+}	Cu^{2+}
Sample 2 (pristine)									
-	**C 1s**				**O 1s**	**Pb4f**		**Cu2p**	
[at. %]	56.80				27.43	**12.00**		**3.75**	
[at. %]	7.84	**42.95**	-	6.01	27.43	**4.90**	**7.10**	1.60	2.15
BE [eV]	282.5	285.0	-	288.8	529.2 531.7	136.7	139.2	930.5	932.9
Sample 2 (scratched)									
[at. %]	57.63				32.31	**3.25**		**6.80**	
[at. %]	-	**36.10**	14.92	6.61	32.31	**0.48**	**2.77**	-	6.80
BE [eV]	-	285.0	286.5	288.9	530.0 531.5 533.1	137.2	138.4	-	932.5
Ox. state	-	C-C H-C	C-O	C=O H-C=O	-	Pb^{3+}	Pb^{4+}	-	Cu^{1+}

Sample 2

Fig. 2 represents the core-level spectra of the pristine surface compared by scratched surface of sample 2. The pristine sample exhibits multiple doublet peaks in the core-level spectra of Cu2p (Fig. 2a) and Pb4f (Fig. 2b), indicating different oxidation states (blue and green curves).



a)



b)

Figure 2. High-resolution XP spectra of: a) Cu2p and b) Pb4f core levels of pristine and scratched surfaces of 1 sample. Open circles are used for experimental data, red line is the envelope of curve fitting procedure, coloured thick lines representing the different constituents of the peaks (oxidation states).

A detailed examination suggests the presence of at least one top layer that is differently charged compared to the bulk sample and this could be associated with Pb_2O presence at the surface. Based on the binding energy and peak shapes, copper in the pristine sample is predominantly in the Cu^{1+} (1.60 at. % for one of the layers and 2.15 at. % for the other layer) oxidation state (Fig. 2a). Further, this is supported by the presence of a low-intensity shake-up satellite in the 938-948 eV energy range.

The lead component appears to be a mixture of Pb^0, Pb^{2+}, and Pb^{4+} oxidation states, though their precise proportions cannot be determined.

An estimation after a curve fitting procedure reveals 4.90 and 7.10 at .% for each of non-contacting layers.

Upon mechanical removal of the top layer, the Cu2p and Pb4f spectra undergo significant changes (Fig. 2b, scratched spectrum). The Cu2p peak is now observed at 932.5 eV, with a low-intensity satellite structure in the 940-950 eV range, characteristic of Cu^{1+} (6.80 at. %) state [14].

Similarly, the Pb4f spectrum changes significantly, enabling a more precise determination of lead oxidation states. The curve-fitting analysis reveals two doublets with BEs of 137.2 eV and 138.4 eV, corresponding to Pb^{3+} (0.48 at. %) and Pb^{4+} (2.77 at. %) oxidation states. Table 1 summarizes the atomic concentrations, binding energies, and oxidation states of the elements detected in samples before and after removing the top contaminated layer. The results confirm that the pristine surface of sample 2 is composed predominantly of hydrocarbon-oxides with minor contributions from the Cu^{1+} and Pb^{4+} ions. After scratching, the surface become rich of Cu^{1+} and Pb^{4+}, metallic copper and oxidized lead (Pb_2O).

Sample 2 deserve more attention due the interesting discovery, namely the migration

processes towards the film surface as a result of elevated temperature. Let us focus on the lead atomic concentration in the pristine and the scratched surfaces. The oxidized lead in pristine sample is 7.1 at. % while correspond one in scratched is 2.77 at. % which result in 2.56 times left over.

Contrariwise, for the metallic component of Pb4f, this left over is 10 times (the bold in Table 1). This, clearly mean strongly defined migration of the lead to the hot surface. Therefore, approximately 60% of the lead content of the sample has floated to the surface. The latter rise immediately the tribological significant of this alloy.

On the surface, the lead-oxides (Pb_2O) concentration is 3 - times greater than the metallic state - Pb. However, for the scratched sample, this ratio is about 8-times, which suggest that the main culprit for the low FC are the lead oxides, in particular - Pb_2O, see XRD Fig. 5b.

In Fig. 3 the qualitative EDX analysis is given for sample 2 in point 1 (intact surface). It is worth to note, that there is a difference in the composition of the wear zone (point 2) and the intact one.

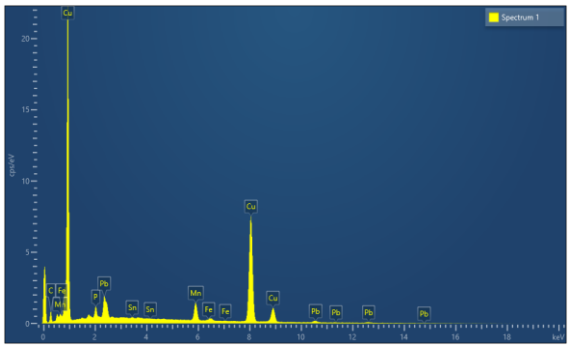


Figure 3. EDX spectrums of sample 2.

The elemental composition of sample 2 taken inside the Tribometer trace (Fig. 4) is deduced from EDX and is displayed on Table 2.

These differences are shown in Table 2 and they are related mainly with the Pb and its oxides (according the XPS and XRD) decrease in the wear zone. This is normal, as the Pb_2O is the main phase responsible for wear lowering.

The XRD spectra of sample 2 show mostly well-pronounced crystalline phases of both Cu-matrix, as well as the additives. As we observed five different phase, for readability, we divided it on two graphics (Fig. 5a - Cu, Pb, SnO_2, Fig. 5b - Mn, Pb_2O). The relative surface composition deduced is as follow: 12% metallic Pb, 13% Pb_2O, 5% Mn, 5% SnO_2 and 65% Cu.

Table 2. Chemical composition of self-lubricating Cu-based material in 2 points for sample 2.

Weight %	Spectrum 1	Spectrum 2
P	1.74	1.91
Mn	5.94	6.06
Fe	0.22	0.29
Cu	81.59	84.23
Sn	0.47	0.49
Pb	10.04	7.00
Total	100.00	100.00

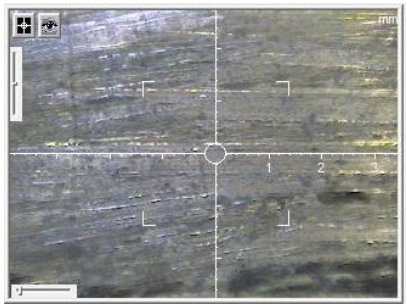
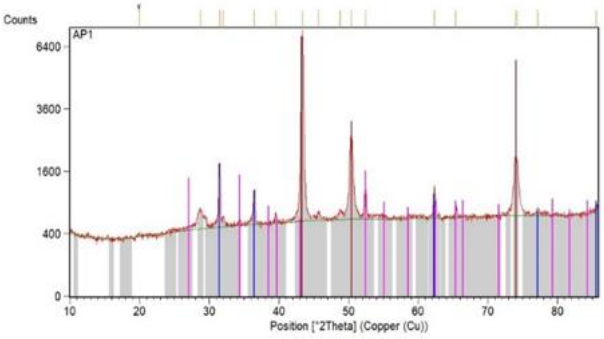


Figure 4. Optical image of the XRF taken on sample 2 in tribemate's trace.

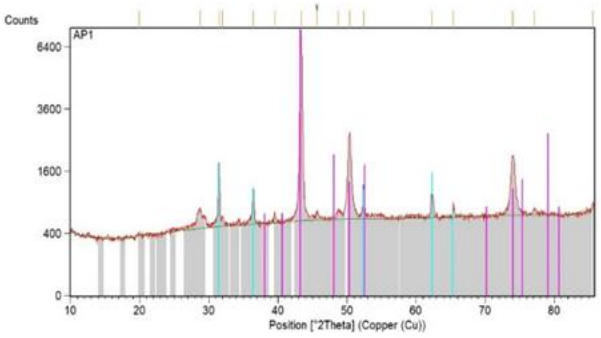
The Sn-oxides serves as a temperature sink, thus its role is seen at working conditions. The process of thermal diffusion is the main factor which rule the migration of elements towards the surface and their subsequent oxidation, generally observed at the self-lubrication of materials.

During dry friction, an increase of the temperature in the contact area and a certain plastic deformation of the surface layer can take place. The heterogeneous structure causes a difference in the coefficients of thermal expansion and diffusion of the main matrix and lead. As a result of these

circumstances, a process of diffusion of lead to the friction surface is formed [8].



a)



b)

Figure 5. XRD spectrums of sample 2, including all observed phases: a) Copper (brown line), Lead (blue line), Tin-oxide (magenta line); b) Manganese (magenta line), Lead oxide Pb_2O (cyan line).

Lead plays the role of a solid lubricant. Fig. 6 presents the microstructure of the material. The light areas represent a network of copper phosphide, the grey one represent a solid solution of Cu-Sn and the dark areas represent the lead.

It is important to relay about the hardness measurements of the pure copper sample and the treated one with the already discussed alloying elements. We found HV 75 for the pure one, and HV 150 for the treated one. These increase is due to the copper phosphide (Cu_3P) which is harder phase and the role of the Sn forming Cu_3Sn and $SnPb_2O_4$. The latter phase is known to form open network on the film surface, and possibly into the bulk. This result in even better hardness and wear resistance by heavy loads. In Table 3, the mean values of the FCs are compared at equal conditions, in vacuum and in air.

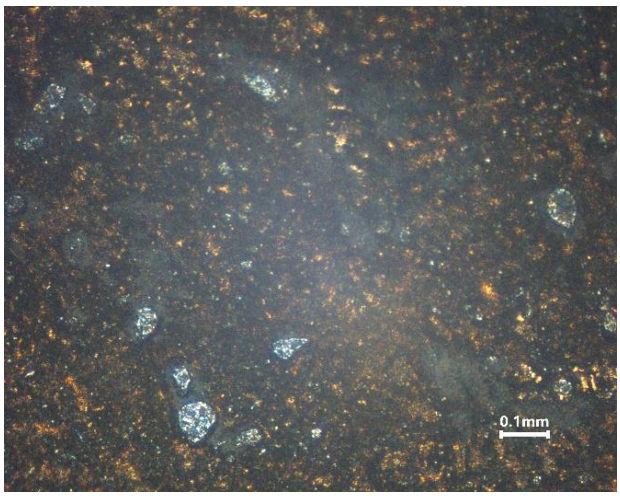
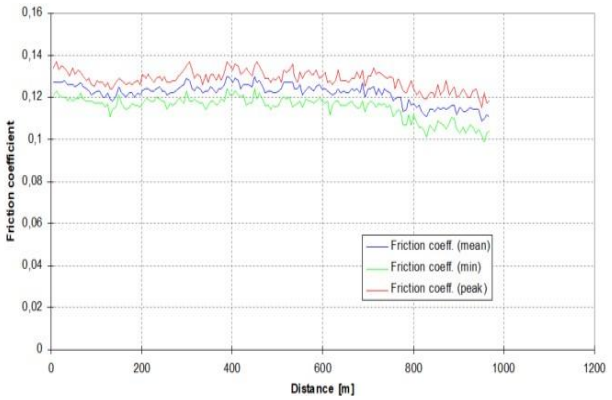
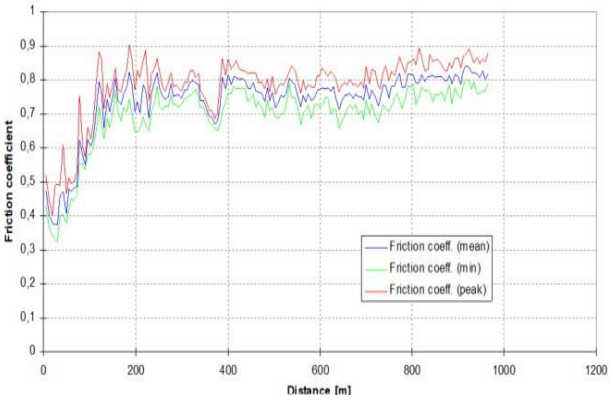


Figure 6. Metallographic image of the microstructure (sample 2)

In Fig. 7, the FC's are given for samples measured in vacuum and on air at 2N (7a) load 1 m/s (7b).



a)



b)

Figure 7. Friction coefiecient at 2N load in: a) Vacuum; b) Air [7]

The friction depends not only on the mechanical irregularities of both contacting surfaces, but also are consequence of molecular and atomic forces, inherent characteristics of each material.

Table 3 Friction coefficients of raw Cu sample and reinforced one in vacuum and in air.

FC μ	Copper Sample 1	Copper* Sample 2	Δμ [%]
on air	0.5	0.8	60↑
vacuum	4.8	0.12	85↓

Upon work conditions, the FC behave as dynamic because processes of diffusion and new phase formations take place and thus structure changes are involved. As a consequence, secondary layer is formed. Due to the additives, the wear of the materials is improved, but external factors could change the chemical and structural state of the surface.

Here, two factors, such as the temperature and oxidation determines a compositional dynamics and new phase formations. We observed formation of cluster oxides which migrate to the surface and are "consumed" by the friction. As a matter a fact, in course of wear of these lubricants, a new supply of those molecules are provided from the bulk. Below are named the processes which take place in dynamic way and they are governed by steady-state mechanism which depends on numerous factors, such as:

- Oxidation, resulting from the interaction of the affected surfaces with the gaseous environment;
- Diffusion or redistribution of elements in the surface layer from the interior of the material to the surface;
- Selective migration of chemical elements due to heating;
- Phase and structural transformations such as new phases and formations;
- Redistribution of stresses, mainly in the initial moments of friction followed by its decrease;
- Appearance of cubic phases, which proves crystallization of the surface layer.

4. CONCLUSION

In the present work, Cu-based alloys with addition of reinforcing elements are considered to improve their tribological and mechanical properties. The alloying elements are P, Pb, Sn and Mn. The both materials, the raw one and the Cu-alloy are studied in respect their structure, morphology and chemical compositions in the intact and the wear surface.

The samples were thoroughly quantified by XRF, XRD and XPS analysis to discover the elemental dynamics and processes of migration, diffusion and segregations were noted. The formation of new phases, such as Pb_2SnO_4, Cu_3P and Cu_3Sn were detected, largely responsible for such significant friction improvement. It has been shown that about 40 times FC lowering in vacuum and 2 times hardness improvements for the treated sample. The metallographic images reveal surface Pb segregations, later proven by XPS and XRD analysis as Pb_2O.

All mentioned and studied processes in complex way describe in-situ phase dynamics, surface migration and oxidation of these competitive solid lubricant. They are applicable in machine parts, including MEM's, in vacuum installation, where Cu lower in oxygen content is essential.

ORCID iDs

Petya TABAKOVA 0009-0004-7795-001X
Anna PETROVA 0000-0003-2765-6512
Snezhana ATANASOVA 0009-0008-2542-528X
Hristo KOLEV 0000-0002-4231-9306
Feyzim HODJAOGLU 0009-0000-0200-9904
Reni ANDREEVA 0000-0001-9656-9768
Ivan ZAHARIEV 0000-0002-4276-344X
Georgi AVDEEV 0000-0002-3465-3339
Korneli GRIGOROV 0000-0002-3176-1780

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