

Article

Tribochemical Interaction of Multicomponent Aluminum Alloys During Sliding Friction with Steel

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Abstract: In this work, aluminum multicomponent alloys were studied after friction with steel in a mixed lubrication regime. The resulting secondary structures on the friction surface were investigated by scanning electron microscopy (SEM), energy dispersive analysis (EDX), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction analysis (XRD). In addition to the mass transfer of steel counterbody particles, phase transformations and new chemical compounds formed as a result of interaction with the lubricant were revealed. The release of elements, mainly magnesium and to a lesser extent zinc, from a solid solution of aluminum alloy was also observed, which indicates the occurrence of a non-spontaneous reaction with a negative entropy production.

Keywords: aluminum alloys; bronze; journal bearings; tribological alloys; friction; friction surface; secondary structures; self-organization; mixed lubrication regime

1. Introduction

Lead and tin-lead bronzes remain the most widely used material for monometallic journal bearings due to a combination of mechanical and tribological properties [1–3]. Considering that today about 23% of the world’s energy is spent on overcoming friction forces and their consequences [4–6], the transition from bronze to aluminum-based alloys can become a driver for the development of the engine-building industry due to significant cost reduction of bearing manufacturing and further repair. Aluminum is three times lighter than copper, and its specific cost is 2.5–2.7 times less, it is easier to process, and its casting requires 15–20% less energy. Moreover, unlike bronze, aluminum is not a surfactant for steel and does not cause its destruction by the Rebinder effect [7]. As a result, additional chemical-thermal treatment of steel shafts might be avoided. These advantages provoke a great interest in anti-friction alloys [8–14].

Normally, tin and lead are the main alloying components for aluminum antifriction alloys [15–24]. Particularly, Al-20Sn-1Cu alloy is acknowledged to be a basic alloy for the development of new antifriction materials due to its good tribological behavior. However, having poor mechanical properties, its application is limited to bimetallic bearings only. Additional alloying with silicon and copper results in solid inclusions of silicon and CuAl₂ in the microstructure, which realizes the Charpy principle under friction and provides conditions for lubricant retention [25,26]. This effect can also be achieved by applying functional coatings [24]. An increase in the content of solid inclusions, such as carbides, nitrides, and oxides, improves wear resistance of the alloy, but negatively affects the wear of the steel counterbody [27,28].

Various methods for obtaining aluminum antifriction alloys provide different types of microstructures. Rusin et al. [29] obtained an alloy with a tin content of 50% while preserving the aluminum skeleton structure. However, tribological properties were improved at the cost of mechanical properties. This drawback was partially solved in [30], where the authors applied the equal-channel angular pressing to improve mechanical properties of the Al-40Sn alloy.

Nevertheless, all these improvements were accompanied by a limited understanding of the processes occurring during friction. The performance of tribosystem is conditional not only from bearing, but lubricant and counterbody as well. Several research groups are focused on the addition of special additives to the lubricant and the study of their interaction with rubbing bodies [31,32]. The authors note that the tribofilm formation on a friction surface responsible for structural and properties changing [32]. In [33], it is noted that the addition of a sulfurized olefin to the lubricant leads to the formation of FeS compounds on steel reducing friction to the Al_2O_3 -FeS contact preventing seizure. A similar interaction mechanism was observed when zinc dialkyl dithiophosphate (ZDDP) was added to the lubricant [33–36]. As a result, friction was reduced to the contact of Al_2O_3 and ZnPO_4 formed on steel, which allowed to significantly improve tribological characteristics. On the other hand, phosphorus-based additives were reported to be detrimental to aluminum-steel contact as they increase wear due to chemical corrosion of aluminum [33,37]. Today, ionic liquids are being introduced as a new class of lubricants for aluminum-steel contact [33,38,39]. Anion parts of ionic liquids adsorb onto a worn metal surface, protecting it from wear. Furthermore, they provide tribofilms with lower shearing strength leading to lower friction coefficient and wear resistance [38]. In addition to the deposition of additives, oxidation and mass transfer of debris during friction, other processes occurring must be taken into account. The authors [40,41] suggest the possibility of tribochemical reactions in contact area leading to the formation of beneficial secondary structures. In papers [42,43], the formation of a boundary film is noted, which was greatly contributed by decomposition, oxidation, and polymerization of the lubricant. Various metals, in particular iron, can catalytically decompose hydrocarbons, which are the basis of most lubricants. In [43–47], attempts were made to describe the tribological processes through the theory of self-organization and thermodynamics of nonequilibrium processes. According to it, dissipative structures forming during friction are accompanied by increasing of negative entropy production. Through the thermodynamics of nonequilibrium processes and the theory of self-organization, it was shown that the bearing wear rate reduces with a decrease in entropy production.

Dissipative structures are associated with secondary structures formation processes occurred during the running-in stage and their development with further friction. To get reasonable results the test methods should be as close as possible to the actual operating conditions. In this regard, sclerometry provides rather limited information about the real tribological properties of the material, since the conditions for the formation of secondary structures are completely different from the real ones [21,48].

This study is a part of an ongoing research aimed at replacing bronzes with aluminum-based alloys [49–51]. The goal of the work is to reveal typical processes taking place on the surface of antifriction aluminum alloys during friction.

2. Materials and Methods

2.1. Tribological Tests

Within the research eight experimental multicomponent cast aluminum alloys were investigated. Tin, lead, copper, silicon, magnesium and zinc were used as alloying components in aluminum (Table 1). Tribological tests were performed on a SMC-2 friction machine (Tochmashpribor, Ivanovo, Russia) with a constant load of 617 N according to the kinematic scheme shown in Figure 1. A roller made of 38HN3MA steel was used as a shaft (Table 2). The experiment was carried out for 40 h with a lubricant feed rate of 0.2 g/min which corresponds to a mixed lubrication regime [52]. The whole set

of test parameters is presented in Table 3. Engine oil M14V2 with the viscosity of 13.5–14.5 mm²/s was used as a lubricant. During the experiment, data were obtained on four parameters: friction coefficient, temperature, mass wear of an aluminum alloy and mass wear of a steel counterbody. The latter two were chosen as the best tribological performance criteria comparing to reference bronze Cu-4Sn-4Zn-17Pb (Table 1). The temperature was measured by a 830-T2 pyrometer (Testo, Lenzkirch, Germany) in 8–10 mm downstream of the contact. Table 1 shows the arithmetical average value of the temperature after 10 measurements with accuracy up to 1 °C. After testing, the samples were washed from oil residues in an ultrasonic bath in chemically pure acetone for 20 min. The dried samples were weighed on a GR-300 analytical balance (A&D, Tokyo, Japan) with an accuracy of 0.0001 g.

Table 1. The composition and wear performance of experimental aluminum alloys.

No.	Elemental Composition, % mass.							Alloy Wear, mg	Steel Wear, mg	Temp., °C	Friction Coefficient
	Sn	Pb	Cu	Si	Zn	Mg	Al				
1	11.0	2.6	3.9	0.1	2.6	-	79.8	1.2	0.6	33	0.20
2	9.8	2.5	4.5	0.6	2.4	1.2	79.0	0.7	0.7	31	0.15
3	9.6	3.2	4.9	0.1	4.4	0.3	77.5	2.0	2.1	37	0.19
4	8.7	3.2	3.4	0.5	2.9	0.4	80.9	2.4	0.8	32	0.22
5	7.6	3.3	4.0	1.0	0.5	0.07	83.5	0.5	0.8	42	0.26
6	6.4	3.0	4.1	0.9	1.9	1.4	82.3	0.9	1.0	38	0.14
7	5.8	2.7	4.1	1.5	2.3	1.5	82.1	0.4	0.6	40	0.18
8	5.4	2.6	3.5	0.8	2.3	1.7	83.7	0.5	0.7	36	0.17
Ref. Bronze	4.1	16.9	75.2	-	3.8	-	-	2.7	4.0	38	0.16

Table 2. The composition of the 38HN3MA steel.

Elements Composition, % mass.												
Ni	Cr	Mn	Si	C	Mo	Fe	Cu	P	S	Al	V	Nb
2.80	0.68	0.63	0.30	0.35	0.48	94.42	0.087	-	0.01	0.018	0.185	0.013

Table 3. Tribological test parameters.

Load, N	Nominal Contact Area, mm ²	Rotation Velocity, rpm	Lubricant Feed Rate, g/min	Lubricant Temperature, °C	Test Duration, h
617	175	500	0.2	20	40

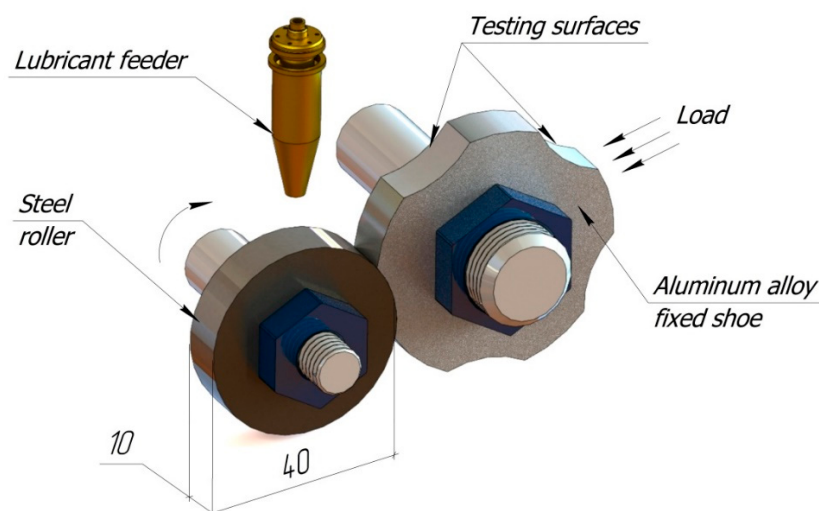


Figure 1. Kinematic configuration of the friction mechanism experiments.

2.2. Surface Roughness Analysis

Cast aluminum cylindrical billets were milled to form surfaces for tribological tests (Figure 1). Steel rollers were polished to $R_a = 0.8 \mu\text{m}$. The roughness of the samples was studied on a Hommelwerke T8000 profilograph-profilometer (Hommelwerke GmbH, VS-Schwenningen, Germany) with a TKU 300/600 probe with a sensitivity of 40 nm and a step resolution of $1 \mu\text{m}$.

2.3. Chemical and Microstructural Characterization

To identify the additives contained in the base oil, the lubricant was studied by infrared spectroscopy on a Vertex 70 infrared Fourier spectrometer (Bruker, Karlsruhe, Germany). It showed that the material in the initial state has a CH_2 hydrocarbon base. The composition also includes additives, that contain sulfur (1.16% wt.) and calcium (0.24% wt.). The total content of other detected elements (Al, Mg, Zn, Si, P, Na, Mo, and Fe) does not exceed 0.3% wt. The infrared spectrum of the M14V2 lubricant is shown in Figure 2. The signal has peaks in the region of $800\text{--}1200 \text{ cm}^{-1}$, which corresponds to C–O bonds in various classes: alcohols, phenols, ethers, etc. The oxidation of the lubricant is the most likely cause of this discrepancy.

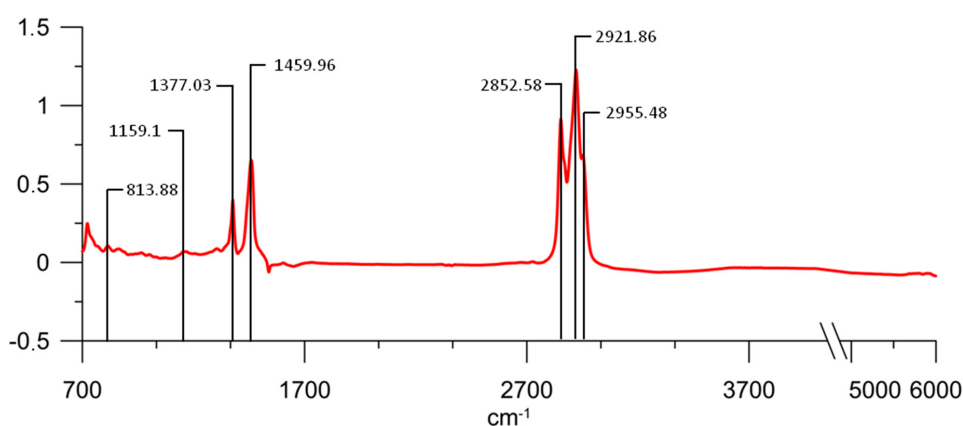


Figure 2. Infrared spectrum of M14V2 lubricant.

The content of elements in the as-cast alloy was tested using a Spectrolab-S emission spectrometer (Spectro Analytical Instruments GmbH, Kleve, Germany). Vickers microhardness of the alloy structure was measured on a specially prepared beveled sample at an angle of 6° to friction surface using Qness Q10 microhardness equipment (ATM Qness GmbH, Golling, Austria) at a load of 0.01 g for 10 s. The initial microstructure and the friction surface were studied using a Vega 3 scanning electron microscope (SEM, Tescan, Brno, Czech Republic) equipped with an X-Act energy dispersive analysis (EDX) module (Oxford Instruments, Abingdon, UK). Images were obtained using a secondary electron detector (SE), which forms a topographic contrast, and a backscattered electron detector (BSE), which forms a composition contrast. EDX was carried out at an accelerating voltage of 20 kV to activate all the main lines of the elements. Since energy lines of sulfur ($\text{S K}\alpha$) and lead ($\text{Pb M}\alpha$) overlap at 2.307–2.347 eV, the former was analyzed at SI line (0.23 eV) and the latter—at $\text{L}\alpha$ line (10.550 eV). By EDX-analysis the elemental composition of the studied areas and the distribution map of the elements were obtained.

To confirm the composition and identify the binding energies of the elements, the samples of aluminum alloys were studied by X-ray photoelectron spectroscopy (XPS) using Thermo Scientific K-alpha (Thermo Fisher Scientific, East Grinstead, UK) equipment with an $\text{Al K}\alpha$ source after preliminary ion etching to a depth of 100 nm.

The phase composition was studied using X-ray diffraction analysis (XRD) on a Bruker D8 Advance diffractometer (Billerica, MA, USA) with a monochromatic radiation of $\text{Cu K}\alpha$ in Bragg-Brentano geometry.

3. Results and Discussion

3.1. Microscopic Investigation

As follows from the theory of self-organization, the processes that occur during friction can lead to a decrease in the wear of a rubbing body [36]. Based on the results of the tribological tests, two alloys were selected with the lowest and highest wear rates No. 7 and No. 4, respectively, to detect differences in changes. Both alloys have the same set of alloying components and microstructure (Figures 3 and 4). In the matrix based on a solid solution of copper, zinc, magnesium, silicon in aluminum there are solid inclusions of the θ -phase (CuAl_2) and silicon, as well as soft inclusions based on tin and lead. The latter are present in the alloy in the form of volume inclusions up to 30–50 microns. Copper-based inclusions are contouring aluminum grains providing additional strength. Zinc and magnesium are part of the aluminum matrix and soft inclusions and do not form own phases or zones of increased concentration.

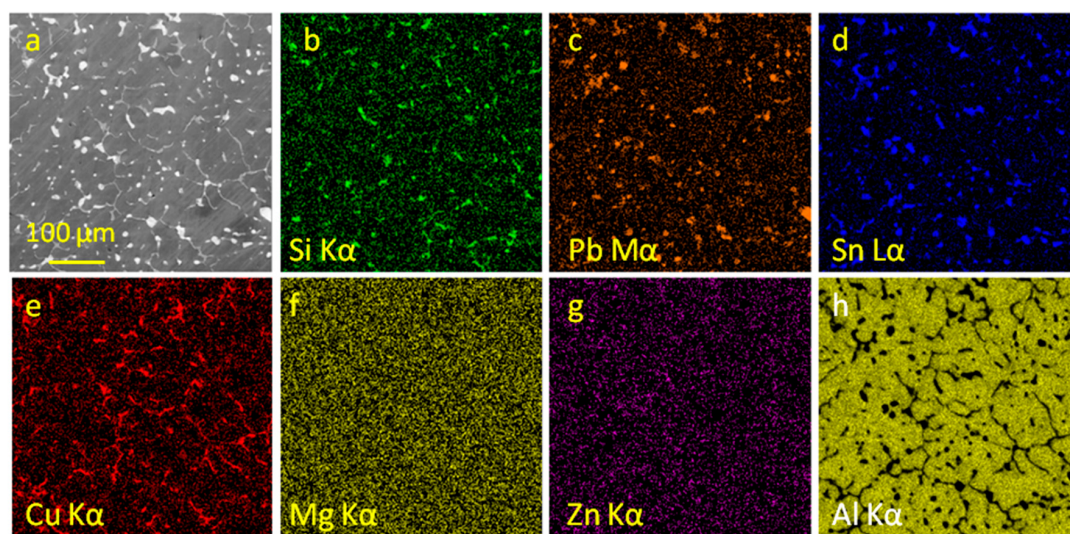


Figure 3. SEM image of a polished aluminum alloy No. 7 (a) and distribution maps of silicon (b), lead (c), tin (d), copper (e), magnesium (f), zinc (g) and aluminum (h).

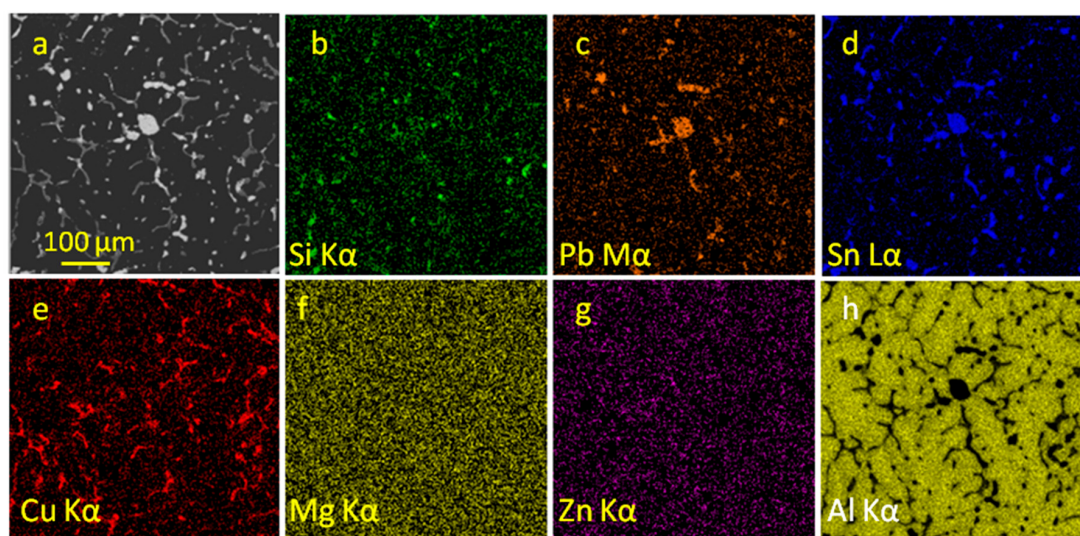


Figure 4. SEM image of a polished aluminum alloy No. 4 (a) and distribution maps of silicon (b), lead (c), tin (d), copper (e), magnesium (f), zinc (g) and aluminum (h).

The surface structure of aluminum alloys No. 7 and 4 during 40 h of testing (Figure 5b,c) underwent significant structural changes compared to the initial surface (Figure 5a). The direction of friction of both alloys can be traced. Alloy No. 7 is characterized by significant smearing of soft inclusions based on lead and tin in the direction of friction. Alloy No. 4 has a small amount of soft phase on the friction surface, and the direction of friction is characterized by the location of the grooves formed. On the surface, cavities are also visible, which were absent in the initial state. Compared to the state after milling, the roughness decreased from $R_a = 0.783 \mu\text{m}$ to $R_a = 0.128 \mu\text{m}$ for alloy No. 7 and $R_a = 0.159 \mu\text{m}$ for alloy No. 4. The roughness decreased by 5–6 times during running-in due to the smoothing of all sizeable protuberances.

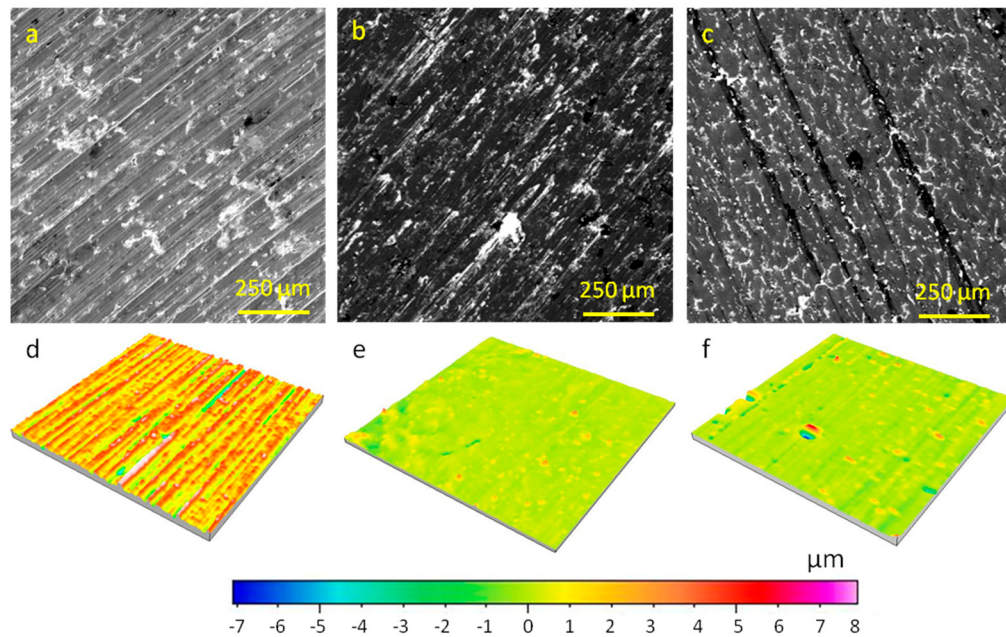


Figure 5. SEM-BSE image of a surface after milling (a), SEM-BSE image of a No. 7 alloy's surface after friction (b), SEM-BSE image of the No. 4 alloy's surface after friction (c), roughness restoration of the surface after milling (d), roughness restoration of the No. 7 alloy's surface after friction (e), roughness restoration of the No. 4 alloy's surface after friction (f).

EDX-analysis of the friction surface, in addition to elements of an aluminum alloy, also showed the presence of lubricant components (Table 4). The content of carbon and oxygen increased significantly. Independent inclusions of iron on the surface appeared due to the mass transfer of particles separated from the steel counterbody due to mechanical running-in. The debris are often the main cause of the formation of grooves until they are absorbed by soft inclusions. The content of tin and lead decreased in both alloys (Table 4). Moreover, the tin content in alloy No. 4 is less than in alloy No. 7, although in the initial state alloy No. 4 contained 1.5 times more tin (Table 1).

Table 4. Alloys No. 4 and No. 7 testing surfaces EDX analysis.

Object	Elemental Composition, % mass.											
	Sn	Pb	Cu	Si	Zn	Mg	Al	Fe	C	O	S	Na
Alloy No. 7 friction surface	3.3	2.6	1.9	0.5	1.4	0.4	39.7	0.2	34.6	15.1	0.3	-
Alloy No. 4 friction surface	2.2	0.7	3.6	0.2	3.4	0.2	56.9	0.4	18.2	13.6	0.1	0.1

In contrast to the emission spectrometer, in the EDX-analysis it is important to take into account the electron penetration depth when interpreting the results, which is $\sim 2 \mu\text{m}$. The smearing of soft inclusions led to an increase in the distribution area of tin and lead. In this regard, the content of

the latter on the friction surface of alloy No. 7 increased relative to the initial content. In alloy No. 4, there is a sharp decrease in tin and lead on the friction surface, which leads to the absence of smearing.

The distribution of elements on the friction surfaces of alloys is shown in Figures 6 and 7, where it can be seen that in some cases the distribution of elements is non-random. First, for alloy No. 7, magnesium precipitates were revealed (Figure 6e), which in the initial state had no zones of increased concentration. These zones were simultaneously enriched in carbon and oxygen. Carbon, in turn, is present on almost the entire friction surface, having different intensities in different local areas. The oxygen distribution map, for the most part, follows the location of the formed grooves. Their appearance is accompanied by constant destruction and the formation of Al_2O_3 oxide films. The more developed the surface, the greater the amount of oxygen. Besides, oxygen is present in the lubricant in the form of various C–O compounds, which also explains its significant amount on the surface. Lead and sulfur also have almost the same distribution maps of elements (Figure 6i,j). Each inclusion of lead from 10 microns turned out to be enriched in sulfur. Iron is present on the friction surface in small quantities in the form of small, up to 5 μm debris (Figure 6l). Zinc, as before friction, remains an element uniformly distributed over the alloy structure (Figure 6h).

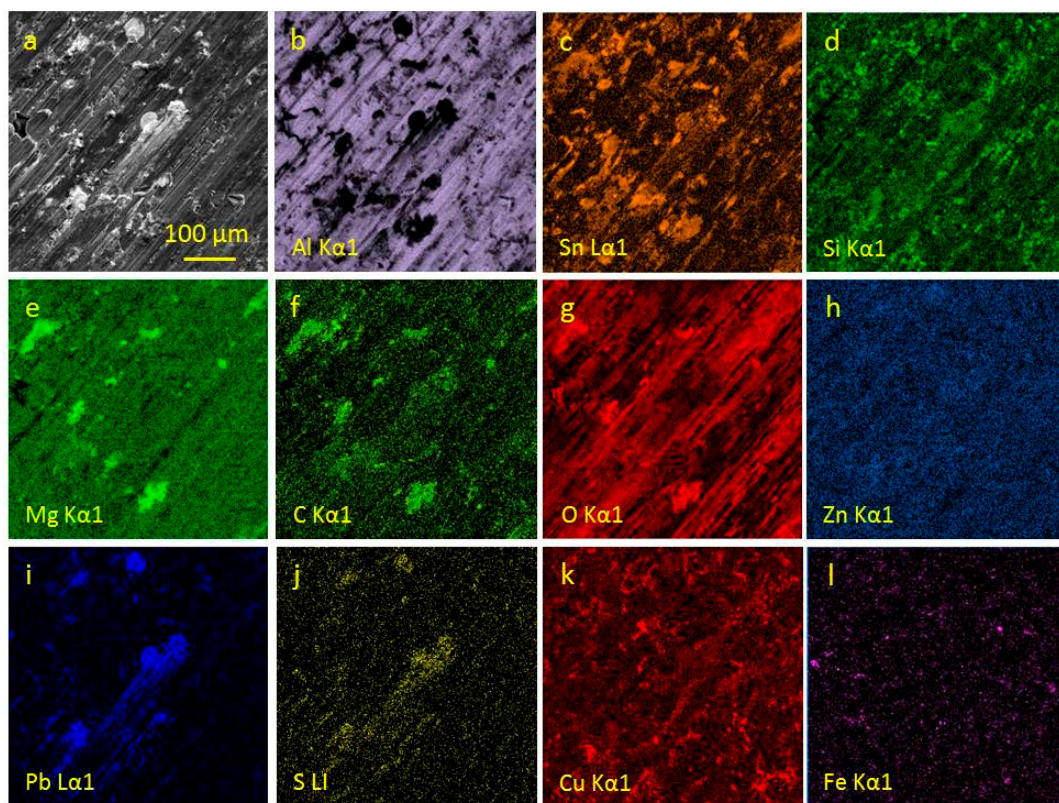


Figure 6. SEM-BSE image of the Alloy No. 7 (a) and distribution maps of aluminum (b), tin (c), silicon (d), magnesium (e), carbon (f), oxygen (g), zinc (h), lead (i), sulfur (j), copper (k), and iron (l).

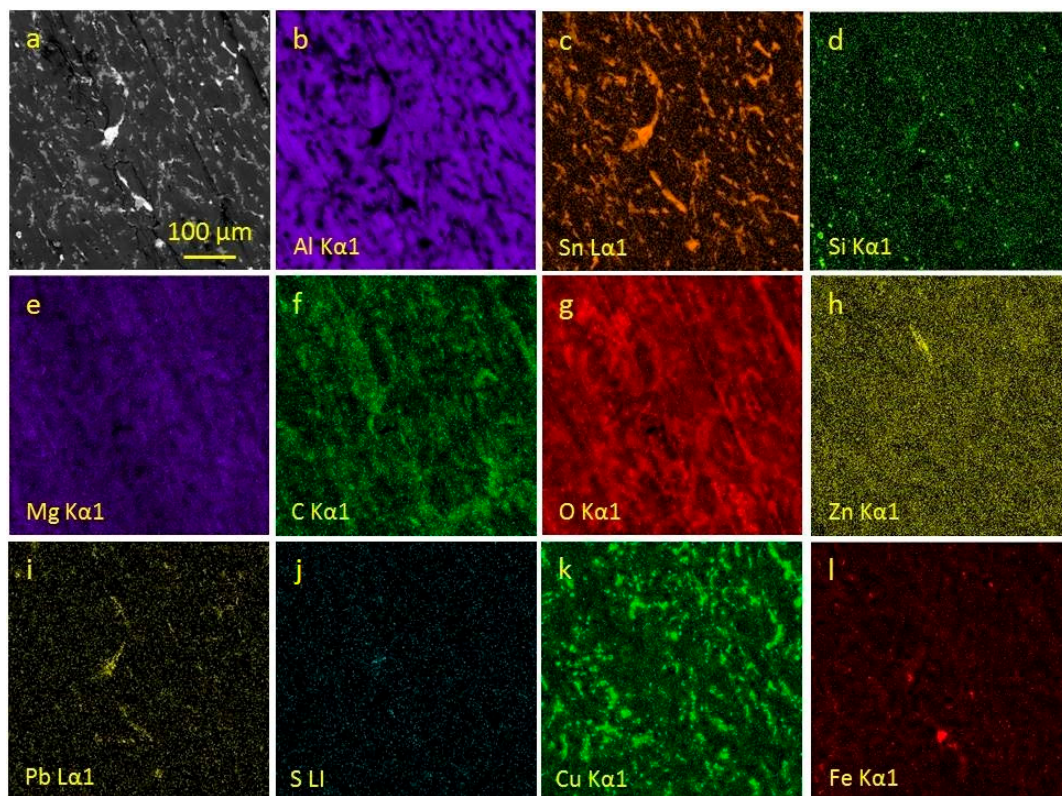


Figure 7. SEM-BSE image of the Alloy No. 4 (a) and distribution maps of aluminum (b), tin (c), silicon (d), magnesium (e), carbon (f), oxygen (g), zinc (h), lead (i), sulfur (j), copper (k), and iron (l).

Patterns found on the surface of alloy No. 7 did not apply to alloy No. 4. First, there is practically no release of magnesium from aluminum solid solution (Figure 7e), despite their commensurate content in the initial state (Table 4). As a result, carbon and oxygen have high content mainly in the formed grooves. A significant decrease in silicon content is also observed. The inclusions, compared to the alloy No. 7, are smaller in size and quantity in the studied area. Lead on the surface is represented by several small elongated inclusions. Its small amount caused the almost complete absence of sulfur on the surface. The copper content, in contrast to other alloy components, increased by 0.2%. This can be explained by the high hardness and strength of the CuAl_2 intermetallic compound, as a result of which the wear rate of such inclusions is lower than that of the other phases. Against the background of the absence of soft structures smearing that could cover copper inclusions and the intensive wear of the remaining components, the copper content on the surface increased. As a result, a large number of solid inclusions formed on the surface, which led to more intensive wear of the steel counterbody. It led to more intensive mass transfer of iron particles up to 10–20 microns and an increase in its content on the surface. In contrast to alloy No. 7, zinc is locally precipitated from aluminum solid solution. No features of its interaction with lubricant products were found. Thus, it can be assumed that the formation of secondary structures for alloys No. 4 and No. 7 proceed differently.

To determine the depth of changes that occurred a beveled sample was studied. Figure 8 clearly shows the deformation of inclusions along friction direction. While the change in elemental composition occurs mainly on the surface, the subsurface layer undergoes plastic deformation to a depth of 3 μm due to large shear stresses. Due to this, the surface of the aluminum matrix becomes hard-drawn and its hardness increases by 10–20% (Table 5). This mechanism is common for all alloys and increases the ability of alloys to resist wear.

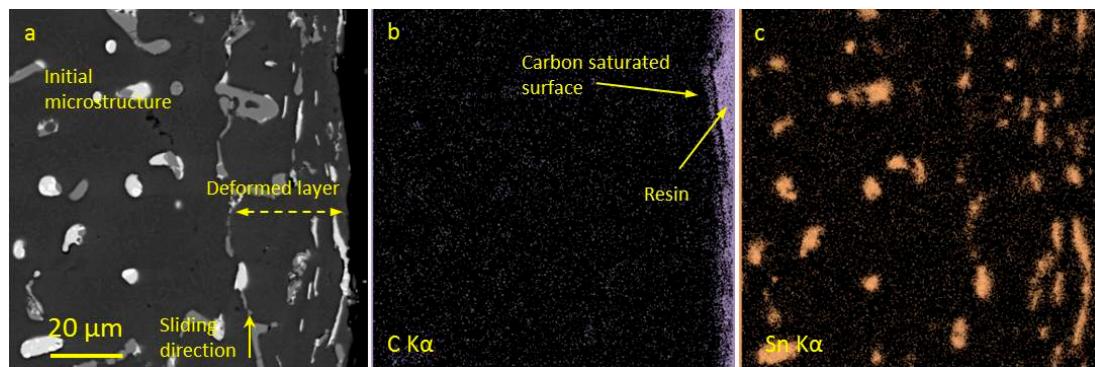


Figure 8. SEM-BSE image of the beveled sample of the alloy No. 7 (a), carbon distribution map (b), tin distribution map (c).

Table 5. Microhardness testing.

Object	HV Microhardness
Alloy No. 7 initial surface	283 ± 23
Alloy No. 7 deformed layer	314 ± 31
Alloy No. 4 initial surface	263 ± 27
Alloy No. 4 deformed layer	309 ± 29

3.2. XPS

The possibility of the spatial detection of elements in the area is one of the main advantages of EDX-analysis. However, to confirm the occurrence of the tribochemical reaction during the friction process, it is necessary to determine the bonds established between the elements using XPS. In this case, the studied region is limited by 2–3 atomic layers. Figure 8 shows the XPS spectra of alloys No. 4 and No. 7, as well as alloy No. 4 in the initial state. The XPS survey spectrum (Figure 8a), in comparison with the sample that was not subjected to friction, shows the presence of several new peaks. First, the peak of iron (~708 eV), confirming the presence of mass transfer from the steel counterbody. Sodium (~1056 eV) from the lubricant is also observed. The intensity of the lead peak for alloy No. 7 increased, which is associated more with the smearing of this element over the surface. Table 6 shows the atomic percentages of the observed elements.

Table 6. Elemental composition, % at.

Alloy	C1s	O1s	Pb4f	Sn3d	Al2p	Mg1s	Zn2p	Cu2p	Fe1s	Si2p	S2p	Others *
No. 7	55.69	22.64	1.69	2.34	9.62	1.59	0.37	0.37	0.41	0.47	3.21	<1
No. 4	62.34	24.95	0.75	0.16	7.42	0.38	0.73	0.12	0.52	0.65	1.16	<1

* Elements Na, F, P, Cl, Ca less than 0.3% at. Each.

The high-resolution spectra of the elements by which a match was found during EDX-analysis are shown in Figure 8b–g. In alloy No. 7, magnesium, which before friction was present in the alloy only in solid solutions, was released after friction, as indicated by the peak of elemental magnesium with a binding energy of 1303.12 ± 0.5 eV. Most of the magnesium is oxidized to magnesium oxide MgO, which has a binding energy of 1304.68 ± 0.5 eV. Under friction conditions and intensive carbon deposition, magnesium carbonate MgCO_3 is formed (1305.74 ± 0.5 eV). Discovered compounds correlate with distribution maps of elements (Figure 5). In alloy No. 4, the intensity of elemental magnesium and MgCO_3 is rather low compared to alloy No. 7, and magnesium oxide is dominant (Figure 9b,e). The most likely cause is a lower amount of magnesium released from the solid solution. Given the low electronegativity of magnesium, it can be concluded that oxide formation is a priority [53], which then reacts with carbon during friction to form magnesium carbonate. One of the reasons for

its formation is the mechanical activation of magnesium oxide particles, due to the constant impact of rubbing objects on it. The process is accompanied by an increase in free energy that is spent on initiating reactions, instead of the physical wear of the body.

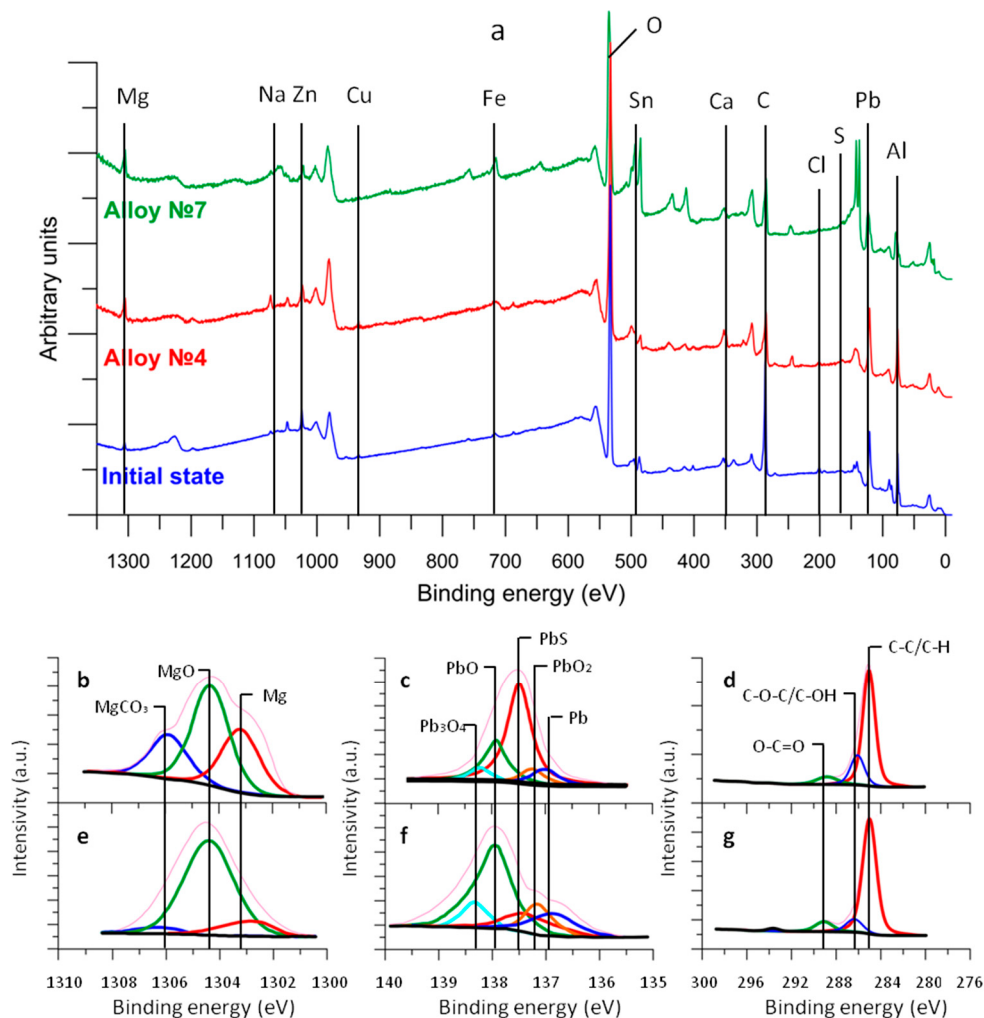


Figure 9. XPS survey (a), high resolution XPS spectra of magnesium (b), lead (c) and carbon (d) of the alloy No. 7 after friction, high resolution XPS spectra of magnesium (e), lead (f) and carbon (g) of the alloy No. 4 after friction.

The solubility of magnesium in aluminum, according to the equilibrium state diagram at room temperature, is about 5%. In addition, aluminum has a higher affinity for oxygen than that of magnesium. Therefore, the release of magnesium from a solid solution is not a spontaneous process and is accompanied by a negative production of entropy. This may be a mechanism of dissipative structures formation [47]. Alloy No. 7 has two times more magnesium on its friction surface than alloy No. 4. Given the same time of the friction test, the intensity of magnesium release from the solid solution of alloy No. 7 is two times higher than that of alloy No. 4. Accordingly, the negative entropy production in alloy No. 7 is approximately two times greater (in absolute value) than in alloy No. 4. The increased wear rate of Alloy No. 4 is probably related to the ability of magnesium to precipitate from a solid solution.

Lead in both alloys after friction is present in a small amount in the elemental state, as indicated by the peak at a binding energy of 136.8 ± 0.5 eV (Figure 8c,f). The main part of lead in alloy No. 4 is in the form of oxides Pb₃O₄ (138.4 ± 0.5 eV), PbO₂ (137.2 ± 0.5 eV) and PbO (137.9 ± 0.5 eV), of which the latter is the dominant compound. On the other hand, alloy No. 7 is characterized by a significant

amount of lead sulfide compound PbS (137.4 ± 0.5). Various lead oxides are also present on the friction surface of alloy No. 7 (Figure 9c). The beneficial effect of lead sulfide upon friction lies in the possibility of the formation of long films on the surface, which are easily transferred to the steel counterbody. The crystal lattice of this compound is symmetrical and can be cleaved along the $\{100\}$ plane. It is noted that sulfur is capable of being transported and reacting with iron at the point of contact with the formation of FeS compound, which is also characterized by a lamellar structure with low shear resistance [33,54]. Thus, the friction in the area is reduced to the contact of two solid lubricants, which can easily wear out under the action of shear stresses.

No significant differences in the interaction with carbon in alloys No. 4 and No. 7 were observed. A greater amount of it occurs in adventitious hydrocarbon contamination C-C/C-H with the binding energy of 285 ± 0.5 eV, the source of which is not only lubricant, but also the environment. The formation of C-O-C/C-OH (286.3 ± 0.5 eV) compounds on the friction surface is seen, which indicates the decomposition of the lubricant and its subsequent polymerization. The O-C=O peak (289.2 eV) represents the presence of carbonates on the surface.

3.3. XRD

To detect changes in the phase composition, an X-ray phase analysis of the samples was carried out before and after friction, as well as a sample of steel 38HN3MA in its initial state (Figure 10). It can be seen that the samples after friction underwent some changes, as indicated by the presence of new peaks compared to the initial state (Table 6). Moreover, there are no steel-related peaks, which would indicate the presence of mass transfer. The number of transferred counterbody particles is small and is below the sensitivity limit of the device.

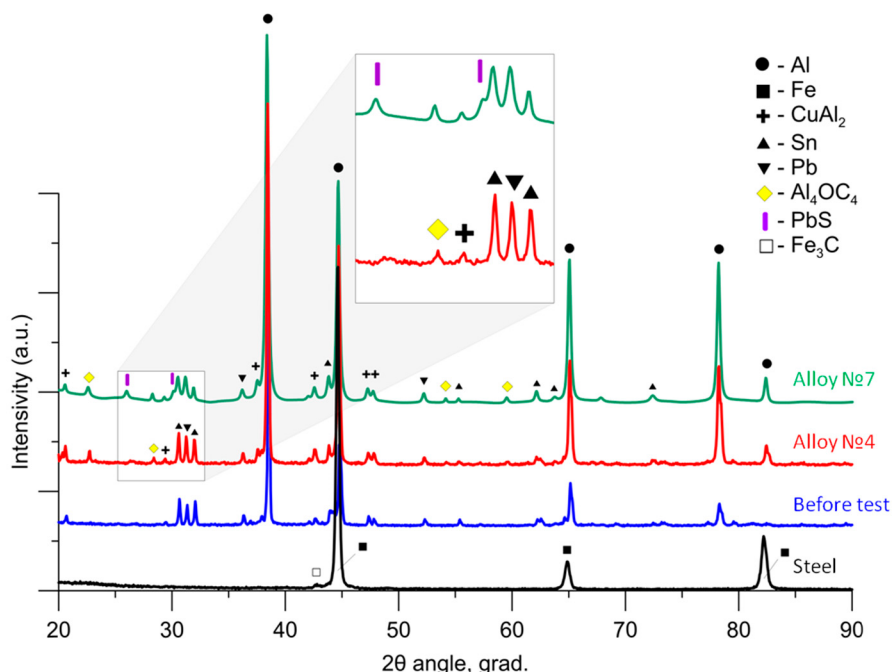


Figure 10. XRD patterns the aluminum alloys and steel before friction test.

The friction surface structure of alloy No. 7 differs from alloy No. 4 by the presence of peaks 1 and 2 (Table 7), which were identified as lead sulfide PbS (96-301-3404), which confirms the XPS-analysis. The newly formed peaks 3–6 (Table 7) have low intensity and, based on interplanar spacings, were identified as aluminum carboxide in various stoichiometry, which is also the result of the interaction of the matrix with the lubricant.

Table 7. Friction induced phase changes.

Peak No.	1	2	3	4	5	6
2θ angle, deg.	26.00	30.12	22.69	28.21	54.42	59.56
Phase	PbS	PbS	Al ₄ OC ₄	Al ₄ OC ₄	Al ₄ OC ₄ /Al ₂ OC	Al ₄ OC ₄ /Al ₂ OC

The formation of the compound occurs on the surface over the entire area of the aluminum matrix, as a result of which such compounds are the basis of the secondary structures formed during friction. The presence of aluminum carboxides after friction is common for both alloys. Compounds Al₂OC and Al₄OC₄ are the main components of ceramics and have high hardness and, as a result, higher wear resistance than the original aluminum matrix. That mechanism of secondary structures formation is a response of the system to the destruction caused by friction and aimed at reducing wear.

4. Conclusions

In this work, secondary structures formed on the friction surface of experimental aluminum alloys rubbing with steel in mixed lubrication regime were studied. The following physical and tribochemical features of their formation were revealed:

Magnesium is capable of precipitating from solid solutions of aluminum and tin during friction, followed by interaction with oxygen and carbon and the formation of MgO, MgCO₃ compounds. The precipitation of magnesium from a solid solution is not a spontaneous process, hence, it is a part of the self-organization process. To summarize, the following conclusions may be put forth:

1. Lead can react with sulfur contained in the lubricant to form sulfur sulfide PbS, the layered structure of which has an additional lubricating effect.
2. Aluminum carboxides are formed on the surface of the aluminum matrix providing increased wear resistance.
3. Shear stress during friction causes plastic deformation of the alloy surface to a depth of up to 3 μm. This leads to an increase in hardness of the surface layer by 10–20%, which increases its wear resistance.

Thus, all structural changes that occur during friction are aimed at reducing body wear. This can occur by absorbing the generated free energy for precipitation of elements, initiation of tribochemical reactions, and formation of layered compounds acting as a solid lubricant. At the same time, there is a general increase in the hardness of the surface layer due to deformations and the formation of solid aluminum carboxides. Such mechanisms of the formation of secondary structures are possible due to the self-organization of alloys during friction. However, the processes of self-organization are different for alloys with different content of elements.

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