Features of the structure and properties of surface layers of babbitt coatings after boundary mode of friction

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The microstructure and properties of the surface layers of the friction surface of the babbitt coating were studied after the boundary mode of friction. Its tribological characteristics were studied in a load-speed mode close to the operating conditions of plain bearings of gas-pumping units; cases of optimal antifriction behavior of the coating were revealed, when the coefficient of friction after short-term steam treatment decreased to 0.02. It was established that the mechanochemical processes in the friction contact zone of the babbitt-steel pair come to end with the formation of a submicrodisperse antifriction surface layer with an average grain size of 310 nm (for the B83 alloy). Near the surface, a fairly ordered fragmentation of the intergranular space with a fragment size of about 12 nm was observed. On the surface of the coating, the presence of an elementally compacted surface layer of a similar thickness was found. Highly dynamic processes of isomorphous replacement of the basic elements of the SnSbCu coating with carbon and oxygen, which are responsible for the appearance of a nanocomposite surface structure, are revealed. Oxygen stabilizes the content of copper in the surface grains, but, on the other hand, causes their depletion in antimony (an element of the strengthening phase). The intensification of mechanochemical oxidation significantly reduces the content of antimony in the surface friction layers of babbitt; this is obviously the main reason that babbitt coatings are not able to provide the necessary bearing capacity of bearings at elevated operating temperatures (above 100–120°C).

Keywords: babbitt coating, friction, surface microstructure.

Особливості структури та властивості поверхневих шарів бабітового покриття після граничного режиму тертя. *М.В.Кіндрачук, В.В.Харченко, О.І.Духота, І.А.Гуменюк, Д.В.Леусенко*

Досліджено мікроструктуру та властивості поверхневих шарів тертьової поверхні бабітового покриття після граничного режиму тертя. При вивченні його трибологічних характеристик за навантажувально-швидкісних умов, наближених до експлуатаційних, для підшипників ковзання газоперекачувального агрегату, виявлено випадки оптимальної антифрикційної поведінки покриття, коли коефіцієнт тертя після короткочасного періоду припрацювання пари зменшувався до величини 0,02. Встановлено, що механохімічні процеси в контактній зоні тертя пари бабіт-сталь завершуються утворенням субмікродисперсного антифрикційного поверхневого шару з середнім діаметром зерен 310 нм (для сплаву Б83). В околі поверхні спостерігається доволі упорядковане фрагментування міжзеренного простору з розміром фрагментів близько 12 нм. На поверхні покриття зафіксовано існування елементно-ущільненого поверхневого шару подібної товщини. Виявлено високо динамічні процеси ізоморфного заміщення базових елементів покриття SnSbCu на вуглець та кисень, що спричинюють виникнення нанокомпозиційно+ поверхневої структури. Кисень стабілізує концентрацію міді у складі

поверхневих зерен, але, натомість, спричиняє їх збіднення на сурму. інтенсифікація механохімічного окиснення, яке суттєво зменшує концентрацію сурми (елементу зміцнювальної фази) в тертьових поверхневих шарах бабіту, й стає, очевидно, головною причиною того, що бабітові покриття не забезпечують необхідної несучої здатності підшипників за підвищених температур експлуатації (вищих за 100–120°С).

1. Introduction

Alloys based on tin and lead (babbitts) are the oldest bearing materials. Such longevity is due to their unrivaled anti-friction properties and excellent workability [1–3]. Nowadays, the B83 and B88 brands of babbitt are used for filling the liners of sliding bearings of gas pumping units. They are high-quality, with strict requirements for their chemical composition, but also quite expensive and scarce alloys. In addition, babbitts do not provide the necessary bearing capacity at elevated operation temperatures. Therefore, there is a need to find alternative high-temperature materials. In particular, an anti-friction eutectic alloy based on iron additionally doped with tin and lead, cheaper than babbitts, has bean developed and the mechanism of its wear has been investigated [4, 6]. Iron, chromium, nickel, and copper in the alloy create a metal matrix in which the strengthening phase, i.e., crystals of titanium diboride and vanadium monocarbide, is evenly distributed. Alloying impurities of tin and lead enhance the positive effect of copper [7], which improves the anti-friction characteristics and wear resistance of the material under conditions of friction without lubrication. In the lubricating environment, the developed alloy is superior to babbitts in terms of high-temperature tribological properties, and it also has increased fatigue resistance. But at close-to-room temperatures, the characteristics of babbitts remain better.

Therefore, studies of the processes of mechanochemical reconstruction of the surface layers of babbitt coatings in the contact zone of friction are promising from the viewpoint of the mechanisms of ensuring the antifriction ability of the material. All babbitts of the most common brands B83, B83C, B88 and B93 have a heterogeneous structure and are a mixture of solid solutions based on tin (soft base) and the intermetallic compound SnSb (hard inclusions). Due to the low fatigue resistance of babbitts, they are used mainly as a working coating material (up to 1 mm thick) for surfaces in sliding pairs. Secondary friction structures, which determine the antifriction and wear resistance of bearings as a whole, arise within the friction contact zone as a result of the mechanochemical rearrangement of the surface layers, which are much thinner (up to 1 μm) compared to the thickness of the babbitt coating [8]. New results of studying the causes of wear resistance of friction surfaces of bronze-steel pairs [9–10] show their special reduced-oxidized state and a complex thin-film structure of surface layers with element-compacted and depleted layers; therefore, it is also necessary to study the correlations of the component composition and elemental density of antifriction babbitt surfaces.

The aim of the work was to study the antifriction mechanisms of babbitt coatings and the features of the thin-film structure of their surface layers which are formed on different parts of the friction surface under conditions of boundary friction, close to the operating conditions of plain bearings of gas-pumping units. For this, the component composition and patterns of changes in the elemental density [7] were analyzed for those surface layers that significantly differed in the fine structure of spectral lines.

2. Experimental

The tribological properties of a babbitt coating with a thickness of about 1 mm were studied on the developed laboratory friction device according to the block-ring kinematic scheme. The nominal area of the friction surface of the babbitt coating (FSBC) on the working surface of the block was 300 mm^2. Babbitt of the B83 grade was chosen for research. A counterbody sample (ring, friction track diameter 50 mm) was made of steel 45 in the hardened state. Surface roughness R_a = 0.32. Turbine oil TP22 was used to lubricate the steam.

The microstructure of the friction surfaces of the FSBC babbitt coating after tribological tests was studied by the methods of metallography, optical and scanning electron microscopy. The thin-film structure of the surface layers was investigated by the methods of microprobe Auger-electron spectroscopy and stepwise sputtering of characteristic microareas of the FSBC with argon ions (device JEOL JAMP-10S). The elemental density of the frictional surface layers of the babbitt was analyzed according to the following characteristic measured under the
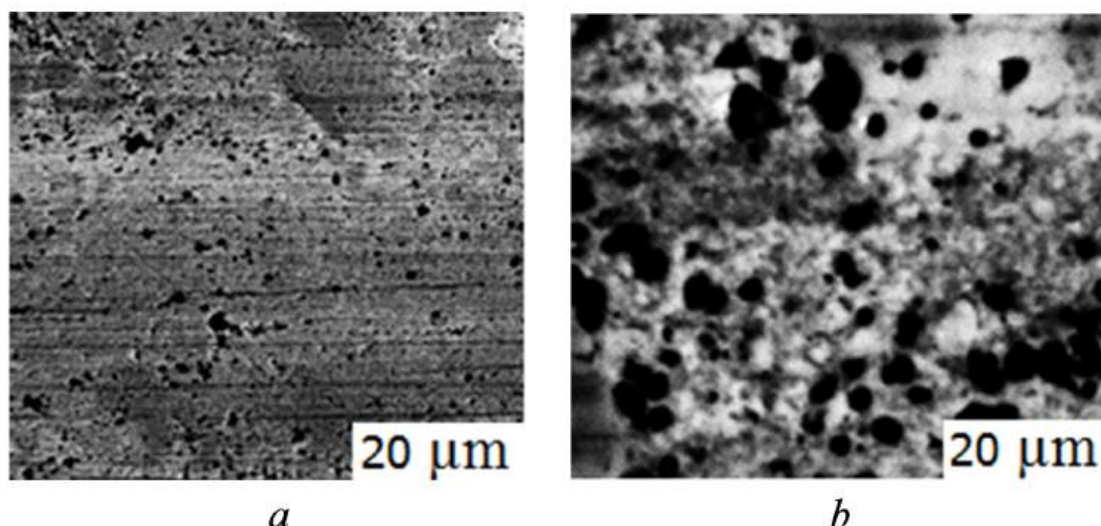
Fig. 1. Microstructure and phase contrast of FSBC. Image: SEM. Specific load 5 MPa; rotation speed 500 min[1961], room temperature. Turbine oil TP22.

condition of a constant diameter of the primary electron beam:

$$Characteristic(h) = (S(h) - S_0)/S_0, \quad (1)$$

where $S(h)$ is the total intensity of Auger lines normalized to the corresponding coefficients of relative sensitivity for all elements of the investigated surface layer located at the depth h, which is proportional to the duration of sputtering of the alloy surface with argon ions; S_0 *cong const* is an averaged value in the "volume" of the metal coating. The relative contents of elements in the FSBC were calculated from the intensities of characteristic lines on the EdN/dE type Auger spectra, using the relative sensitivity coefficients [8].

3. Results and discussion

When studying the tribological characteristics of the model pair "block (with a babbitt coating) - ring (steel)" under loading-speed conditions close to those existing during the operation of the sliding bearings of the gas pumping unit, some cases of optimal antifriction behavior of the babbitt coating were identified: a decrease in the friction coefficient (after short-term running-in friction pairs) up to 0.02. Samples of friction surfaces in these cases were selected for further research. An example of such a surface is illustrated in Fig. 1 The volume wear intensity of the babbitt coating under a specific load of 5 MPa and a speed of rotation of the steel ring of 500 min[1961]

was 0.07 mm^3/mm^2 per 1 km of the friction path.

When analyzing the topographic and phase contrast of the PCBK, characteristic surface zones of two types are revealed (Fig. 1, a): zone 1 of predominantly dark contrast, which occupies most of the friction surface, and zone 2 of light contrast, which is inherent in separate relatively thin sliding strips. Microzones 1 and 2 were observed simultaneously on many areas of FSBC (Fig. 1, b). The microstructure of the surface zones of dark contrast is finer (average grain diameter 0.31 μm with a spread in the range of 0.23–0.37 μm) compared to the microstructure of light contrast zones (0.56 μm with a spread in the range of 0.42–0.65 μm).

In order to average the results, the subsequent Auger analysis of FSBC was used so that it covered simultaneously to 15 submicrograins of zone 1 or to 5 micrograins of zone 2. Therefore, both the grain boundaries and the intergranular phases contributed to the results obtained. Auger-spectral analysis of various microareas of FSBC revealed a fundamental difference in the basic elemental and impurity composition and in the degree of surface layer oxidation of zones 1 and 2, which affected not only the amplitudes, but also the fine structure of the spectral lines (Fig. 2).

The calculation of the content of elements for different surface layers in different sections of the FSBC showed that during friction within microzones 1, in general, the surface layers of the alloy are depleted

Table 1. Elemental composition of FSBC microzones and alloy B83 (Figs. 1, 2)

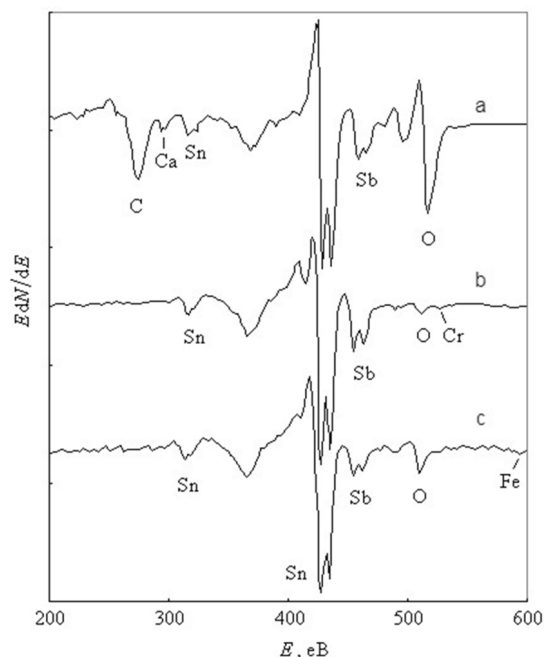| Surface	Depth, nm	Content of elements, at. %					
		Sn	Sb	Cu	O	C	The rest
Microzone 1	0	39.2	10.6	0.4	26.1	18.0	Ca, Al
	70	81.3	10.7	3.3	2.1	0.5	Cr, Mn
Microzone 2	70	76.7	5.6	8.0	5.7	0	Fe, Al
B83		79.1	10.2	10.7			

Fig. 2. Fine structure of Auger lines of tin (a) on the surface and (b, c) in the subsurface layers at a depth of 70 nm from FSBC for microareas: (a, b) zone 1; (c) zone 2.
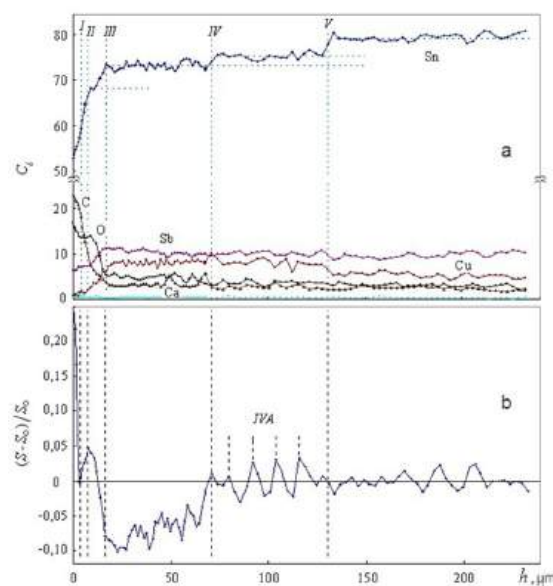

Fig. 3. Profiles of (a) element content and (b) element density of the surface layer for a characteristic microsection of zone 1 in FSBC (see Fig. 1). Roman numerals mark the boundaries between different surface layers.

in copper, and in microzones 2 — in antimony (Table 1).

It should be noted that the surface layer of zone 1 is more saturated with carbon compared to zone 2. The micro-impurity states of zones 1 and 2 are also different, which may be due to different contact interactions of the corresponding FSBC areas with the surface of the steel counterbody. The presence of microimpurities of iron in the surface layers of zone 2 is probably due to the transfer of counterbody microfragments to the babbitt coating. A much higher degree of oxidation of the subsurface layers of zone 2 compared to zone 1 indicates a stronger contact interaction of the microareas of zone 2 with the counterbody (Table 1). It is obvious that micrograins of zone 2 are oxidized conglomerates of submicrograins of zone 1 (Fig. 1, b).

The evaluations performed made it possible to conclude that the above-mentioned antifrictionality of the babbitt coating is related to the processes of mechanochemical restructuring and specific properties of its surface layers within zone 1 covering most of the friction surface (Fig. 1). This conclusion requires a thorough study of the thin-film structure of the surface layer of this zone. The distribution profiles of the elemental composition and density (according to criterion (1)) of the surface layer of zone 1 analyzed to a depth of 230 nm (minimum grain size of this zone) from the surface are shown in Fig. 3.

Analysis of the profiles in Fig. 3 reveals the presence of several characteristic layers in the structure of FSBC: *0–I* — elementally densified layer with the maximum carbon content ; *0–II* — elementally densified layer with the maximum oxygen con-

tent; *II−III* — transitional layer between the densified and depleted layers; *III−IB* — elementally depleted layer with the maximum contents of antimony and copper; *IV−V* — conditionally "nanofragmented" layer; *V-230* — subsurface layer with the contents of tin and antimony corresponding to those in the alloy B83 except for the 2−3 times reduced content of copper.

Thus, these results demonstrate the redistribution of the basic elements of the babbitt coating within its surface submicrograins (Fig. 1). The composition of layers *III−V* is closest to the alloy B83 in terms of the content of antimony and copper. The elemental density of the "nanofragmented" layer *IV−V*, averaged over the cross-section of several surface grains of zone 1 (Fig. 1), varies quasi-periodically with "depleted-densified" type oscillations. The compaction of this layer is accompanied by sharp "ups" in the carbon content and "downs" in the copper content. This made it possible to identify the boundaries of the fragments marked within layers *IV−V* as IVA subboundaries (Fig. 3b) and to determine their localization.

Taking into account the cross-section of the middle of the submicrograins of zone 1 (Fig. 1) by the boundary VD and the sharpness of the IVA subboundaries, we note a rather ordered fragmentation of the intergranular space of the surface layer with a fragment size of about 12 nm (Fig. 3, b). Note, the size of the fragments also corresponds to the thickness of the oxide densified surface layer 0−II, III.

Similar submicrograins (as in Fig. 1) were also observed on the friction surface of bronze [6, 7] under the conditions of the "selective transfer" effect in the bronze-steel pair. On the bronze surfaces, a surface elementally densified layer was formed with the sealing characteristics of babbitt (Fig. 3b), but mainly under the influence of carbon. Carbon penetrated much deeper, even beyond the boundaries of the surface submicrograins, into the subsurface layer of bronze to 2 µm thick, and created an isomorphic mixture with copper atoms [9]; it was the basic phase in the nanodispersed composite structure of the "servo film" and determined its elemental-densified state [7]. As a result, elementally depleted interlayer *III−IV* (Fig. 3, b) in the surface layer of bronze, characteristic to babbitt, was not formed in this case.

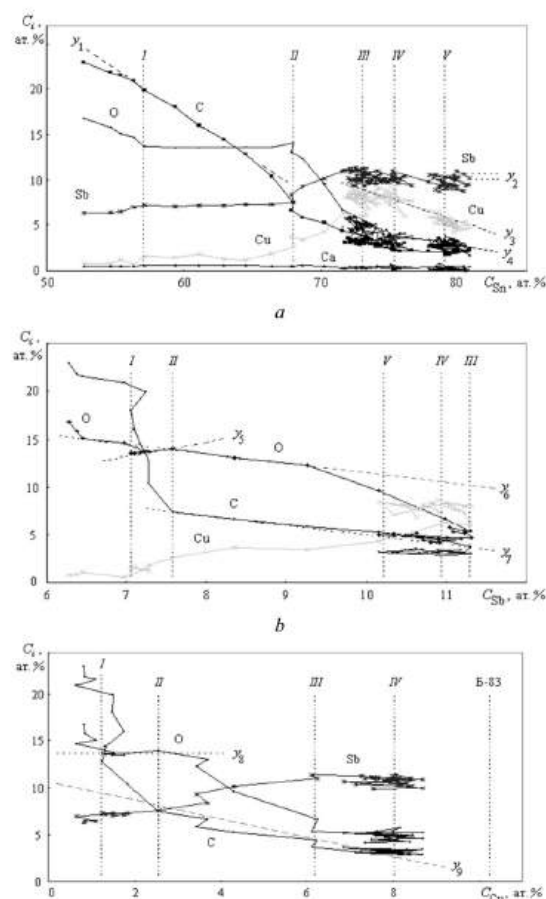It is also worth noting that the densified surface layer can be a separate thin-film

Fig. 4. Correlation dependences between the contents of basic elements (Sn, Sb, Cu) and impurities of the babbitt coating in the surface layer of zone 1 (see Fig. 1), constructed according to the data in Fig. 3 for the surface layer: (a) 0−240 nm; (b, c) 0−IV.

phase that is held by adhesion forces on the surface of the elementally depleted interlayer *III−IV*. Thus, its thickness may depend on the properties of the lubricating medium components. For example, it has been found that under the influence of oil-soluble finely-dispersed hydroxysilicate of magnesium and iron, a surface abrasive-wear-resistant structure is formed on the friction surfaces of a steel pair, which includes the elementally-densified adhesive surface layer with a submicron thickness of 130−160 nm [10].

In order to study the phase composition of the revealed surface layers of the babbitt coating (Fig. 3), it is reasonable to consider the correlations between the contents of its basic elements (Sn, Sb, Cu) and impurities (Fig. 4). Such correlation dependences may be considered in terms of phase diagrams of the thin surface layer of the metal.

Table 2. Parameters of equation (2) for extrapolation straight lines y_1–y_9 (Fig. 4)

Parameter	y_1	y_2 (B 83)	y_3	y_4	y_5	y_6	y_7	y_8	y_9
a	−1	0	−0.5	−0.25	1.5	−1	−1	0	−1
x_0, at.	77.2	0	91.0	91.0	7.2	21.5	15.0	0	10.7
y_0, at.	0	10.7 (Cu) 10.2 (Sb)	0	0	13.7	0	0	13.7	0

The analysis showed that certain sections of the correlation dependences in Fig. 4 can be extrapolated by straight line segments:

$$y(x) = a(x-x_0) + y_0, \qquad (2)$$

where $y(x)$ and y_0 are the contents of elements according to the ordinate axis of Fig. 4; x and x_0 are contents of elements according to the abscissa axis of the corresponding correlation dependence; and a is a constant coefficient.

Segments of the horizontal lines y_2 and y_8 indicate characteristic contents of elements in the corresponding layers (Fig. 4, a, c). Values of a, x_0 and y_0 for all extrapolation lines y_1 – y_9 in Fig. 4 are listed in Table 2.

Linear extrapolations y_1, y_6, y_7 and y_9 (Fig. 4) with a characteristic coefficient $a = -1$ indicate isomorphic replacement of elements x and y in nanostructured phases [9], which in the corresponding surface layers have contents calculated by the expression:

$$y+x = x_0. \qquad (3)$$

The presence of two phases having isomorphic changes in the contents of carbon and tin (Fig. 4, straight line y_1) or antimony and oxygen, (straight line y_6), indicates a nanocomposite structure of the densified layer *0–II* with a ratio of the indicated phases of 77.2:21.5 (or 3.6:1), respectively.

Note that the fine structure of the spectral line of carbon on the surface of zone 1 (Fig. 2, a) is typical rather for carbides than for for adsorbed hydrocarbon [11]. Calculation of the element contents (Table 1) revealed the presence of hypothetical tin carbide with a stoichiometry close to that of Sn_2C. Since tin does not form carbide compounds under normal conditions, the detected carbide should be considered thermodynamically unstable and capable of structural rearrangement and adaptation.

A similar elementally-densified complex structure, but within a fairly thick (up to 2 μm) surface layer has been observed in the friction surfaces of bronze [6, 7]. The isomorphism of carbon and copper along with iron and oxygen was revealed.

Within the layer *I–II*, the isomorphic replacement of antimony with oxygen (straight line y_6) is interrupted by the formation of an oxide phase that corresponds to the high-temperature antimony dioxide SbO_2 according the ratio of antimony and oxygen contents (Fig. 4, a). However, extrapolation of the y_5 line shows that in the range of antimony contents of 7.1–7.6 at.%, oxygen content changes proportionally in accordance with the composition of ordinary sesquioxide Sb_2O_3 (Fig. 4, b; Table 2).

In addition, an isomorphism of carbon and antimony (Fig. 4, straight line y_7) along with carbon and copper (straight line y_9) was found in the subsurface layers *II–III–IV*. The performed linear extrapolations indicate the binding of antimony and copper atoms in those layers.

The maximum content of copper 10.2 at. %, which is close to its content in the B83 alloy (Table 1), was reached only at boundary IV (Fig. 3, a), where the isomorphic replacement of copper atoms with carbon stops (Fig. 4, c, straight line y_9). In the direction from boundary *IV* to boundary *V*, the content of copper decreases, which correlates with a decrease in the content of oxygen (extrapolations y_3 and y_4); this is due to relatively small fluctuations in the contents of antimony and carbon as compared to their constant averaged levels (Fig. 4, a). In this case, the ratio between copper and oxygen atoms corresponds to the Cu_2O oxide stoichiometry (Table 2). Note, that if the content of this copper oxide decreases to zero (Table 2; y_3 and y_4; equation (2)), the elemental composition of the surface layer becomes similar to that of alloy B83, except for the carbon admixture of about 2 at. %.

According to the above results, the mechanism of the formation of the anti-friction structure (zone 1) of the surface layer

of the babbitt coating SnSbCu (alloy B83) is as follows.

During mechanochemical activation in the friction contact zone, the inner part (core) of the surface grains of the alloy is steadily depleted of copper. At the same time, due to oxidation, a subsurface layer *III–V* is formed, which contains copper oxides and limits the mobility of copper atoms. In this layer, the contents of copper and antimony are close to those typical for the B83 alloy. From boundary *IV* to the surface, we observe isomorphic replacement of copper atoms with carbon. A densified nanosized (thickness from 4 to 12 nm) surface layer is formed on the grain surfaces, which is probably bound to the subsurface layers by adhesion forces [10].

The isomorphic replacement of copper atoms in the *II–III* interlayer and tin atoms in the adhesive surface layer *0–II* with carbon correlates with an increase in the elemental densification of the surface layer, as well as, in general, with a decrease in tin and copper contents in the surface grain structure. The latter probably contributes to the appearance of the element-depleted state of the subsurface layer *III–IV* with a thickness of 55–60 nm. Antimony atoms in the surface adhesive layer are isomorphically replaced with oxygen and create an oxide phase in the *I–II* interlayer, which can significantly affect the properties of the entire antifriction surface structure of the babbit coating.

The mechanochemical activation of oxidation in FSBC microareas of the, as a result of microseizures, local overloads or heating in the contact zone leads to the formation of copper oxides and stabilization of the copper content in the composition of surface grains. On the other hand, it causes a significant depletion in antimony, which ends with the formation of surface areas of zone 2 (Fig. 1; Table 1). Therefore, it is reasonable to study the initial stages of destruction of the babbitt coating (Fig. 5), which come to end with the adaptability of the structure to the steady-state mode of friction.

The results of the study of the microstructure of significantly destroyed areas of the friction surface indicate the typical triangular shape of the damage (Fig. 5, microarea 1). Each damage occurs with the formation of the microzones described above: microzone 2 near the "top" of the triangle, from which the destruction process begins and develops, and the characteristic
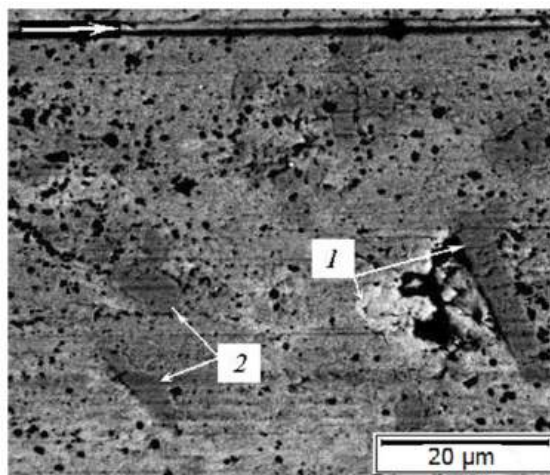

Fig. 5. Peculiaries of destruction of FSBC microareas.

dark band of microzone 1 at the triangle base, where the destruction stops. The adaptability of the coating structure through the formation of a transverse band of microzone 1 under normal conditions of boundary friction most often manifests itself even at the initial stages, i.e., without the appearance of triangular forms of damage (Fig. 5, microareas 2). This indicates the highly dynamic nature of the studied mechanochemical transformations of the surface layer of the coating, which come to end with the formation of surface microzones 1 and 2.

4. Conclusions

Mechanochemical processes in the friction contact zone of the babbitt-steel pair are completed with the formation of a submicrodisperse antifriction surface layer (with an average grain size of 310 nm for the B83 alloy). Near the surface, a rather ordered fragmentation of the intergranular space is observed with a fragment size of about 12 nm. On the coating surface, the presence of an elementally-densified surface layer of a similar thickness was revealed. It has been established that highly dynamic processes of isomorphic substitution of carbon and oxygen for the main elements of the SnSbCu coating lead to the appearance of a nanocomposite surface structure. Carbon causes depletion of surface sub-micrograins in copper and partly in tin, which, however, contributes to the anti-friction structure and the elemental depletion of the subsurface 55–60 nm thick layer. Oxygen stabilizes the content of copper in the composition of surface grains but, on the other

hand, causes their depletion in antimony. The intensification of mechanochemical oxidation significantly reduces the content of antimony (an element of the strengthening phase) in the FSBC; this obviously becomes the main reason that babbitt coatings do not provide the necessary bearing capacity of bearings at elevated operating temperatures (over 100–120°C).

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