

EFFECT OF DIFFUSIONAL REDISTRIBUTION OF ALLOYING ELEMENTS ON THE WEAR RESISTANCE OF COPPER ALLOYS

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Plastic deformation leads to a change in the structure, phase composition, and physical and mechanical properties of the surface layers of friction couples. The high rates of heating and cooling of the surface during friction, substantially exceeding the heating and cooling rates during ordinary heat treatment, affect the kinetics of the structural changes. Repeated thermal and mechanical effects lead to substantial diffusional flows of atoms in surface layers with a thickness of several tens of microns. Diffusional redistribution of alloying elements is of particular importance during friction in the presence of a surface-active substance (SAS) as a lubricant, when shearing is facilitated in surface layers as the result of the physicochemical interaction of molecules of lubricant with atoms of the contacting materials.

Copper-tin alloys are of particular interest.

Increasing the tin content of a copper-tin alloy to 1.5-2.0% improves the operating conditions of the boundary lubricant, while larger tin concentrations do not increase the temperature resistance of lubricating materials [1]. Studies of the changes in the composition of the deformed zone of an alloy based on copper (during friction in various lubricating media) with a thickness of several interatomic distances with use of Auger spectroscopy [2] and a thickness of 5-30 μm [1] showed that the concentration of tin increases as the contacting surface is approached. In this case it is possible for nonequilibrium solid solutions to be formed and for intermetallic compounds to be precipitated in separate sections of the contact zone. Precipitation of intermetallic compound ϵ (Cu_3Sn) in the surface layer of a copper-tin alloy during friction causes intensive destruction of the zone of deformation and sharply impairs the parameters of friction and wear [3, 11].

The most common alloying elements in commercial tin bronzes are phosphorus, lead, and zinc. The wear of tin bronzes decreases by approximately one order when the phosphorus content is raised from 0.05 to 0.25% [4], and phosphorus also improves the antiscoring properties of bronze [5]. It was shown in [6], however, that under conditions of boundary lubrication tin bronzes without phosphorus have higher wear resistance than bronzes with phosphorus. The high wear resistance of phosphorus-free bronzes is evidently due to inclusions of tin oxide with a size of 0.2-1.0 μm .

Lead inclusions greatly reduce the ductility and weaken copper. Therefore, this alloy is incapable of undergoing substantial plastic deformation under conditions of friction, and fractures. If lead forms a thin metallic film on the supporting surface then the friction characteristics and wear resistance improve [7, 8]. The effect of zinc on friction of tin bronzes has not been investigated. It can be assumed on the basis of [9] that under conditions of a steep gradient of dislocation density zinc has a positive effect on the resistance of tin bronzes during friction.

This work concerns the diffusional redistribution of tin through the depth of the deformed zone in tin bronzes during friction with various lubricating materials in order to determine the effect of the lubricant on the character of diffusion processes during contact and the interaction of the redistributed alloying elements.

We investigated commercial alloys containing 10, 6.5, 5, and 4% Sn (bronzes BrOF10-1, BrOF6.5-0.15, BrOF4-0.25, BrOS5-25). The first three bronzes contained 1, 0.15, and 0.25% P, respectively, while BrOS5-25 contained 25% Pb.

Friction tests were made in the 77MT-1 machine with back and forth movement, an average sliding speed of 0.1 m/sec, and load 1 kgf/mm². The counterbody was quenched steel 45. The lubricants were Au spindle oil, commercial glycerin (in which copper alloys are almost unresistant to wear), and a commercial

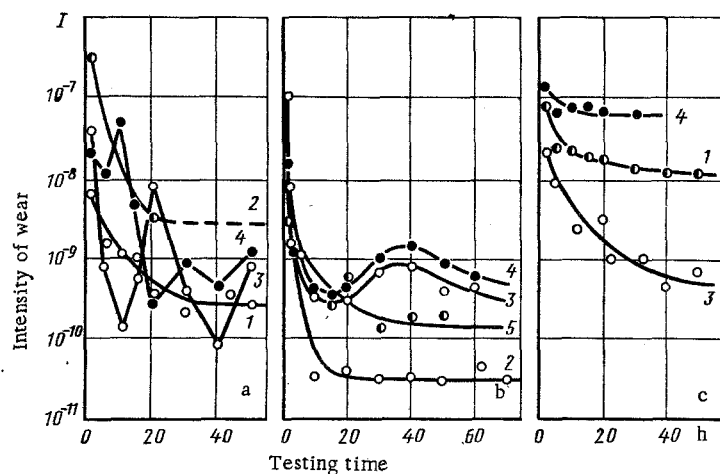


Fig. 1. Intensity of wear of tin bronzes during friction in lubricants. a) BrOF10-1; b) BrOF6.5-0.15; c) BrOS5-25. 1) AU spindle oil; 2) glycerin; 3) PGV without additives; 4) PGV with an additive; 5) BrOF4-0.25 and PGV without an additive.

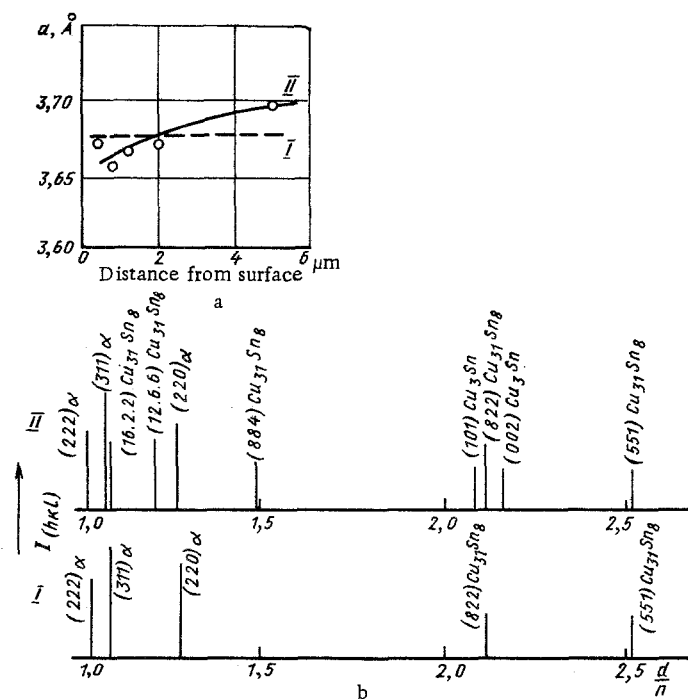


Fig. 2. Structural changes in the surface layers of bronze BrOF10-1 during friction in glycerin. a) Change in the lattice constant of the α solid solution; b) line diagrams of metallic phases. I) Original condition; II) after friction.

lubricant based on glycerin - PGV. PGV with additives was also tested. The wear was determined from the weight change. The redistribution of alloying elements was determined from the lattice constant of the α solid solution.

We used the sliding beam method [10], which permits a layer-by-layer analysis of layers with a thickness from tenths of a microns to several microns that are intermediate between layers used for microscopic analysis, electron diffraction analysis, and x-ray analysis. The images were made in K_{α} Co radiation; the angle was varied from 1 to 20°.

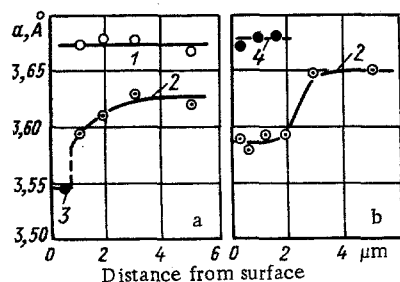


Fig. 3

Fig. 3. Change in the lattice constant during friction of bronze BrOF-6.5-0.15 in glycerin. a) Condition of selective transfer; b) disruption of the condition of selective transfer. 1) Original condition; 2) after friction; 3) film of copper; 4) intermetallic compound.

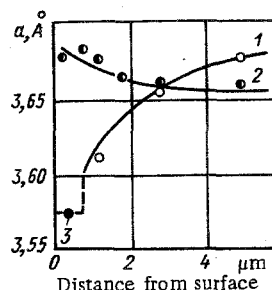


Fig. 4

Fig. 4. Change in the lattice constant of the α solid solution in bronze BrOS5-25 through the depth of the deformed zone. 1) Friction in PGV without an additive; 2) in PGV with the additive; 3) film of copper.

The lattice constant was determined by the graphoanalytic method, using the Minsk-22 computer and a special program with an accuracy of ± 0.004 Å, taking into account interference lines (220), (311), and (222).

The wear of bronze BrOF10-1 decreases monotonically in inactive mineral oil (Fig. 1). With friction in glycerin, in which SAS are formed, the wear changes by jumps and the mean value is about ten times larger than in spindle oil. The jumps in PGV, containing 40% glycerin, are as much as 100 times the value reached in the entire test. A reduction of the tin content in bronze BrOF6.5-0.15 (Fig. 1b) leads to a reduction of wear by two orders in glycerin, but the jumps in the PGV lubricant are less evident. With further reduction of the tin content (bronze BrOF4-0.25, curve 5) the wear also decreases and the jumps disappear. It should be noted that wear increases in the PVG lubricant with an anticorrosion additive (Fig. 1c).

An analysis of the literature data and the wear test results indicates the complex character of the processes in the zone of contact. We consider that it is due to the diffusional redistribution of tin in thin surface layers of the alloys, leading to a change in the properties of the metal in the contact zone and the boundary layers of the lubricant.

Figure 2 shows the results of x-ray analysis of the surface layer of bronze BrOF10-1 before and after friction tests in glycerin (similar data were obtained in PGV, based on glycerin). The slight reduction of the lattice constant in a layer with a thickness of ~ 2 μm indicates a reduction of the tin content. At a greater depth the tin concentration is higher than the original, which indicates that deformation during friction extends to a depth larger than 5 μm .

More substantial changes were observed in the phase composition of the alloy (Fig. 2b). Two phases were detected before the friction tests: The α solid solution and the $\text{Cu}_{31}\text{Sn}_8$ intermetallic compound (Fig. 2b, I). After friction, the intensity of x-ray lines of $\text{Cu}_{31}\text{Sn}_8$ increases and additional lines appear (Fig. 2b, II). New lines of Cu_3Sn appear on x-ray patterns of surface layers with a thickness of ~ 1 μm . This phase results from the decomposition of the α solid solution (indicated by some reduction of the lattice constant) and, evidently, of the intermetallic compound $\text{Cu}_{31}\text{Sn}_8$. Such changes in structure were not observed in tests in mineral oil.

Thus, during friction of alloy BrOF10-1 in a lubricant containing SAS there is not only a diffusional flow of tin atoms parallel to the surface of contact in a deformed zone with a thickness from tenths to several microns, accompanied by impoverishment of the α solid solution in tin, but also a change in the phase composition of the material. The diffusional redistribution of tin has a characteristic feature — an increase of the average concentration of tin in surface layers as the result of the increasing quantity of intermetallic compound. The driving force of the diffusion of tin to the surface of contact is the change in the chemical potential of the metal under the influence of external factors (pressure, temperature) and the more intensive electrochemical process of the solution of anodic components of the alloy in the lubricant [11].

The effect of SAS on diffusional processes in the zone of deformation during friction is especially clear in alloys in which phase transformations are inhibited under ordinary conditions of deformation — during friction of bronze BrOF6.5-0.15, for example.

Figure 3 shows the change in the lattice constant of the solid solution in bronze BrOF6.5-0.15 during friction in glycerin with decomposition of the solid solution and in the absence of it. In the latter case the concentration of tin in the surface layer decreases (as the result of interaction with the lubricant). A film of copper 1 μ m thick, with a specific structural condition, is formed on the surface (Fig. 3a) [12]. This is responsible for the low value of the parameters of friction and wear (Fig. 1b, curve 2). The formation of intermetallic compounds resulting from decomposition of the solid solution (Fig. 3b) destroys the copper film and causes a sharp increase of friction and wear. The increase of wear during friction of bronze BrOF6.5-0.15 in the PGV lubricant after testing for 20 h (Fig. 1b) is evidently due to partial decomposition of the solid solution, but after 40 h a copper film is again formed and wear decreases.

Figure 4 shows the character of diffusional redistribution of tin in the α solid solution of bronze BrOS5-25 during friction in the PGV lubricant. During friction in a lubricant without an additive the tin concentration decreases in the surface layer, while a film of copper is formed on the surface [12]. With the additive the solution of anodic components of the alloy is suppressed, leading to an increase of the tin concentration in the surface layer; the wear resistance decreases (Fig. 1c). The lead from the surface layers is completely dissolved in the lubricant during friction in the PGV lubricant without the additive; its concentration gradually increases to the original value in deeper layers. Lead is found throughout the depth of the deformed zone during friction in PGV with the additive.

CONCLUSIONS

1. Under conditions of friction and wear of an equilibrium solid solution one observes solution of anodic components of the alloy in the lubricant and formation on the contact surface of a plasticized film of pure copper with a specific structure — low dislocation density and high density of vacancies. In this case the wear resistance increases sharply — to the point where wear is practically absent.

2. During friction of unstable alloys and alloys susceptible to phase transformations the conditions are favorable for the formation of intermetallic compounds in local areas, which changes in principle the mechanism of the contact interaction — the wear resistance decreases considerably.

3. Equilibrium and a single phase are the basic conditions for high wear resistance of copper-tin alloys during friction in surface-active lubricants.

LITERATURE CITED

1. A. Roberts and A. Cameron, *Trans. ASLE*, **18**, No. 4, 270 (1975).
2. J. Ferrante and D. Buckley, *Trans. ASLE*, **1**, No. 15, 18 (1972).
3. I. Oda, M. Kimura, and K. Nakajima, *Wear*, **20**, No. 2, 159 (1972).
4. B. Lunn, *Wear*, **8**, No. 5, 401 (1965).
5. M. M. Khrushchov et al., "Friction of antifriction bronzes and brasses with and without lubrication," in: *Friction and Wear in Machines* [in Russian], Izd. Akad. Nauk SSSR (1962), p. 36.
6. A. De Gee and G. Vaessen, *First European Trib. Congress*, 1973, p. 137.
7. L. F. Kolesnichenko, É. G. Mamykin, and A. I. Yuga, "Working capacity of Cu-Pb alloys under conditions of sliding friction," in: *Problems of Friction and Wear* [in Russian], No. 4, Tekhnika, Kiev (1974), p. 69.
8. F. P. Bowden and D. Taybor, *Friction and Lubrication of Solids* [Russian translation], Mashinostroenie, Moscow (1968).
9. M. A. Krishtal and M. A. Vyboishchik, "Variation of the parameters of diffusion along dislocations with the valence of diffusing elements," *Fiz. Met. Metalloved.*, **38**, No. 2, 356 (1974).
10. L. M. Rybakova, L. I. Kuksenova, and S. V. Bosov, "X-ray analysis of structural changes in a thin surface layer of metal during friction," *Zavod. Lab.*, No. 3, 293 (1973).
11. L. I. Kuksenova and L. M. Rybakova, "Role of diffusion processes during friction of copper alloys," *Fiz. Khim. Obrab. Mater.*, No. 1, 123 (1978).
12. L. M. Rybakova and L. I. Kuksenova, "Structure of the surface layer formed in the zone of contact during friction of copper under conditions of selective transfer," *Fiz.-Khim. Mekh. Mater.*, No. 1, 100 (1976).