



# The surface self-organization in process friction and corrosion of composite materials

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## ABSTRACT

**Purpose:** The analysis of numerous phenomena that concern the possibilities of metal surface self-organization in friction and corrosion processes.

**Design/methodology/approach:** The design of structural materials resistant to wear and corrosion.

**Findings:** The paper presents the surface self-organization process of composite materials. The surface shows common properties in friction and corrosion.

**Research limitations/implications:** The research has been carried out with the application of Auger spectroscopy. The physical chemical phenomena have been found, such as segregation and surface self-organization that take place during friction and corrosion processes.

**Practical implications:** Eutectic alloys and metal alloys can be used to obtain high quality coatings resistant to wear and corrosion.

**Originality/value:** The atom segregation has been found in friction processes and the forming of special undersurface layer in the liquid phase  $Li_{17}, Pb_{83}$ .

**Keywords:** Composites; Corrosion; Surface; Wear

## MATERIALS

### 1. Introduction

The surface of structural material has the properties at the macrolevel that are similar to the ones of the grain boundary or mosaic block at the microlevel. The operating properties of structural materials can be changed purposefully due to creating the certain structural phase and energy state in the thin surface layers. It can be possible by means of forming the certain surface coatings or original barrier layers with ensuring an optimum thermodynamic state existence. Any structural phase state is stable at the first sight. But it exists for rather a short time and transforms into the new unstable level owing to the processes that are responsible for the increase of total entropy and therefore they decrease material free energy. As a result the subsequent transformation into the quasistable state is provoked and so on. It is necessary to create the conditions under which these transformations will occur with the

least regularity. The above unbalanced state causes directly the probability of the system existence with self-organization [1-4].

During friction the outside factors such as a medium composition, temperatures, moistening, the level of the contact load, the interaction duration etc. have an essential influence on the surface state of structural materials. To ensure the long-term service of structural materials, it is necessary to form the fine-grained or fine-fibered surface structure with uniform distribution and large packing density of separate structure fragments.

### 2. Results and discussing

The physical-mechanical and chemical processes take place during surface friction of materials and therefore cause the

process of wear. It results in the emerge of many friction theories explaining nature and phenomena variety during wear in terms of mechanics, molecular physics, science of materials and thermodynamics [5-9].

The well-defined mechanical and chemical processes take place in the contact surfaces areas during the friction of material. It does not result in the formation of juvenile surfaces or chemisorbed coatings such as oxide films [10]. During the shear process, Cragelsky states the positive strength gradient concept. The outer lubricate layers or adsorptive plasticization of material causes the localized positive gradient of shear resistance [7].

At stated above, the friction process essentially depends on the surface atoms segregation. It has been observed in alloys of Fe-C, Fe-Al, Fe-Si, Cu-Al, Cu-Sc systems where C, Si, Al atoms migrate forward the surface during friction. It has also been indicated that segregated carbon atoms have uncertain effect on wear resistance of materials. On the one hand the carbon on the friction areas leads to the reduction of adhesive interaction of contact materials and on the other hand it decreases the lubrication effectiveness. The change of mechanical properties the surface layers is caused by Rebinder effect. The segregation of carbon and silicon atoms is found out at the friction strengthening treatment of Armco-Fe, steel of 12X18H10T (316SS) [11]. The indicated phenomenon is observed during the wear process concerning eutectic composite disperse strengthened alloys of Fe-Mn-C-B-Si system. The C, B, Si atoms migrate forward the surface in these systems [12].

The most general model of the friction surface is suggested by Burakowski [15]. The oxidized wear theory concerning material surface during the friction is presented at the Kostetsky model, which shows that the quasimorphous oversaturated solid solutions of O, S, P in metal are formed at the metal surface. They consist of dislocationless fragmented structure of clusters and they possess an anomalous ductility [5,14]. The five-layer model of friction surface is presented by Z. Lawrowski, in which, the real mechanism of the friction processes is shown.

The authors have investigated the wear resistance of layers of Fe-Mn-C-B-Si system. It showed that they had the high wear resistance in the friction pair with steel 45 because the segregation process occurred [13]. It has also been proved by the results of Auger spectroscopy of surface layers which indicated the C, B, Si contents increasing. The carbon contents have been changed from 2.4 to 2.7 at. %, the boron contents have been changed from 8.8 to 33 at. % and silicon contents - from 3 to 11.4 at. % in Fe-Mn-C-B-Si-Ni-Cr-Al-Sn system. The peak shape of spectrum carbon indicates that carbon being in free state could act as a solid lubrication. According to the  $B_2O_3$ - $SiO_2$  equilibrium diagram, the melt point of boron trioxide is 458°C and the one of silicon dioxide is 1650°C. Owing to the B and Si atoms migration towards the friction surface, the probability of oxide forming increases in this surface. At the friction pair LH 15 steel (0.95% C and 1.5 % Cr) - boron carbide ( $B_4C$ ) the complex nonstoichiometric boron oxides have been found increase at the boron carbide surface. Allowing for the temperature elevating above 500°C at the contact area it should be waited for  $B_2O_3$  film acting as lubrication. With prolonged wear time, the friction coefficient is increased, because of the secondary structure forming at the steel surface. This causes increase of the molecular component of friction coefficient and leads to the spallation of boron oxide film from the surface (Fig.1a). The carbon

concentration is reduced exponentially from the surface towards the depth of LH 15 steel. The oxides are formed at the undersurface layer owing to the contrary oxygen diffusion (Fig.1b).

Thus, the tribological properties of materials depend on the surface structural phase and the stress state which are changed during friction due to the material ability to the surface self-organization. It is indicated by the process of atoms segregation at the surface with the next secondary structures formed found out at the authors investigations.

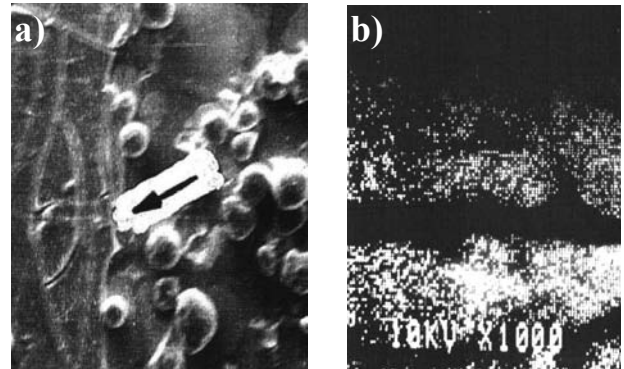


Fig. 1 a) The boron oxides formed at the surface friction of boron carbide, b) The Auger spectroscopy redistribution of C and O atoms at the friction surface of LH 15 steel (b)

The corrosion process has the features in common with the friction process but the passing of the physical chemical phenomena at material-medium interface is different. It can be possible to consider these differ (at the first sight) phenomena in united viewpoint, to create the generalized model of the surface phenomena during friction and corrosion. It is followed from the analysis of the plural theories Petch, Swann and Staihle [16,17,18], explaining the different types of corrosion damages.

The decreasing of surface free energy caused by the adsorption processes relieves the oscillation of the surface layer atoms and it reduces their binding forces. This facilitates the corrosion process development.

At the low surface energy the surface film has the plain dislocation structure which facilitates the forming of sliding stairs of large sizes. It leads to increase the stress concentration in the grain body and promotes the intercrystalline rupture. The surface cell-type dislocation structure relieves the grain stress transferring the crack origins to the sliding stairs at the grain boundaries. However, the sliding stairs start being resolved towards horizontal direction before they have time to be formed. This process is slowed down due to the sliding stairs enrichment by alloying element atoms that migrate from the grain body to its boundary. It has been proved by the investigation of the steels with different nickel contents. At 2...5 % Ni contents in steel the segregation processes are hindered. In the same time with the 10...18 % Ni contents the surface film enrichment by nickel takes place. At the sliding stairs and surface film the little difference of nickel concentration slows down the film solution. The tensile stresses in the film facilitate the active local selective its solution. The compression in it on the contrary slows down the selective corrosion processes.

The theory of grain boundary depletion of alloying elements and the segregation theory explain the intercrystalline corrosion (ICC) process in the most complete form. These theories are connected with the processes of alloying elements redistribution between grain body and grain boundary and with the surface segregation processes.

The liquid metal corrosion also depends on either the selective solution of alloying elements or chemical interaction at the liquid-solid interface or ICC processes. In a result the change of structure, phase composition and properties is observed exactly at the surface layers of structural materials. At the same time the interaction mechanism at the liquid-solid interface depends on temperature, the duration of isothermal exposure, type of corrosive medium and on the surface state. The elements redistribution at the interface or inside phase volume occur due to the adsorption, diffusion processes and chemical interaction processes.

Let's consider the interaction mechanism on the example of EI-450 alloy (0.13% C, 11.1% Cr, 0.5% V, 0.5% Mn, 0.2 % W, 1% Nb, 1.6% Mo, 0.3% Si) exposed to liquid lead and bismuth at the temperatures up to 500°C and above 700°C. The schematic model of this mechanism is presented in Fig.2, where  $j_A^p, j_B^p$  - the solution flows of A, B alloy components dissolved in liquid;  $j_A^s, j_B^s$  - limit solubility of alloy components;  $\gamma(A, B)^s$  - the solid solution forming of variable concentration due to the  $j_A^p, j_B^p$  flows.

Assume that the solution rate of B component is higher of the one of A component. Then, with B component depleting at the surface layers the phase transition  $\gamma-\alpha$  becomes possible. The  $\alpha$ -solid solution layer is found out more resistant in liquid and at the next step the solution process depends on the B component diffusion through this layer (this flow is denoted by  $j_B^s$ ). It has a certain rate of interface move ensuring the layer forming with thickness of  $\delta_{in}$  at the appropriate thickness of dissolved layer ( $\delta_p$ ). The diffusive flows in solid are consistent with the contrary vacation flows. There are two versions of interaction (the position of I and II in Fig.2) dependent on the relation of  $j_A^s, j_B^s$  and  $j_B^p$  flows.

In the former case, the occupation of vacant places formed because of the intensive  $\gamma_B^p$  flow at  $\delta_{in}$  layer occurs due to the supplying of A, B components atoms from solid (flow  $j_A^s, j_B^s$ ). If this flow has been compensated the  $\alpha(A, B)^s$  layer forming occurs breaking the structure integrity. In such case the corrosion damages are shown as some size reduction ( $\delta_{in}$  layer) of material and as some change of composition, structure and properties of these surface areas.

When the contrary flows have not been compensated the  $\delta_{in}^1$  layer with friable porous structure is formed. The porous distribution through the profile is not uniform: next to the surface their concentration is increased. Because of this the components distribution is not uniform at the damaged layer. In this case the processes of mass transport of the main alloying and doping (C, N) elements are observed. Thus, such mechanism takes place at the temperatures up to 500°C when the solution flow of alloy components has no time to be compensated by diffusive processes in solid. It results in the forming of vacancies unbalanced concentration and promotes the Frenkel effect development. Taking into account the test temperature and results of micro X-ray spectrum analysis it has been concluded that the surface layers structure is changed due to solution mostly of chromium. It takes place owing to iron and carbon solubility is a half order of magnitude lowers that chromium solubility at the indicated

temperatures in liquid lead and bismuth. Besides that, the carbon concentration is small in alloyed ferrite. Hence the chromium solution process does not depend on the solid-phase diffusion. At the same time the thickness increase of friable areas and the samples mass losses have a linear dependence.

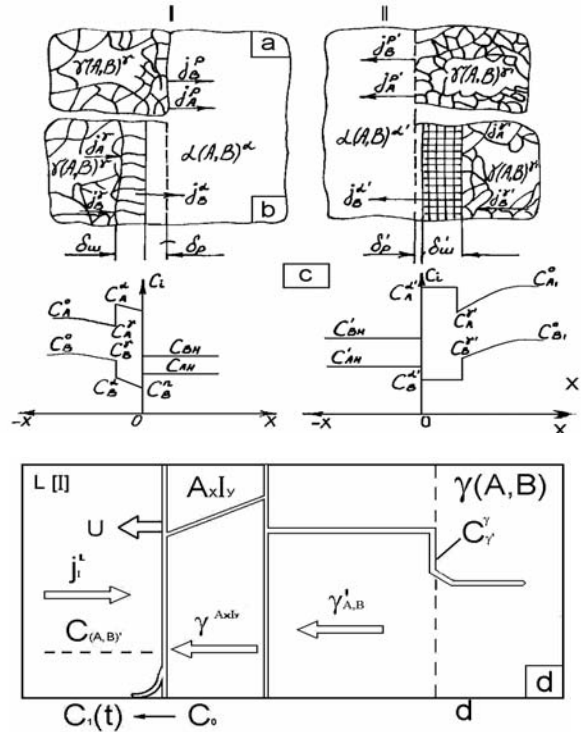


Fig. 2. The scheme of binary alloy corrosion (a) in liquid (b) with distribution of the component concentrations (c) and flows at the phase (d): I – without the creation friable zones, II - with the creation of friable zones

The temperature increasing of isothermal exposure up to 700...800°C results in the intensification of exfoliation processes of solid solution owing to the diffusive processes speeding up. The disposition of change of microhardness and local thermal electrical driving force through the samples depth, parabolic dependence of samples mass change and interaction zone sizes indicate that the interaction process depends on the diffusive factor. The change of chromium and carbon concentration in solid solution due to the partial solution of carbon phase in it and the regular flow of these elements (Cr, C) into liquid prove it. These processes result in the unstable surface thermodynamic state and change of chromium equilibrium concentration in ferrite and promote the chromium redistribution between solid solution and carbide phase. Thus, with chromium content reduced to 6,5 wt. % in ferrite the tetragonal carbide (Fe, C)<sub>7</sub>C<sub>3</sub> is formed where the composition change occurs depending on the atoms correlation between iron and chromium. In this case, the chromium concentration changes at the range of 6.5... 1 wt. % in solid solution it is waited the more probability for Fe<sub>2</sub>Cr<sub>5</sub>C<sub>3</sub> carbide forming. With the chromium concentration reduced to 1...0.75 wt. % in solid solution the FeCr<sub>3</sub>C<sub>3</sub> carbide is formed.

The changes of composition and structure state of structural material shown in the forming of the chromium deficient  $\alpha$ -solid solution and nonstoichiometric carbides at the surface depend on outside flow of chromium and partly carbon into liquid. At the same time the structural indications of intercrystalline corrosion appear.

The similar phenomena at the interaction investigation of the vanadium alloys of V-Cr-Ti system in liquid  $\text{Li}_{17}\text{Pb}_{83}$  under the isothermal conditions at the temperature range of 350...700°C are observed by authors. In alloys with chromium content of more than 17.15% and titanium content of 12.5% the titanium migration towards surface is observed simultaneously with chromium depletion at the undersurface layers due to its solution in liquid. At the interaction of titanium and liquid contained oxygen, the titanium oxide layer is formed becoming a peculiar barrier and slowing down the selective chromium solution.

### 3. Conclusions

The artificial creating of areas with the peculiar substructure and stress state at the surface layers [3] or obtaining it due to the contact interaction is an attempt of "a priori" increasing the duration of thermodynamic state existence to ensure the surface self-organization conditions. The outside factors make active the adsorption and diffusion processes at the interface or into these phase. So the initiation of the diffusive flow direction results in the making control of transferred elements. In this way the conditions of necessary phase forming in undersurface layers is created. The controlling and supporting of kinetics of these processes make the possible of maintaining the metastable structural phase and corresponding energy state at the surface to insure the predetermined operating properties.

One possible way is to prepare "a priori" the structure material surface to ensure the high rate supply of necessary alloying and doping elements not only to compensate these elements because of the solution flows  $j_A^p$ ,  $\gamma_B^p$  and also for reactive diffusion as well. It results in the forming of the thermodynamic stable phases with corrosion solution resistance (Fig. 2 d) [19]. In such way the conditions for free passing of the self-organization processes are made. In this case, instead of the dissipative structures, the peculiar barrier layers are formed at the surface under the pretext of high alloying solid solution which is strengthened by disperse impurities of carbide, nitride, carbonitride or intermetallic phases. The latter phase has the function of slowing down the mass transfer processes through the interface. Proceeding from the research well-founded methods of surface engineering, the authors consider that it is possible to control the surface property purposefully with the regulation the change process of arising and existence of the self-organization phenomenon.

So it has been shown that the nature of the surface self-organization phenomenon has the common features with differences at the kinetics and peculiarities of mechanism during friction and corrosion. It should be emphasize that the diffusive processes act as exactly an "information carrier". The surface receives the peculiar signal depending on the outer factors (temperature, friction loading, medium composition, moistening).

According to this signal the change of surface structural phase and energy state occur. As a result, the level of the operating properties is ensured corresponding to the real condition.

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