

Nonequilibrium Processes of Segregation and Diffusion in Metal-Polymer Tribosystems

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Abstract. The article presents the results of exchange-diffusion processes between chemical elements in metal-polymer tribosystems (between a metal wheel of a rolling stock and a composite polymer brake shoe). The effect of the segregation processes on the strength characteristics of the working surface of a tribosystem is estimated by quantum chemical calculations, Auger and X-ray photoelectron spectroscopies.

INTRODUCTION

The achievements attained in the physics of the solid state, including contemporary concepts of the electronic structure of matter, the theory of dislocations, quantum chemical calculations, structural and energy self-organization in friction processes and a significant development of experimental methods like X-ray diffraction, X-ray spectroscopy, X-ray electron spectroscopy, Auger electron spectroscopy, etc. allow tribomechanical, triboelectric, diffusion and segregation processes in the surface layers of a metal-polymer tribosystem to be investigated more thoroughly and deeply [1].



FIGURE 1. An exterior view of mass transfer plates on a decommissioned wheel



FIGURE 2. An exterior view of a composite brake shoe with the introduction of mass transfer plates

TEST METHODS AND MATERIALS

The paper considers only diffusion-segregation processes on the example of the braking system of freight rolling stock, which includes a friction unit and a wheel-brake shoe. The mechanical and thermal stresses generated in the wheel during braking contribute to the development of cracks in the near-surface layer and the premature destruction of the metal counterbody, the wheel rolling surface (Fig. 1), this being manifested in metal smearing on the friction block surface conjugated to the wheel (Fig. 2). It was revealed in [1] that the temperature stresses arise from the presence of a maximum temperature in the subsurface layer due to a change in the boundary conditions, rather than

on the friction surface. Any area of the wheel rolling surface after being under the shoe is cooled during the motion, and this leads to a negative temperature gradient. In practice, some temperature gradients may cause such stresses in the surface layer of the friction unit that friction occurs during plastic contact even if the bulk temperature of the friction unit is low, and specific pressures can cause only elastic deformations under ordinary conditions. It is known that diverse solid, liquid, and gaseous products of different nature precipitate at friction as a result of thermal and mechanical destruction of polymers in the zone of contact with metal. There is a large amount of hydrogen among the given products. In its turn, hydrogen is actively adsorbed by the contact area of the metal. This process leads to metal destruction and the transfer of solid metal particles from this surface to a softer polymer material. It is established that the following three factors contribute to it: the concentration gradient, the mechanical stress gradient and the temperature gradient. Hydrogen penetration into the metal leads to the decarburization of steel and methane formation, which promote the occurrence of microcracks in the steel bulk and reduces its strength properties.

To study the process of segregation from the wheel and its detached fragments and to conduct an experiment, samples were cut out from the wheel and its detached wear fragments. In addition, the parameters of the crystal lattice and the volumetric composition at different depths of the wheel and wear products were studied. Auger and X-ray photoelectron spectroscopy [2] has revealed the atoms of the following elements at the chips and surfaces of defect areas (Table 1): *Fe* (iron matrix), sulfur and phosphorus impurities, the alloying elements *C*, *Cu*, *Mn*, *Cr*, *Si*, and the elements *K*, *Ca*, *Ba*, *Zn*.

TABLE 1. The concentration of elements in the bulk and in the surface layer of the wheel, at%, obtained by Auger electron spectroscopy (AES)

Investigated area of the wheel	Elements found in various areas of the wheel material														
	Elements belonging to the wheel material								Elements not belonging to the wheel material						
	Fe	Cu	C	Cr	Mn	P	Ni	S	Si	Ba	Sr	Zn	O	Ca	K
Wheel initial material	95.43	0.07	2.7	0.03	0.87	0.08	0.19	0.03	0.6	–	–	–	–	–	–
Surface of the dent	33.94	2.6	30.8	0.07	–	1.4	–	1.53	–	6.9	7.1	1.7	10.5	3.1	0.36
At depth <i>h</i> , 1 mm	51.32	1.8	28.9	–	–	–	–	1.41	–	3.8	1.8	–	9.6	1.08	0.29
At depth <i>h</i> , 6 mm	55.1	1.9	30.2	–	–	0.72	–	0.38	–	2.1	1.6	0.9	6.5	0.6	–

The elements found on the wheel rolling surface have different sources; for example, Ba and Zn atoms are from the brake shoe, and K and Ca are from the environment. Silicon is present both in the environment and in the wheel material. Atoms of potassium and calcium can be contained both in the environment and in various technological materials used in servicing the test bench. In addition, an increase in the carbon content was noted in the wear products. The main result of the research is that the amount of alloying and impurity elements considerably exceeds their initial volumetric concentration on the surface of the wear products of the wheel. It indicates the progress of intensive diffusion processes in the nonequilibrium system of friction pairs, leading to the redistribution of chemical elements in the system.

The morphology of wear products has attracted much attention, as it has a compact plate-like shape with a substantial extent in two spatial dimensions. Infinitesimal wear particles with a size smaller than the grain size have not been detected. It allows concluding that the fracture has an intercrystallite character rather than a transcrystallite one) [2, 3].

The results of the research presented in Table 1 claim the increased concentrations of elements of adsorption or segregation nature on friction surfaces, wear particles and in subsurface layers at different depths. At the homological temperatures of the tests $T \leq 0.5 T_m$, most of the atoms of the elements adsorbed and segregated on the friction and fracture surfaces will get to these surfaces through grain boundaries by grain boundary diffusion (even under nonequilibrium conditions). Taking this into consideration, as well as the instrumentally detected increased content of elements over the depth of the subsurface layer, it can be assumed that small-angle boundaries, dislocation clusters and packing defects may be possible areas for the concentration of these elements. However, a fixed supersaturation of the concentration of the elements suggests that grain boundaries are the most likely the localization of alloying elements.

Segregated atoms at grain boundaries can significantly affect the strength characteristics of materials as a result of replacing the bond between metal atoms by a stronger or weaker “metal – segregated atom” bond. To support the above-mentioned point of view, we made quantum chemical calculations to estimate the energy sufficient to break the bond between the grains. Knowing the binding energies of adsorption and segregation clusters, it is possible to

calculate the energy E_d required for the cluster fracture (disintegration) with the formation of two parts simulating the grains in the model cluster. Its values are defined by the formula

$$E_d = |E_s - E_a - E_g|,$$

where E_s is the binding energy of the segregation cluster; E_g is the binding energy of a cluster containing one pure iron grain; E_a is the binding energy of the adsorption cluster. Similarly, we calculated the binding energy of pure iron cluster, assuming that the 30-atom cluster $Fe_{13}Fe_4Fe_{13}$ disintegrates into separate $Fe_{13}Fe_4$ and Fe_{13} fragments.

TABLE 2. Disintegration energy (in eV) of segregation complexes in the model of a 5-layer plate with a boundary surface (110)

Periods	Groups of elements										
	I	II	III	IV	V	VI	VII	VIII			
1	H										He
	1.0										0.0
2	Li	Be	B	C	N	O	F				Ne
	1.6	2.7	4.0	3.7	2.0	0.7	0.3				0.0
3	Na	Mg	Al	Si	P	S	Cl				Ar
	1.4	1.8	2.3	2.1	0.8	0.0	0.0				0.0
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	
	1.7	2.6	2.8	3.2	3.4	3.3	2.9	2.6	2.4	2.1	
5	Cu	Zn	Ga	Ge	As	Se	Br				Kr
	1.7	1.3	1.6	0.7	0.1	0.0	0.0				0.0
6	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	
	1.4	2.2	2.5	2.7	2.8	2.6	2.3	2.0	1.8	1.3	
7	Ag	Cd	In	Sn	Sb	Te	I				Xe
	1.1	0.8	0.7	0.4	0.1	0.1	0.1				0.0

The energy of interatomic interactions in the grain boundary area containing segregated atoms can be estimated as follows. It follows from the calculated data that the chemical bond properties of impurity and alloying elements with iron in the considered cluster are periodically dependent on the charge of the atomic nucleus of these elements (Table 2), and that the value of the chemical bond is responsible for its hardening or softening.

The results presented in Table 2 actually reflect an important property, which is a compatibility of various elements with iron at the boundaries of its grains. Compared with the Fe–Fe bond, the chemical bond of the elements from the beginning of any of the periods with iron is weak; however, as the element number increases, it first increases, and then it decreases in the second half of the period. When moving top-down along the main and branching subgroups, the bond tends to weaken. The obtained results make it possible to conclude that the properties of the chemical bond of the elements of the five periods with iron depend periodically on the charge of the nucleus of the atoms of these elements, and this completely corresponds to Mendeleev’s law. Figure 3 demonstrates the dependence of the disintegration energy E_d on the atomic number of the X element for various cluster models [4, 5].

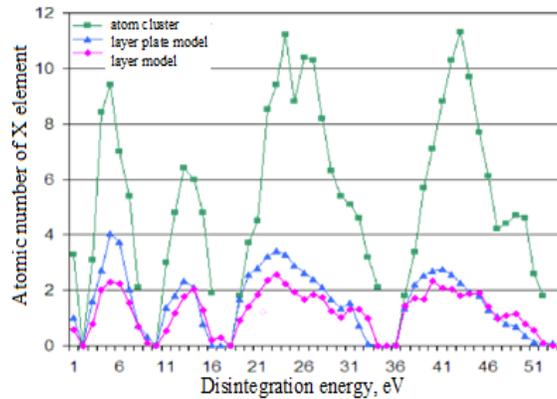


FIGURE 3. The dependence of the disintegration energy E_d on the atomic number of the X element: the upper curve refers to the cluster model and the lower one represents two-period plate models

Moreover, the physical and mechanical characteristics of the samples cut out of the examined wheel material at different distances from the normal to the surface were studied.

SUMMARY

It has been established that the value of ultimate strength on the fracture of the samples containing the surface layer of the rolling of the wheel ($\sigma_u = 920$ MPa) is significantly lower than the value of σ_u for samples remote from the surface of the layer ($\sigma_u \approx 1$ GPa).

Furthermore, it is demonstrated that the removal of a thin millimeter layer containing the rolling surface of the first samples changes the form of the dependencies. Therefore, we have obtained maximum values for the first studied layer, which decrease monotonically from layer to layer. The nature of the Young's modulus over depth is consistent with the change in ultimate strength; when it increases, the value of the Young's modulus decreases, and vice versa [2].

CONCLUSION

As it follows from the calculation results, some segregated atoms (boron, vanadium, chromium) strengthen the intercrystallite bond in iron, while other atoms (magnesium, sulfur, phosphorus, and zinc) soften them, this being due to the energy required for the disintegration of segregation complexes. These results correspond to empirical data about the properties of the elements.

The analysis of the data on the impurity composition of the working surface of a railway wheel, which limits its service life, and the curve of the distribution of the mechanical properties (ultimate strength and the Young's modulus) through the depth of the wheel has shown that the presence of impurity elements in the wheel surface layers deteriorates its mechanical properties.

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