

METALLIC SURFACES AND FILMS

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Structure and Properties of Multicomponent Surface Layers on Steel

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The structure and properties of a multicomponent diffusion layer obtained on steel as a result of joint saturation with boron and other elements (silicon, molybdenum, tungsten) during chemical-thermal treatment (CTT) are investigated in this work. As a result of multicomponent saturation of the steel surface pre-treated by deformation of various intensities (electrolyte plasma, pressing, explosion) a multiphase microstructure of the diffusion layer with higher micromechanical characteristics of the steel surface in comparison with ordinary boron saturation is obtained. As established, the pre-treatment of steel surface at saturation under conditions of a multicomponent CTT accelerates diffusion processes and contributes to the spread of finely dispersed inclusions from refractory boride compounds to a greater depth. This ensures the formation of a multilayer complex coating with unique properties.

Key words: multicomponent saturation, multiphase microstructure, deformation pre-treatment, borides, wear resistance.

У даній роботі досліджено структуру і властивості багатокомпонентного дифузійного шару, одержаного на сталі в результаті спільного насичення Бором та іншими елементами (Силіцій, Молибден, Вольфрам) при хіміко-термічній обробці (ХТО). У результаті багатокомпонентного насичення поверхні сталі, попередньо обробленої деформацією різної інтенсивності (електролітна плазма, пресування, вибух), отримана багатофазна мікро-структура дифузійного шару з більш високими мікромеханічними характеристиками поверхні сталі порівняно зі звичайним насиченням Бором. Встановлено, що попередня обробка поверхні сталі при насиченні в умо-

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вах багатокомпонентного ХТО прискорює дифузійні процеси і сприяє поширенню тонкодисперсних включень з тугоплавких боридів на велику глибину. Це забезпечує формування багатошарового комплексного покриття з унікальними властивостями.

Ключові слова: багатокомпонентне насичення, багатофазна мікроструктура, попередня деформаційна обробка, бориди, зносостійкість.

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1. INTRODUCTION

The structure and properties of the surface layers of machine parts and tools have an important influence on their working capacity, since during exploitation it is the surface layers that are most intensively subjected to temperature-force and aggressive influences. In some cases, chemical-thermal treatment (CTT) is the only possible means of obtaining the required operational properties of not only the surface, but also product as a whole. Such properties can be achieved by creating a surface layer with a multiphase structure obtained as a result of multicomponent saturation. Multicomponent saturation with different elements makes it possible to create multilayer composite materials with unique properties [1–3]. The increased wear and corrosion resistance of the boron-molybdenum layer and the lower brittleness of the boron-tungsten layer are observed in comparison with the boron layer [4–6]. It is of interest to create coatings on the surface of iron-based alloys during CTT in a multicomponent mixture of three or more elements, as the least studied and not found in the literature, for example, boron-molybdenum-tungsten, boron-molybdenum-silicon. Therefore, the purpose of this work is a study of the structure and properties of a multicomponent diffusion layer obtained on steel as a result of joint saturation with boron and other elements (silicon, molybdenum, tungsten) in order to create a multilayer complex coating with increased hardening micromechanical characteristics that provide wear resistance in a wide temperature range [7, 8].

2. EXPERIMENTAL AND THEORETICAL DETAILS

Saturation is carried out in a powder medium with boron carbide B_4C , activators KBF_4 , Na_2CO_3 , alloying additives WO_3 , MoO_2 , Si (0.1), SiO at temperature of 1223 K for $t = 4$ hours. As samples we used steel 40, 45. Some of the samples are pre-treated in electrolyte plasma obtained in an aqueous boron-containing electrolyte solution in the regime: $U = 60–90$ V, $j = 0.98–1.7$ A/cm², $t = 20$ min [9, 10]; with a load under the press of 10 tons (when the weight acts on an area of 0.64–1 cm² cor-

responds to a pressure of 0.156–1 GPa), explosion treatment [11]. The intensity of linear wear is determined by the SMU-2 friction machine. The friction is carried out according to the scheme ‘shaft-partial insert’ at a load of 4 MPa, which corresponds to the middle of the load segment of constant friction, the sliding speed is 1.3 m/s, the duration of friction is 0.5 hours, the length of the path in the sum at friction is 10 km, counter body is hardened steel 45. Metallographic analysis of the obtained samples is performed using a microscope NEOPHOT-21 and microhardness PMT3. The calculation of the critical stress intensity factor of the first deformation mode (K_{1C}) is carried out according to [12]. The identification of the phase components is performed by X-ray diffractometer analysis on the DRON-2 diffractometer in iron radiation. The heat resistance is determined by increasing the mass of the sample relative to the surface unit (specific mass gain) after exposure for 40 hours at 1273 K in an air atmosphere.

3. RESULTS AND DISCUSSION

The microstructure of the diffusion layer, presented on Figs. 1–3, is obtained as a result of multicomponent saturation, including the diffusion of boron and alloying components into the surface of steel pre-treated to deformation of various intensities (electrolyte plasma, pressing, and explosion).

The results of layer-by-layer X-ray diffraction analysis of the surface after saturation with boron, molybdenum, tungsten showed that, along with iron borides FeB, Fe₂B, there are Mo₂B, δ -MoB, W₂B₉, WB₄,

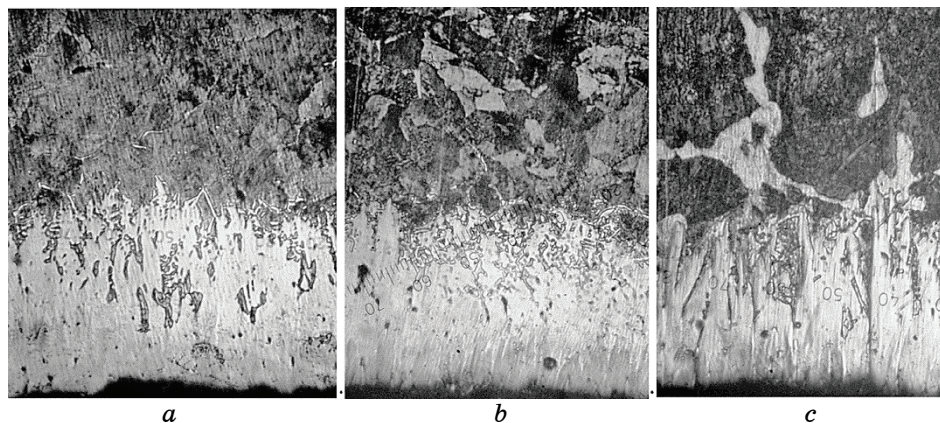


Fig. 1. Microstructure of diffusion layer at multicomponent saturation (boron-molybdenum-tungsten) of steel 40 ($\times 400$): without pre-treatment (a), pre-treated in electrolyte plasma (b), pre-treated under pressure (c).

β -WB, and Fe_3Mo , Fe_2W , Fe_7W_6 , as well as ternary compounds $\text{Fe}_{13}\text{Mo}_2\text{B}_5$, FeW_3C , $\text{Fe}_3\text{W}_3\text{C}$, Mo_2BC . The depth of the obtained layer is 150 ± 20 microns depending on the treatment method.

Iron monoboride makes up about 30% of the total boride layer. The microhardness of the coating in the monoboride zone ranges from 33 to 21 GPa, and in the diboride zone from 17 GPa to 15 GPa. The morphology of the boride layer does not have a pronounced needle shape of borides, as in the usual boronation of this steel grade. The space between the highly branched needles is filled with separate inclusions of borides (Fig. 1). According to [1], molybdenum and tungsten borides do not form when saturated with boron and molybdenum, as well as boron and tungsten.

However, with simultaneous saturation with boron, molybdenum, and tungsten, the X-ray diffraction data suggest that molybdenum, diffusing after boron, forms ternary compounds Fe_2MoB_4 and Mo_2BC in the Fe_2B zone, and Mo_2B , δ - MoB are formed mainly in the FeB zone closer to the surface where the concentration of boron is quite high.

Here, mainly at the surface, tungsten borides are formed: $\text{WO}_3 + \text{B}_4\text{C} + \text{C} \rightarrow \text{W}_2\text{B}_5 + \text{CO}$, $\text{W}_2\text{B}_5 + 2\text{B}_2\text{O}_5 \leftrightarrow 2\text{WO}_2 + 9\text{B}$, $\text{W}_2\text{B}_5 + 3\text{B} \leftrightarrow \text{W}_2\text{B}_4$.

The addition of tungsten to the saturating mixture according to the results of metallographic analysis increases the fragility of the low boron phase Fe_2B and the amount of high boron phase FeB .

The results of layer-by-layer X-ray diffraction analysis of the surface after saturation with boron, molybdenum, and silicon showed that, along with iron borides FeB and Fe_2B , there are phases, which are located as follows: the outer zone up to 200 μm deep contains iron bo-

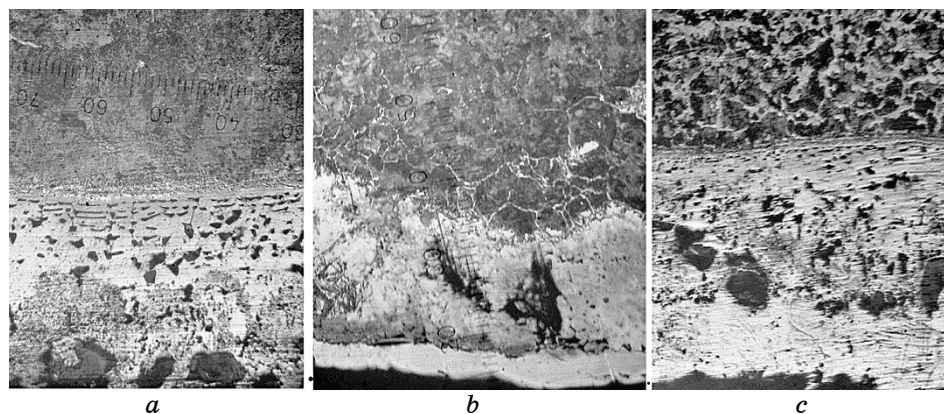


Fig. 2. Microstructure of diffusion layer at multicomponent saturation (boron-molybdenum-silicon) of steel 40 ($\times 50$): without pre-treatment (a), pre-treated in electrolyte plasma (b), pre-treated by explosion [11] (c).

rides doped with silicon and molybdenum (FeB , Fe_2B , Mo_2FeB_4 , Fe_4B_2 , FeMo_2B_2 , Fe_3SiB_2 , $\text{B}(\text{Fe}, \text{Si})_3$), Mo_2B_5 , then goes the zone to a depth of 300–350 microns, consisting of solid inclusions (hardness 8–13 GPa) in the field with lower hardness (4–6 GPa) (FeMo_2B_2 , Fe_7Mo_3 , Fe_2B , Mo_2B_5 , $\text{Mo}_5(\text{B}, \text{Si})_3$, Fe_5Si_3 , Fe_3Si , $\text{Fe}_2\text{Si}_{0.4}\text{B}_{0.6}$, Mo_5Si_3). At the boundary with the base (Fig. 2) there is a zone with a thickness of 10–20 μm with a hardness of 6.6 GPa, to which a light band with a thickness of 20–30 μm with a microhardness of 3–4 GPa is adjacent. In the formed diffusion layer there is also a redistribution of Mo and Si according to the principle of least action. At this stage of saturation, microinclusions are formed from iron compounds with diffusing components (double and triple phases), which are located mainly along the boundaries of the boride phase — iron monoboride and on the interphase boundaries. The alternation of solid and less solid zone contributes to the improvement of the micromechanical characteristics (Table 1), namely the reduction of micro-fragility, increase of the wear resistance and heat resistance of the coating. Moreover, the heat resistance of the coating is increased by 10% compared to [3] (3 g/m² against 2.7 g/m²).

According to the results of metallographic analysis (Table 1), the pre-treatment of various intensities deformation on the steel samples affects the depth and micromechanical characteristics of the diffusion layer obtained after CTT in a multicomponent environment. The formed diffusion layer with a depth ranging from 300 to 450 μm and sublayer with a structure characteristic of the concentration peritectic heterogeneity of Fe–C–Si–B with the possible presence of Mo (Fig. 2) does not have clear boundaries. The layer contains inclusions whose microhardness is 15–16 GPa, and, in addition, a zone with a depth of

TABLE 1. The values of depth of diffusion layer h , microhardness H_μ , resistance to brittle fracture K_{1C} , intensity of linear wear I_n depending on the type of steel 40 pre-treatment.

No.	Type of pre-treatment	$h, \pm 20 \mu\text{m}$		H_μ, GPa		$K_{1C}, \text{MPa}\cdot\text{m}^{1/2}$		$I_n \cdot 10^{-9} \pm 0.01$
		Diffusion layer	Sub-layers	Diffusion layer	Sub-layers	Diffusion layer	Sub-layers	
1	Electrolyte plasma	70–140	250–350	11–14 (18–20)	4–8 (3–4)	6.0–6.1	6.5–6.6	0.28
2	Load under pressure	130–200	600–720	13–15 (20–22)	6–10 (3–4)	6.1–6.2	6.4–6.6	0.22
3	—	120–180	300–400	13–16 (20–23)	6–10 (3–4)	6.0–6.1	6.4–6.6	0.26
4	Explosion deformation	150–210	750–850	14–17 (20–21)	6–12 (3–4)	6.2–6.3	6.4–6.7	0.18

10–20 μm and a hardness of 6.6 GPa is formed on the border with the base (Fig. 2, c). It should be noted that a similar structure is characteristic of all the presented methods for saturation of boron, molybdenum, silicon.

Pre-treatment of steel in an electrolyte plasma allowed to increase the depth of the diffusion layer, compared with untreated one, by 1.5 to 3 times. In addition, steel pre-treatment in electrolyte plasma, according to layer-by-layer X-ray diffraction analysis, promotes the diffusion of alloying elements over long distances with the formation of a greater number of finely dispersed refractory compounds, such as Mo_2B , $\delta\text{-MoB}$, W_2B_9 , WB_4 , $\beta\text{-WB}$, Fe_2MoB_4 , Mo_2BC . Due to this, the microhardness of the coating in the monoboride zone ranges from 33 to 21 GPa, which provides higher micromechanical characteristics of the steel surface.

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Pre-treatment by pressure promotes the formation of a diffusion

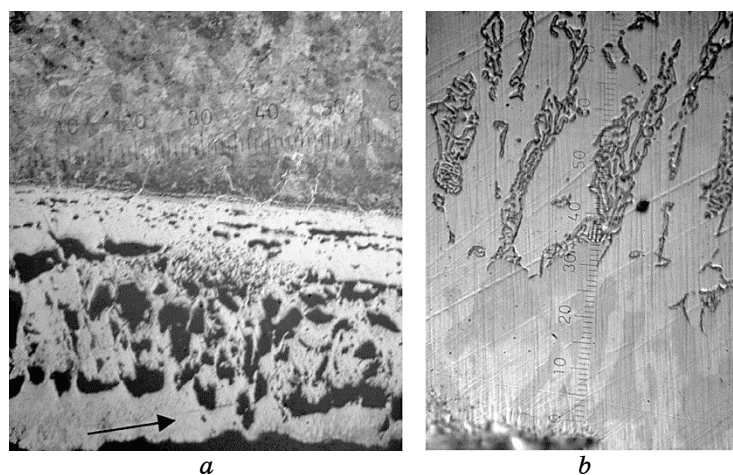


Fig. 3. Microstructure of diffusion layer at multicomponent saturation (boron–molybdenum–silicon) of steel 40: pre-treated by pressure with fragments at point 1 at magnification (a), $\times 1000$ (b).

layer structure in many ways similar to that formed after pre-treatment by explosion. For example, the presence of eutectoid (Fig. 3, *b*) is characteristic of both surface treatments. It should be noted the eutectoid is formed on the highly branched boride phases of FeB. The interruption of the continuity for the boride phase FeB and eutectoid formation to a greater degree is more inherent in samples with pre-treatment by pressure (Fig. 3, *b*).

Explosion pre-treatment promotes to the formation of the diffusion layer with a maximum depth of 900–980 μm and microhardness of 13–14 GPa. After pre-treatment by pressing, the diffusion layer is thinner on 100–150 μm and includes more soft structures (4 GPa). This difference shows that the intensity of deformations during surface pre-treatment affects the diffusion rate and facilitates the movement of alloying elements over long distances with the formation of finely dispersed boride inclusions.

Compared with borosilication [2, 10], the boromolybdosilicated coating has a 20–22% greater thickness of the diffusion layer, high hardness and resistance to fragile destruction, less intensity of linear wear, increased heat resistance by 10% due to the doping of the boride layer with silicon and molybdenum and the formation of a sublayer having a multiphase composite structure from microcrystalline inclusions of compounds with Si and Mo, boron and iron.

4. CONCLUSION

Thus, the uses of the present mixture for multicomponent diffusion saturation allows obtaining the complex coating of modified boride layer and sublayer on the steel surface, which provides high hardness, resistance to fragile destruction, and wear resistance over a wide range of temperatures. Steel surface pre-treatment plays a significant role at saturation in the conditions of multicomponent CTT: it accelerates diffusion processes and promotes the distribution of finely dispersed inclusions from refractory compounds to a greater depth. This provides higher micromechanical characteristics of the steel surface compared to conventional boron saturation.

The processes of multicomponent saturation make it possible to form a multiphase structure of the surface layer with a set of useful properties. Moreover, such a combination of hardened product properties, which cannot be obtained by other methods, can be obtained by chemical-thermal treatment. In this case, CTT can be considered not as a specific operation of manufacturing a parts, but as a method of obtaining a fundamentally new structural material. Multicomponent saturation with different elements makes it possible to create multi-layer composite materials with unique properties.

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