Investigation of the microstructure of diffusion coatings of carbon steel obtained by simultaneous diffusion saturation with boron, chromium and titanium

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Abstract. The mechanism of boron diffusion under conditions of simultaneous saturation of steels with boron, chromium and titanium are poorly represented in the literature. It is noted that exactly three-component saturation with boron, chromium and titanium allows to obtain diffusion coatings with unique properties. The microhardness of such coatings can achieve 5000 HV, which corresponds to the microhardness of boron carbide B\(_4\)C. In addition, such coatings, depending on the saturation parameters and the saturable material, can also show high durability values. The microstructure of the diffusion coatings on carbon steels Grade C and steel 1045 has been studied. It has been shown that during the simultaneous diffusion of boron, chromium and titanium under the boride layer additional perlite volumes are formed. The perlite that existed in the steel before the diffusion processes, as a result of diffusion, is fragmented.

1. Introduction

Parameters of boron diffusion under conditions of simultaneous saturation of steels with boron, chromium and titanium were investigated in [1]. However, the parameters of diffusion of boron, chromium and titanium under conditions of simultaneous three-component diffusion are poorly represented. As noted in [1, 2], that exactly three-component saturation with boron, chromium and titanium allows to obtain diffusion coatings with unique properties: the microhardness of such coatings can reach 5000 HV, which corresponds to the microhardness of boron carbide B\(_4\)C. In addition, such coatings, depending on the saturation parameters and the saturable material, can also show high wear and corrosion resistance. At the same time, a sufficiently detailed description of the mechanisms of simultaneous diffusion of boron, chromium and titanium atoms is not given. The parameters of the saturation process and their influence on the structure of the diffusion coating and its final mechanical and operational properties are not considered.

2. Materials, methods and results

In the present work, the saturation process was carried out in accordance with recommendations [3-7] from powder saturating mixtures based on boron carbide [8, 9]. The microstructure was examined...
using the ThixometPro software and hardware complex, and also TESCAN MIRA 3 electron microscope.

Figure 1 shows the microstructure of the upper part of the transition zone located beneath the boride layer with simultaneous diffusion saturation of Grade C steel. It is noteworthy that in this region there is practically no ferrite, although in the initial steel the share of ferrite achieves 80% (Figure 2). In this case, the overwhelming number of cementite slabs is broken into fragments having average dimensions about 20-45x180-680 nm in the plane of the section. Moreover, there is considerable texture of the cementite plates in the boron diffusion direction: from the boride coating in the direction to the core of the sample. Such a texture is formed as a result of the joint diffusion of boron, chromium, titanium into the interior of the material: all components of structures that interfere with diffusion fluxes dissolve, whereas components of structures parallel to the concentration gradient have great chances to avoid dissolution or grow from the embryo to acceptable sizes.

The image was obtained using Thixo® software and hardware complex, which include Thixo® software and Carl Zeiss Axio Observer Z1m optical microscope. In addition, to identify this structure used special research methods [10–14] – the method of "circular polarization" (C-DIC) and also special etching.

Special etching is used to contrastly reveal the structure of the transition zone located under the boride layer, since etching separately with an alcoholic solution of iodine, sodium picrate or an alcoholic solution of hydrofluoric acid do not allow to get clear images.

Figure 3 shows a photograph of the microstructure of the boundary of the subordinate zone with the directly boride layer.

As can be seen from the image, the perlite newly formed during the boriding is structured in the direction of the concentration gradient. Figure 3 shows an image of borated perlite with fragmented cementite plates. Blocks of perlite, cementite plates in which are located along the normal to the direction of the gradient of boron concentrations, all underwent fragmentation, whereas the plates of the newly formed perlite were lined along the concentration gradient lines and did not undergo significant fragmentation.

The structure shown in Figure 3 is a grain of perlite, which existed from the beginning, before the borating process and which was completely fragmented as a result of the diffusion of boron. The individual blocks that make up the grain shown in Figure 1 are quite clearly seen – the orientation of the cementite in these blocks is somewhat out of sync. In addition, cementite plates in blocks oriented at a smaller angle to the boron diffusion direction are fragmented to a lesser extent than plates in blocks perpendicular to the concentration gradient. This observation confirms that diffusion of boron proceeds along a mixed (reactionary and diffusional along the phase boundaries) mechanism, because boron atoms have extremely low solubility both in $\alpha$- and $\gamma$-phases and this solubility limited by a level of thousandths of a percent. Thus, the only way to realize any significant values of diffusion, as well as the formation of a boride coating, is the reaction diffusion mechanism.

The image of the microstructure of the damaged perlite on steel 45 during the simultaneous diffusion of boron, chromium and titanium is shown in Figure 4.

The distribution of microhardness along the cross section of the diffusion layer is shown in Figure 5.

The distribution of microhardness along the cross section of the diffusion layer shows that the three-component saturation increases by approximately 1.3-1.5 times the microhardness of the coating. The microhardness of the boride layer increases because of the formation of borides of chromium and titanium having higher hardness values than iron borides. Due to the diffusion of chromium and titanium, chrome and titanium carbides are formed under the boride layer (spherical particles on carbide plates in the pearlite phase, Figure 4). The enrichment of the transition zone with chromium and titanium carbides increases the microhardness of the transition zone.

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![Figure 1](image1.png)

**Figure 1.** Panoramic image of the diffusion layer on GradeC steel obtained by simultaneous saturation with boron, chromium and titanium. Optical microscopy.

![Figure 2](image2.png)

**Figure 2.** The structure of the boronizing layer on carbon steels. Optical microscopy.
Figure 3. Microstructure of perlite with fragmented cementite plates. Optical microscopy.

Figure 4. Microstructure of damaged perlite during diffusion saturation of steel with 45 boron, chromium and titanium. Electron microscopy.
3. Conclusions

Diffusion of boron proceeds along a mixed (reactionary and diffusional along the phase boundaries) mechanism, because boron atoms have extremely low solubility, limited by a level of thousandths of percent. The diffusion of chromium and titanium is possible both in the phase boundaries and in the defects of the crystal structure. The reaction mechanism is only way to form a boride coating. Iron borides are additionally doped with chromium and titanium. Thus, as a result of the diffusion saturation of steels with boron, chromium and titanium, the hardness of the diffusion coating and its thickness are increased in comparison with one-component boronizing.

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