Features of the formation of a diffusion layer and the mechanism of diffusion during boronizing of steels

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Abstract. The paper presents the results of studies on the formation of a diffusion layer during the boriding of steel with a carbon content of 0.38 wt\%. The study of diffusion coatings by SEM and TEM methods allows one to more clearly determine the mechanisms of diffusion of boron atoms and the formation of diffusion boride coatings. Diffusion of boron in the processes of diffusion boriding of iron-carbon alloys proceeds by a mixed mechanism: the delivery of active boron atoms to the diffusion front proceeds along the grain and phase boundaries. The reaction mechanism is realized by a gradual substitution of carbon with boron in iron carbides. Due to the continuous diffusion of boron, the reaction boundary is constantly moving in the direction from the surface to the core of the saturated material. In this case, as the diffusion proceeds, the concentration of carbon atoms under the boride layer constantly increases. This provides resistance to diffusion of boron atoms by the atomic mechanism and provokes diffusion by the reaction mechanism.

1. Introduction

The most common cause of failure of machine parts and tools is the wear of their working surface. It prevails in more than 75\% of cases. The problem of increasing the wear resistance of the tool is now becoming increasingly relevant. In this regard, various methods of surface hardening, including diffusion, are widely demanded. This trend is due to the problem of saving alloying metals (manganese, chromium, cobalt, tungsten, vanadium, molybdenum, niobium, etc.) and the transition to the consumption of economically alloyed steels. The use of diffusion hardening and protective coatings can significantly reduce the cost of production and improve the performance of the created products. In some cases, chemical and thermal treatment is the only possible means of obtaining the required performance properties not only of the surface, but also of the product as a whole.

Boriding occupies a special place among the processes of chemical and thermal treatment. Increased interest in the process of boriding is caused by the possibility of obtaining mono- or multiphase boride layers in the surface area of the processed products, characterized by a unique complex of physicochemical properties and its acceptability for processing a wide range of structural and tool steels and alloys. Boron-based coatings are the leaders in improving properties such as wear resistance, heat resistance and hardness. However, the processes of diffusion of boron and related elements in the diffusion hardening of the surface of steels have not been sufficiently studied. At the same time, while
the zone of continuous borides is still being studied, as a rule, insufficient attention is paid to the transition zone. Although some studies show that the structure and physical and mechanical properties of the transition zone have a significant impact on the performance of the entire coating.

An important place is occupied by the question of the mechanism of boron diffusion in the boriding of steels and alloys and the formation of diffusion coatings. It has not been fully resolved and is still debatable [1-14]. Some authors adhere to the reaction mechanism of formation of boride coatings directly as a result of the chemical reaction between iron and boron. Other authors claim that first a solid solution of boron in iron is formed, and after reaching the limit concentrations by a chemical reaction between iron and boron borides are formed. There is no clear understanding of both diffusion mechanisms and methods of process control in order to obtain coatings of a given composition and with the required properties, and this leads to the appearance of technological recommendations that differ 2 to 50 times in labor and energy costs for diffusion boriding. Therefore, the study of the process of formation of the diffusion layer and the mechanism of boron diffusion in the boriding of steels is an important task.

2. Methods

In this paper, we study the process of formation of boride coatings on carbon steel with a carbon content of 0.38 wt. %. Saturation was carried out in an airtight container of a powder mixture based on boron carbide [15] at a temperature of 920°C for 2.5 hours [16-18]. The microstructure of the boride layer and the transition zone was studied on transverse microspheres using optical and scanning electron microscopy. To study the methods of transmission electron microscopy, tempelts 0.2 mm thick were cut using an electroerosive machine. The cutting mode was chosen in such a way that it did not introduce additional deformation and, therefore, did not affect the structure of the sample. Foils were polished electrolytically. The composition of the electrolyte was as follows: saturated solution of phosphoric acid, chrome anhydride. The temperature of the electrolyte during the preparation of foils was 30-50°C. The phase composition was characterized by diffraction patterns obtained by the methods of x-ray diffraction analysis and diffraction electron microscopy.

3. Results and discussion

The studies show that boron diffuses along the grain and phase boundaries [1–3]. At the same time, due to the limited solubility of boron in iron, saturated solid solutions of boron in iron are formed relatively quickly. Along with this, boron alloys the iron carbides by substitution reactions, replacing part of the carbon in cementite. Carbon displaced from cementite together with boron creates additional volumes of boronizing cementite Fe₃(C, B) at some distance from the reaction front of iron boride formation. This can explain the significant volumes of perlite in the transition zone. Often the content of perlite in the transition zone reaches 100% when bordering steels with a carbon content of more than 0.4 wt % (figure 1). The structure of the transition zone is presented in more detail in figure 2.

As can be seen from figures 1 and 2, the content of perlite in the transition zone reaches 95-98% by volume. At the same time, the thickness of the transition zone and, accordingly, the volume occupied by it, significantly exceed the thickness and volume of the boride zone (4-6 times). Even taking into account the fact that from the zone of the boride layer carbon is displaced almost completely, the formation of such a large amount of cementite with the participation of only the amount of carbon displaced by boron is impossible.

The data of energy dispersion analysis, as well as diffraction patterns and electron diffraction patterns obtained by SEM methods confirm the doping of cementite transition zone. The content of boron in cementite ranges to 0.8 (Fe₃(C₀.2, B₀.8)) in the upper part of the transition zone. The minimum concentration of boron in boronizing cementite corresponds to the gross formula Fe₃(C₀.8, B₀.2) and this compound is predominantly in the lower part of the transition zone, at a depth of about 800 µm from the surface. Figure 2 shows that the cementite formed as a result of diffusion boriding has a thinner structure compared to the cementite that existed initially and underwent boriding.
The corresponding microstructures obtained by SEM methods are shown in figures 3 and 4. The microstructure of boronizing cementite, shown in Figure 4, is represented by fragments of plates destroyed by boron diffusion. At the same time, on the side faces of the plate fragments, the nuclei of boride phases of different composition having a globular shape and a size of about 20-50 nm are noticeable.

Boron diffusion predominantly occurs along the grain and phase boundaries, as well as along substructural units (subgrains), and at some distance from the reaction front, the formation of particles of carboborides \( \text{Fe}_{23}(\text{C}, \text{B})_6 \) and \( \text{Fe}_6(\text{C}, \text{B}) \) occurs. As the boron content in carboborides increases, their chemical composition approaches the boron cementite \( \text{Fe}_3\text{B} \). This compound is unstable at diffusion boriding temperatures and decomposes according to the reaction \( \text{Fe}_3\text{B} = \text{Fe} + \text{Fe}_2\text{B} \). As boron further diffuses along the interface between the boride needle and the iron matrix, the phase composition is balanced and passes into the \( \text{Fe}_2\text{B} \) compound. This argument is supported by darker areas on cementite plates in figure 4.

It should be noted that, along with the carboboride mechanism of the formation of iron hemiboride, its formation also occurs as a result of a direct reaction between iron and boron at the border of the boride needle, and the direct reaction of the formation of iron hemiboride \( \text{Fe}_2\text{B} \) at the initial stage is predominant. As the process of boron diffusion develops deeper into the iron matrix and carbon is displaced by boron, the concentration of carbon atoms increases at the border of the boride layer. As the concentration of carbon atoms approaches approximately 0.8 wt. %, the reactions of direct formation of borides by direct interaction of boron and iron and the reaction of obtaining borides through the decomposition of borated cementite \( \text{Fe}_3\text{B} \) have approximately equal proportions. This assumption is indirectly confirmed by the fact that at the initial stages of the boriding process, no destroyed cementite plates are observed in the transition zone. Whereas the formation of the pearlite structure under the boride layer is observed practically from the very beginning of diffusion boriding.
Figure 3. Microstructure of diffusion boride layer and transition zone obtained by SEM methods, general microstructure, BSE.

Figure 4. Microstructure of transition zone obtained by SEM methods, microstructure of boronizing cementite plates, BSE.

Directly in the transition zone itself, under the influence of diffusing boron, a partial dissolution of cementite occurs, as a result of which it takes the form of fragmented plates. Fragmentation and destruction of cementite plates in borated pearlite probably occurs as a result of boron diffusion, which is accompanied by phase transformations with a change in volume. When analyzing the microstructures shown, it is obvious that boron atoms prefer to diffuse over areas depleted by carbon (subsequently, it is ferrite after cooling). At the same time, the grain boundaries and ferrite grains are enriched with boron, while the destruction of cementite plates in perlite has not yet occurred.

4. Conclusion

The following conclusions can be made from the results of the present study.

1. Boron diffusion in the processes of diffusion boriding of iron-carbon alloys proceeds by a mixed mechanism: the delivery of active boron atoms to the diffusion front proceeds along the grain and phase boundaries. The reaction mechanism is realized by the gradual substitution of carbon with boron in iron carbides.

2. A significant contribution is made by the mechanism of the reaction of the formation of iron borides, which is implemented according to a two-stage scheme as follows: \[ \text{Fe}_2\text{C} + \text{B} + \text{Fe} \rightarrow \text{Fe}_3\text{(C,B)}, \]

and the boron content in borating cementite ranges from 20 to 80 at. %. When adding new amounts of boron atoms, the boron content in cementite reaches 100 at. %. When replacing carbon with boron, forms additonal amounts of iron carboborides \[ \text{Fe}_2\text{(C,B)} \text{ and } \text{Fe}_{23}\text{(C,B)}6. \]

3. Iron atoms, reacting at the border of the nuclei of boride phases directly with boron diffusing along the borders of these nuclei, form additional volumes of iron hemiboride \[ \text{Fe}_2\text{B}, \]

and subsequently monoboride \[ \text{FeB}. \]

4. Due to the continuous diffusion of boron, the reaction boundary is constantly moving in the direction from the surface to the core of the saturated material. In this case, as evolution the diffusion processes in time, the concentration of diffusing atoms of carbon in the boundary layer are constantly increasing, providing resistance to the processes of physical diffusion of active atoms of boron.
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