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# **METALLIC SURFACES AND FILMS**

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# Features of Diffusion Processes Occurring at Saturation with Atomic Elements and Formation of Surface Layer with Composite Structure

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One of the most effective ways to reduce the brittleness of boride layers is the formation of layers with a composite structure. To create a composite structure of the diffusion layer, it is proposed to form, in addition to borides, several additional phases that are located in the layer arbitrarily or in an orderly manner. For this purpose, the samples made of 38Cr2MoAl steel are strengthened by a complex chemical-thermal treatment, namely, boriding is carried out after cementation or nitrocementation. The analysis of microstructures shows that after various modes of surface hardening of steel, it can be argued that complex chemical-thermal treatment leads to the formation of a composite structure of steel with the grinding of borides in the layer, the dispersion of which increases with an increase in the temperature of diffusion saturation. The paper shows that the main mechanisms of boron diffusion are such mechanisms as reaction (the movement of atoms is carried out by moving the chemical reaction front); diffusion along dislocations, block boundaries, subgrains and grains, etc. reaction diffusion occurs by diffusing boron everywhere the boride layer to the main reaction front, which is located at the boundary of two phases: iron-boride  $Fe_2B$  and boride  $Fe_2B$ boride FeB. First, the embryos are formed, and then-the needles of boride Fe<sub>2</sub>B. These needles grow until they close and form a continuous layer of Fe<sub>2</sub>B borides. Individual needles are then formed on the surface of this boride layer, which also form a second continuous layer of FeB boride. The needle-like structure of the boride layer indicates rapid growth of boride zones in the di-

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rection perpendicular to the surface of the samples, while along the surface the development of these phases was insignificant. This formation is due to the peculiarities of the structure of these phases, due to which boron atoms move rapidly only in a certain direction. As found, the boride layer displaces the carbon that is in the layer hardened by cementation (nitrocementation) deep into the steel. Due to the preliminary hardening treatment by cementation (nitrocementation), boride needles with rounded edges are formed and then crushed to the depth of the diffusion layer, which is due to the presence of a large number of carbides (nitrides, carbonitrides) in the surface layer, which do not allow boride needles to grow in the direction perpendicular to the surface of the samples due to their high density. Grinding and rounding of boride needles has a positive effect on the further operation of the product, thereby making it possible to eliminate stress concentrators and local zones that can cause cracks in the presence of sharp needles and reduces surface brittleness due to the formation of a crushed composite structure.

Key words: composite structure, diffusion layers, complex treatment, boriding, cementation, nitrocementation.

Одним з ефективних способів зниження крихкості боридних шарів є формування шарів з композиційною структурою. Для утворення композиційної структури дифузійного шару пропонується сформувати крім боридів, декілька додаткових фаз, які розташовані у шарі довільно або впорядковано. Для цього зразки зі сталі З8Х2МЮА зміцнювали комплексною хеміко-термічною обробкою, а саме, здійснювали борування після цементації або нітроцементації. Аналіз мікроструктур показав, що після різних режимів поверхневого зміцнення сталі, можна стверджувати, що комплексна хеміко-термічна обробка приводить до формування композиційної структури сталі з подрібненням боридів у прошарку, дисперсність яких збільшується з підвищенням температури дифузійного насичення. Встановлено, що шар боридів витісняє вглиб сталі вуглець, який знаходився у прошарку, зміцненому методом цементації (нітроцементації). За рахунок попередньої зміцнювальної обробки методом цементації (нітроцементації) відбувається формування боридних голок із заокругленими краями та подальшим їх подрібненням вглиб дифузійного шару, що пов'язано з наявністю великої кількості карбідів (нітридів, карбонітридів) у поверхневому шарі, які не дають можливості зростати голкам боридів у напрямку, перпендикулярному до поверхні зразків за рахунок їхньої великої щільності. Подрібнення та заокруглення боридних голок має позитивний вплив на подальшу експлуатацію виробу саме тим, що дає можливість усунути концентратори напружень та локальні зони, які можуть бути причиною появи тріщини за наявності гострих голок, та знижує поверхневу крихкість завдяки формуванню подрібненої композиційної структури.

Ключові слова: композиційна структура, дифузійні шари, комплексна обробка, борування, цементація, нітроцементація.

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### **1. INTRODUCTION**

Chemical-thermal treatment combines thermal and chemical simultaneous effects on the surface layer of the part in order to obtain the necessary composition, structure and properties [1-3]. During processing, the metal surface is saturated with the corresponding element (carbon, nitrogen, boron, aluminium, chromium, silicon, titanium, *etc.*) by its diffusion deep into the product at high temperature in the atomic state of the external environment.

The widespread use of chemical-thermal treatment in various branches of technology is explained by the fact that most machine parts and various mechanisms operate under conditions of wear, cavitation, cyclic loads, corrosion at cryogenic or high temperatures, at which maximum stresses occur in the surface layers of the metal [4].

The essence of the chemical-thermal treatment process is to saturate the surface layers of the product with one or several elements at once in combination with a certain heat treatment, which, depending on the type of who, can be performed before and after surface saturation. Therefore, during chemical and thermal treatment, the structure and properties of the surface of the part are determined by both changes in the chemical composition of the surface and heat treatment [5, 6].

Diffusion that causes phase recrystallization (with the formation of new phases) is often called reactive or reactive diffusion. This type of diffusion occurs when steel is saturated with carbon, nitrogen [3, 4, 7], chromium, silicon, *etc*.

Diffusion in metals is based on an atomic process in which each free atom performs more or less random displacements, that is, a series of jumps between different equilibrium positions in the lattice. The concept of 'diffusion' is applied not to the motion of individual atoms, but to the macroscopic flow of substances. Macroscopic movements of matter are the result of a huge number of small movements of individual atoms. The driving force of diffusion is the gradient of the chemical potential, which can be caused by various reasons. With respect to chemical and heat treatment, the gradient of the chemical potential is determined by the concentration gradient [8].

The development of the process of diffusion of atoms of the saturating medium leads to the formation of a diffusion layer, which is understood as the surface layer of the part material, which differs from the initial matrix material in chemical composition, structure and properties. The material of the part matrix under a diffusion reinforced layer that is not disturbed by the chemical action of the saturating medium is called the core [9].

One of the most effective ways to reduce the brittleness of boride layers is to form layers with a composite structure. To form the compositional structure of the diffusion layer, it is proposed to form, in addition to the borides, several additional phases, which are located in the layer arbitrarily or in an ordered way. These additional phases should have a lower hardness compared to borides. Layers consisting only of iron borides, despite their high hardness, have increased wear under the operating conditions of products in the presence of shock loads. The reason for this is the discoloration of individual sections of the layer due to its high brittleness [10–12]. Layers with a composite structure do not have this disadvantage. The presence of less solid additional phases in the layer reduces the overall fragility of such a layer, and in the absence of borides in the layer makes it wear-resistant, that is, the layer is built on the 'Sharpie' principle [13–15], during wear of which the surface acquires a microrelief due to structural heterogeneity. In addition, composite borage layers have a low stress state due to stress relaxation at the interface boundaries of the boride-solid solution phases [16].

Thus, the composite structure of the diffusion layer should reduce its brittleness and ensure high wear resistance of the product. To obtain a composite structure, various methods are used, including the most promising ones, based on the use of laser and electron beam heating. The main task of using concentrated energy sources is to design a layer with separated borides. At the same time, it is advisable to replace the compact needle-like or globular structure of borides with a dispersed one with their arbitrary orientation. The use of these heating methods makes it possible to process in the thermal cycling mode, which also leads to the formation of a composite structure of layers during both the diffusion-crystallization and diffusion mechanisms of their formation.

### 2. EXPERIMENTAL/THEORETICAL DETAILS

# 2.1. Obtaining a Composite Structure by Complex Chemical and Thermal Treatment (Boriding after Carburization)

To create the compositionality of the structure, samples made of 38Cr2MoAl steel are reinforced by complex chemical-thermal treatment, namely, boriding is carried out after carburization [17, 18] according to the modes presented in Table 1 composition of the carburizing medium: charcoal with activators (barium carbonate and soda ash in the amount of 10-40% by weight of coal). Composition of the boriding mixture: 65-85% mass of amorphous boron, 5-10% mass of potassium tetrafluoroborate, 5-20% mass of boron nitride, 5-15% mass of dolomite. After boriding, quenching from the temperature of chemical-thermal treatment is performed, followed by a low tempering to partially relieve internal stresses.

The diffusion layers of alloy steel after complex saturation with car-

Mode number	Cementation	Boriding
1	At 800°C duration 2 hours	At 800°C duration 2 hours
2	At 850°C duration 2 hours	At 850°C duration 2 hours
3	At 900°C duration 2 hours	At 900°C duration 2 hours
4	At 950°C duration 2 hours	$ m At950^{\circ}Cduration2hours$

**TABLE 1.** The modes of complex chemical-thermal treatment of alloy steel38Cr2MoAl.

bon and boron consist of a boride zone, carboboride and carbide, which smoothly pass into the core structure.

It is established that the boron layer consists of two zones: the boride zone—chemical compounds of boron and iron and the transition zone a solid solution of boron in iron. The boride zone has a characteristic needle-like structure. Boride needles, growing together at the base, form a continuous boron layer.

Alloying elements in steels do not form their own borides, but alloying iron borides. Depending on the nature of the interaction of alloying elements with iron boride, they are redistributed during the formation of the boron layer. The boron layer is only part of the total reinforced layer. When boring steels, a transition zone is located under the boride zone, which differs from the core in structure.

Electron microscopy of 38Cr2MoAl steel after complex chemical and thermal treatment according to mode No. 1, which consisted of carburization followed by boriding at a temperature of 800°C for 2 hours (Table 1) is shown in Fig. 1.

The elemental composition of the diffusion layer of steel is determined by energy-dispersive recording of the intensity of the lines of characteristic X-ray radiation of the sample, which occurs as a result



Fig. 1. Electron microscopy of 38Cr2MoAl steel after complex chemical-thermal treatment according to mode No. 1.

of irradiation of the micro-volume of the sample with an electronic probe (Fig. 2). Spectrograms are obtained for all the studied points indicated in Fig. 2.

In Figures 3-5 shows the structures of composite layers of steel 38Cr2MoAl after complex chemical-thermal treatment according to modes Nos. 2-4, which consisted in carburization with subsequent



Fig. 2. Intensity of the lines of characteristic X-ray radiation of the 38Cr2MoAl steel sample: at Point 1 (*a*), at Point 2 (*b*), at Point 3 (*c*).



Continuation of Fig. 2.

boriding at a temperature of  $850^{\circ}$ C for 2 hours, carburization with subsequent boriding at a temperature of 900°C for 2 hours and which consisted in carburization with subsequent boriding at a temperature of 950°C for 2 hours (Table 1) respectively.

Received data (Figs. 1, 2) confirmed the presence of a carbide layer between the surface layer of borides and the core of the steel sample, namely the carbon content at Point 2 (Fig. 2, b) has the highest rate (1.22%) with a gradual decrease in carbon (Point 3—1.07\%) compared to the boride layer—Point 1 (0.07%) and the steel core, according to



Fig. 3. Electron microscopy of 38Cr2MoAl steel after complex chemicalthermal treatment according to mode No. 2, which consisted of carburization followed by boriding at temperature of  $850^{\circ}$ C for 2 hours (Table 1).



**Fig. 4.** Electron microscopy of 38Cr2MoAl steel after complex chemicalthermal treatment according to mode No. 3, which consisted of carburization followed by boriding at temperature of 900°C for 2 hours (Table 1).

the marking of which, the carbon content is up to 0.42%. Similar data are obtained for processing modes Nos. 2-4 (Table 1).

It is established that the boride layer displaces carbon, which is in the layer reinforced by carburization, deep into the steel. Due to the preliminary strengthening treatment by carburization, boride needles with rounded edges are formed and then crushed deep into the diffusion layer, which is associated with the presence of a large amount of carbides in the surface layer, which do not allow boride needles to grow in the direction perpendicular to the surface of samples due to their high density. Grinding and rounding of boride needles has a positive effect on the further operation of the product, which makes it possible to eliminate stress concentrators and local zones that can cause cracks



Fig. 5. Electron microscopy of 38Cr2MoAl steel after complex chemicalthermal treatment according to mode No. 4, which consisted of carburization followed by boriding at temperature of  $950^{\circ}$ C for 2 hours (Table 1).

in the presence of sharp needles.

The service properties of boride layers are determined by the set of properties of borides and sublayers. The sublayer plays the greatest role in the heat treatment of borated parts, which creates a solid substrate for the boride layer and prevents its penetration, as well as during the formation of the stress state of the part. In this case, it is necessary to adjust the heating temperature for quenching, taking into account the changed chemical composition of the sublayer, in order to obtain an optimal set of properties of the part. A certain importance for the wear processes is the sublayer, which is strengthened by preliminary chemical and thermal treatment. Due to its higher hardness and the presence of carbides, it provides further increased wear resistance of the part compared to the wear resistance of the core after wear of the boride layer.

A characteristic property of boride layers is their high hardness. Iron boride FeB has a microhardness of 22 GPa, and iron boride  $Fe_2B$ has a microhardness of 18 GPa. An increase the carbon content in the steel leads to a decrease in the hardness of FeB boride and practically does not effect on the hardness of Fe<sub>2</sub>B boride. As the boriding temperature of carbon steels increases, the hardness of FeB decreases slightly, and  $Fe_2B$  increases slightly. The saturation time practically does not effect on the hardness of the boride phases. The high microhardness of the boron layer is not inferior to the microhardness of hardened medium-carbon steel. These allow the use of boriding to increase the wear resistance of products. Thus, after analysing the change in microstructures after various modes of surface hardening of steel, it can be argued that complex chemical and thermal treatment leads to the formation of a composite structure of steel with the grinding of borides in the interlayer, the dispersion of which increases with increasing diffusion saturation temperature.

# 2.2. Obtaining a Composite Structure by Complex Chemical and Thermal Treatment (Boriding after Nitrocementation)

To create a compositional structure, samples made of 38Cr2MoAl steel are reinforced by complex chemical-thermal treatment [22], namely, boriding is carried out after nitrocementation. Nitrocementation of the samples is carried out at a temperature of 550°C for 5 hours, and then control is performed according to the modes presented in Table 2 composition of the nitrocementation medium: urea  $(NH_2)_2CO$  (95%) and NaF activator (5%). Composition of the boriding mixture: 65– 85% mass of amorphous boron, 5–10% mass of potassium tetrafluoroborate, 5–20% of mass boron nitride, 5–15% of mass dolomite. After boriding, quenching from the temperature of the chemicalthermal treatment is performed, followed by a low tempering to par-

Mode number	Nitrocementation	Boriding
1 2 3 4	At $550^\circ$ C duration 5 hours	At 800°C duration 2 hours At 850°C duration 2 hours At 900°C duration 2 hours At 950°C duration 2 hours

**TABLE 2.** The modes of complex chemical-thermal treatment of alloy steel38Cr2MoAl.

tially relieve internal stresses.

When the boriding temperature increases from 800 to  $1000^{\circ}$ C in alloy steel, the boride layer and transition zone increase significantly. The boride layer has a crushed structure with dispersion particles, the amount of which decreases from the surface of the sample to its core.

Electron microscopy of 38Cr2MoAl steel after complex chemicalthermal treatment according to modes No. 1–4 (Table 2) is shown in Figs. 6–9. Energy-dispersive registration of the intensity of lines of characteristic X-ray radiation of a sample made of alloy steel after complex chemical and thermal treatment according to mode No. 1 (Table 2) showed the presence of carbon at Point 1 (Fig. 6) 0.81% and 0.95%—at Point 2.

The boriding temperature of  $950^{\circ}$ C provided the presence of carbon at Point 1 (Fig. 9) 1.02% and 1.42%—at Point 2.

Studies are shown that pre-nitrocementation made it possible to obtain a layer of borides with subsequent struggle with curved and crushed boride needles, which eliminates stress concentrators. This fact has positive effect on the operational properties of the reinforced



**Fig. 6.** Electron microscopy of 38Cr2MoAl steel after complex chemicalthermal treatment according to mode No. 4, which consisted of nitrocementation at temperature of 550°C for 5 hours, followed by boriding at temperature of 800°C for 2 hours (Table 2).

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Fig. 7. Electron microscopy of 38Cr2MoAl steel after complex chemicalthermal treatment according to mode No. 4, which consisted of nitrocementation at temperature of  $550^{\circ}$ C for 5 hours, followed by boriding at temperature of  $850^{\circ}$ C for 2 hours (Table 2).



Fig. 8. Electron microscopy of 38Cr2MoAl steel after complex chemicalthermal treatment according to mode No. 4, which consisted of nitrocementation at temperature of  $550^{\circ}$ C for 5 hours, followed by boriding at temperature of 900°C for 2 hours (Table 2).

layer, reducing its brittleness due to the formation of a crushed composite structure.

## **3. RESULTS AND DISCUSSION**

The most likely mechanism of diffusion in solid substitution solutions and pure metals is, as is known [20], the vacancy mechanism. The process of diffusion in the vacancy mechanism is carried out by moving an atom to a neighbouring vacancy and forming a new vacancy in the old place. Thus, there is a continuous diffusion of vacancies. A convincing



**Fig. 9.** Electron microscopy of 38Cr2MoAl steel after complex chemicalthermal treatment according to mode No. 4, which consisted of nitrocementation at temperature of 550°C for 5 hours, followed by boriding at temperature of 950°C for 2 hours (Table 2).

confirmation of the vacancy mechanism of diffusion in solid substitution solutions is the Kirkendall effect [20]. This is also evidenced by theoretical calculations of the activation energy required to move atoms using one of the listed mechanisms.

Elements with a smaller atomic radius have the highest diffusion coefficient in iron. Among carbon, nitrogen, and boron, nitrogen has the smallest atomic radius, which is 0.75 Å, while carbon and boron have the smallest atomic radius of 0.77 Å and 0.97 Å, respectively. The atomic radius of iron is 1.26 Å.

In the case of boron diffusion in iron, the vacancy mechanism raises significant doubts, since in the case of diffusion by the vacancy mechanism, we can talk about solutions. But according to the Hume-Roseri rules [21], for the formation of substitution solutions, solubility is possible if the crystal lattice of the solvent and the soluble element are the same. Iron, as a rule, has two types of crystal lattices—b.c.c under standard conditions and h.c.c.—at temperatures above *AC1*, and boron either does not have a crystal lattice at all (amorphous modification) or has a more complex rhombohedral crystal lattice (crystal modification). The formation of a solid solution is possible if the atomic radii of the solvent and solute differ by no more than 14-15%. For iron and boron, the difference is  $\{(1.26-0.97)/0.97\}\cdot 100\% = 29\%$ , for nitrogen and carbon, this difference is even greater—68% and 63%, respectively, which significantly exceeds 14 and 15%.

According to this phenomenon, the formation of substitution solutions between iron, carbon and nitrogen is out of the question. Thus, based on the above, we can conclude that the diffusion of nitrogen and carbon in the proposed methods of chemical and thermal treatment occurs by introducing, which does not contradict the existing theory. On the other hand, according to the Hume-Roseri rule, maximum solubility is achieved if the solvent and the substance to be dissolved have the same valence. In this case, metals with a lower valence tend to dissolve in metals with a higher valence. Boron has a valence equal to three, iron can have a valence equal to two or three. Also, the solvent and solute should have the closest possible electronegativity (the difference should not exceed 0.2-0.4). If the recommended difference is exceeded, substances tend to form compounds instead of solutions. The electronegativity of boron on the Pauling scale is 2.04, iron is 1.83, and thus, the difference is 0.21.

To form solid insertion solutions, an atom of a dissolved element must have a radius smaller than the size of voids or pores in the solvent crystal lattice. But be greater than the size of the smallest possible pore, namely a tetrahedral pore, that is, the Hegg rule must be fulfilled [22]: 0.25 atomic radius of the solvent  $\leq$  atomic radius of the dissolved element  $\leq$  0.59 atomic radius of the solvent. For iron and boron, this rule does not apply and is: 0.315 Å < 0.97 Å > 0.743 Å.

For iron, nitrogen, and carbon, the Hegg rule also does not hold and is 0.315 Å < 0.75 Å > 0.743 Å and 0.315 Å < 0.77 Å > 0.743 Å, respectively.

Thus, for the formation of a solid nitrogen, carbon, or boron substitution solution in iron, the atoms of the diffusing elements are too small, and for the formation of a solid injection solution, they are too large in the case of boron. Therefore, the diffusion of boron in iron by the vacancy mechanism is almost impossible. This is also evidenced by the limited solubility of boron in iron at the level of 0.003-0.008%. Thus, we can conclude that the main mechanisms of boron diffusion will be such mechanisms as reaction (the movement of atoms is carried out by moving the chemical reaction front); diffusion along dislocations, block boundaries, subgrains and grains, *etc.* Reaction diffusion occurs by diffusing boron throughout the boride layer to the main reaction Front, which is located at the boundary of two phases: iron-boride Fe<sub>2</sub>B and boride Fe<sub>2</sub>B-boride FeB.

In the developed complex chemical and thermal treatments, pretreatments before boriding do not affect the main regularities of boride layer formation in comparison with the process of atomic boron saturation. Microstructures of the boride layer have the form of needles that are oriented perpendicular to the surface of the samples. First, the embryos are formed, and then the needles of boride  $Fe_2B$ . These needles grow until they close and form a continuous layer of  $Fe_2B$  borides. Individual needles are then formed on the surface of this boride layer, which also form a second continuous layer of FeB boride. The needle-like structure of the boride layer indicates rapid growth of boride zones in the direction perpendicular to the surface of the samples, while along the surface the development of these phases is insignificant. This formation is due to the peculiarities of the structure of these phases, due to which boron atoms move rapidly only in a certain direction. The size of the C faces for the rhombic crystallographic lattice of boride FeB and tetragonal boride Fe<sub>2</sub>B have the smallest values compared to the sizes of other faces and are 2.952 Å and 4.249 Å, respectively. The formation of lattices of these borides occurs in the direction of the *c*-axis, which corresponds to the C faces, and is located perpendicular to the surface of the samples and coincides with the location of the needle axis, that is, with the direction of boron diffusion. Thus, the needles of FeB and Fe<sub>2</sub>B crystals arise due to the fact that the embryos of this phase are oriented to the sample surface and the crystallographic directions of the lattices are oriented along the normal to the diffusion front, which causes the appearance of anisotropy of the diffusion rate and rapid growth of phases in the predominant direction to the core. Thus, the rapid growth of borides is associated with the peculiarities of their structure, which consist in the existence of such crystallographic directions in which the diffusion of atomic boron is significantly facilitated.

Such regularities of the formation of a boride layer in the developed processes of saturation with atomic elements do not contradict the existing theory of the formation of boride layers.

### **4. CONCLUSION**

Obtaining the microstructure of surface layers of 38Cr2MoAl steel under complex chemical and thermal treatment, which consist of a boride and transition zone containing carbonitrides of alloying elements formed during preliminary nitrocementation. Experimental data showed that the thickness of the boride layer and transition zone increases with increasing boriding temperature from 800°C to 950°C after nitrocementation at a processing temperature of 550°C. The surface microhardness confirms the presence of two borides, namely FeB with a hardness of 22 GPa and Fe<sub>2</sub>B with a hardness of 18–16 GPa.

Complex chemical and thermal treatment of 38Cr2MoAl steel, which included sequential carburization, nitrocementation and boriding under various modes, made it possible to create a compositionality of the structure, namely, to form a boride layer with a transition zone containing nitrides, carbonitrides and carbides. The resulting transition zone makes it possible to increase the operational properties of machine parts and tools by reducing the micro-fragility of the diffusion layer.

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