

EFFECT OF CARBIDE COATINGS ON CORROSION OF IRON-BASED COMPOSITE MATERIALS

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Abstract- Increasing the properties of iron-based abrasive composition materials by volume and surface alloying is of scientific and technical importance. Since increasing the properties of composite materials by volume alloying causes a number of difficulties, surface alloying is often used to improve the properties of this type of materials. Therefore, in order to increase the properties, successive saturation processes of their surface layer with one or more carbide-forming elements are carried out. It was found that the properties enhancement with one-component coatings differs from the properties of multi-component coatings. It is clear that as a result of the saturation of the surface layer of the abrasive composition materials with certain elements, coatings with different composition are created in them. Carbide, nitride, boride and other coatings allow to obtain the necessary results. Therefore, the improvement of the structure and properties of iron-based abrasive composition materials directly depends on the coatings formed as a result of hammering the surface layer of construction materials with various elements. In the article, the effect of carbide, nitride and boride-containing coatings on the structure and properties of iron-based abrasive composition materials was considered. The distribution of chromium in the depth of the diffusion layer was studied by the method of micro-X-ray spectral analysis. The greatest concentration of chromium is observed on the surface, which increases as the degree of carbonization of the material increases. The change of the amount of chromium on the depth of the carbide zone obeys a linear law. At the boundary of the carbide zone, its concentration is approximately the same in the studied materials and is 58-61%. In connection with the increase in the initial carbonization degree of the surface zone, the increase in the concentration of chromium is accompanied by the increase in the microhardness of the carbide coating. Based on the data of X-ray structural studies, the studied carbide coatings have the same phase composition $(Cr, Fe)_{23}C_6$, $(Cr, Fe)_7C_3$. The structure of the transition zone and its layers is determined by the degree of carbonization of the material during the initial processing. At relatively low temperatures (875 and 925 °C) in cementitized iron, as in the case of JQr 0.5 composition, a weakly tanned zone (20-25 μm thick) of an extremely

saturated γ -solid solution with a microhardness $H_{100} = 6100-7000$ MPa, formed in the process of cooling from the air chroming temperature directly under the carbide layer is located. Behind it is a zone of high etching ability, which is caused by the eutectoid decomposition of the solid solution of chromium and carbon in γ -iron. The intermediate zone of annealed iron cementitized at 975-1025 °C undergoes eutectoid decomposition during cooling in air and metallographically is detected as a band with high etching ability.

Keywords Carbide, Imprint, Diffusion, Cementification, Boring.

1. INTRODUCTION

Issues such as strengthening the properties of the working surfaces of baked composite materials have not been studied in detail. To improve the properties of the working surfaces of these materials, it can be considered more efficient to use a chemical-thermal processing operation. Therefore, a more in-depth study of the chemical-thermal processing of abrasive composition materials and, as a result, improving the operating properties of the working surfaces of the details is a scientific and practical issue [3, 10, 11]. At the same time, by saturating the properties of iron-based composite materials with certain elements, it is possible to obtain properties that show high quality on their working surfaces. From this point of view, the article is relevant as an issue that meets the requirements of the time, and the issues investigated there can be considered scientifically and practically comprehensive [4, 5]. From this point of view, in the article, the issue of carbon and boron saturation of the surface layer of abrasive composition materials was carefully considered and its efficiency was studied.

2. PROBLEM SOLVING

It is known that cooking is a necessary parameter of the technological process for the preparation of ovuntu compositions. The temperature-time regimes of cooking are close to the regimes of chemical-thermal processing.

Therefore, any studies of cooking and chemical-thermal-thermal processing processes are of great interest, because in a positive solution to the considered problem, the cooking process can be canceled as a free process, shortening the total duration of processing, and making the preparation of rubbing compositions subjected to diffusion saturation easier. It is possible to reduce the value. Composite materials obtained from compact materials are mainly characterized by the presence of macro, micro and submicroscopic porosity in them, the high imperfection of interparticle boundaries compared to intragrain boundaries, great inhomogeneity in terms of chemical composition, high extraction (oxygen, nitrogen, hydrogen, etc.) are different.

The main distinguishing feature of baked composite materials is the presence of residual porosity, which is characterized by the ratio of the actual density of the material expressed as a percentage to its theoretical density. Carbide coatings have high corrosion resistance only if there is a sufficiently hard "base" underneath them. A comparison of the mechanical properties after plating and chroming (Figure 1) shows that they change in the same way. The difference in quantity allows to evaluate the specific effect of the chroming process. After coating, the depth of the diffusion layer increases by 2-2.5 times. In this case, the concentration of carbon decreases sharply. In samples cemented at temperatures of 875 and 925 °C, the maximum concentration of carbon in the layer is 0.3 and 35%, respectively. It is clear that with such amount of carbon, the penetration depth of iron-carbon material is low.

The hardness of samples subjected to chroming is lower than the samples after plating, and the impact viscosity is higher. This is due to the lower concentration of carbon in the substrate, which is part of it. In this case, the study of the distribution of microhardness on the depth of the carbide layer shows that the depth of penetration and the ability to penetrate the cemented samples at 975 and 925 °C are less significant (Figure 1). In this case, high hardness equal to $H_{100} = (6000-7000)$ MPa is observed only in the intermediate zone. The microhardness of the base does not exceed $H_{100} = (6000-7000)$ MPa and smoothly decreases from the intermediate zone to the core. In the case of surface hardness, the carbide layer and the thin intermediate zone are crushed, as a result of which its value does not exceed 25 HRC.

Otherwise, crushing occurs during the operation process. In order to obtain a sufficiently deep (1.0-1.5 mm) solid "substrate" ($H_{100} = (6000-4000)$ MPa) under the carbide coating, the initial cementation temperature should be 975-1250 °C, the optimal duration should be 4-8 hours [6]. Dense abrasive compositions are obtained by double - cold pressing and baking, hot pressing, impregnation with liquid metals and baking in the presence of a liquid phase. For iron and iron-carbon bi-welded materials, the tool is usually used in double pressing and baking. It is recommended to conduct the first firing at a temperature of 700-900 °C, and the second firing at 1150 °C. In this case, the density of wrought iron reaches 7.3-7.5 g/cm³,

and the density of wrought steel reaches 7.3 g/cm³ [7].

The main purpose of co-saturation with carbon and nitrogen is to increase the surface hardness and corrosion resistance of iron-based abrasive compositions. The analysis of the impact of porosity on the nitro cementing process shows that the nature of the dependence of the depth of the nitrosed layer on the density of the material is similar to that of cementation [8, 9, 11].

The depth of the diffusion layer is influenced by the chemical composition of the alloy. Alloying iron with copper and nickel in the amount of 2-7% helps to increase the saturation speed. In this case, a smoother distribution of saturating elements on the gas is observed. The amount of nitrogen and carbon in the diffused layer depends on the saturation conditions. As we increase the carbon potential of the saturated medium, the concentration of carbon increases and the concentration of nitrogen decreases. When keeping the carbon potential at the same level of 0.5-0.7% and reducing the amount of ammonia from 3% to 1%, the amount of nitrogen in the layer decreases, which leads to an increase in the critical temperature of the tabulation.

After quenching in oil, the nitrocemented layer carbonitride elements have a structure consisting of martensite and a small amount of residual austenite. In the case of a low amount of nitrogen in the layer, carbonitride elements form troostite-martensite structure. In this regard, successive saturation of baked iron-based low-carbon materials with elements that form carbides and borides allows to significantly increase their physical and mechanical properties [1, 2]. The depth, composition, and structure of the diffusion layer formed in the process of chrome-plating of carbonized materials primarily depends on the initial depth of the cemented layer, the concentration of carbon, and the character of its distribution. It is known that the corrosion resistance of diffusion coatings depends on the technological parameters of the saturation process, as in other properties, and has maximum values at certain values of the latter. The study of the effect of saturation conditions (temperature, time, composition of the environment, etc.) on the corrosion resistance of carbide coatings was performed using the Box-Wilson method. Good resistance to thermal corrosion of carbide coatings is determined by high values of the following initial mechanical properties: hardness, yield strength and yield strength, and the ability to maintain the original structure and properties when heated to high temperatures.

Studies on the effect of temperature on the hardness of chromium carbides show that their high hardness, equal to $H_{200} = 10000$ MPa, is maintained up to 6500 °C. The specified properties provide high resistance to ignition of carbide coatings and significantly expand the area of oxidative wear. Oxidative corrosion depends on the rate of formation and dissolution of the second structure in the rubbing process [6]. The high resistance of carbides to plastic deformation, the ability to create thin layers of oxides that prevent the diffusion of oxygen to a great depth, sharply reduce the rate of formation of the second structure and reduce the intensity of oxidative corrosion.

The diffusion layer consists of a carbide zone, an intermediate zone and a layer. The initial cementation process of iron and XX3 composition was carried out in carburizers, and XX6 and XX9 compositions were carried out in special carburizers with the following composition, % (by mass): 85% charcoal +15% sodium bicarbonate ($T=975\text{ }^{\circ}\text{C}$, $\tau=4$ hours). The depth of boride layers is lower and their integrity is higher in cemented compositions compared to compositions with the same initial composition. This is due to the retarding effect of carbon on the boronization process. This difference in depth increases gradually as the amount of chromium increases.

This is explained by the increase in the concentration of carbon in the cemented layer and the decrease in the speed of its "absorption" in the process of storage in boron [3, 5]. If after chroming, the impact viscosity and bending strength were higher than the samples after reaching the limit, and the surface hardness was lower, but after boronizing, the opposite regularity is observed. This is explained by the opposite interaction of boron and carbon and the lower temperatures of boronization compared to chromium. In the formation of the boride coating, carbon is forced into the transition zone. Below the transition zone is the base. Due to the fact that boriding is carried out at a lower temperature than chroming, the depth of the base in borinated samples is less (about 20%), then concentration of carbon is higher than in chromized samples.

The increase in the concentration of carbon in the base is explained by its lack of solubility with borides. In addition, the initial cementation temperature of wrought iron may be lower than that of chromium plating, approximately $500\text{ }^{\circ}\text{C}$, in order to obtain a base with a fairly high carbon content (more than 0.4%) in the case of boronization. The microstructure of the composition of the saturating mixture and the saturating conditions on the depth of the boride layer in carbonized iron and iron-chromium compositions with 3.6 and 9% chromium in the composition is given in Figure 2. The initial cementation process of iron and XX3 composition was carried out in bonyuj carburizers, and XX6 and XX9 compositions were carried out in special carburizers with the following composition, % (by mass); 85% charcoal +15% sodium bicarbonate ($T=975\text{ }^{\circ}\text{C}$, $\tau=4$ hours).

The depth of the boride layers is lower and their integrity is higher in the cemented compositions compared to the compositions with the same initial composition, which is related to the retarding effect of carbon on the boriding process. This difference in depth increases as the amount of chromium increases. This is explained by the increase in the concentration of carbon in the cemented layer and the decrease in the speed of its absorption during the storage process. In addition, chromium slows down the diffusion of carbon in austenite and complicates the process of pushing it with the boride layer that grows into the depth of the composition.

Therefore, diffusion processes in cemented iron-chromium compositions require additional energy and time costs. X-ray microstructure analysis showed that the amount of chromium in the intermediate zone cemented at 875-925 and 975-1025 $^{\circ}\text{C}$ is different.

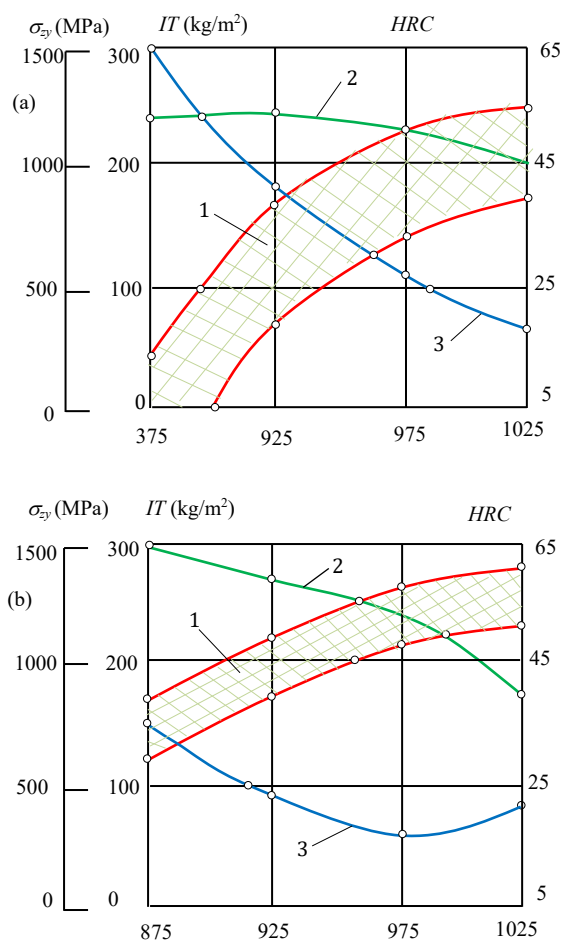


Figure 1. Initial cementation temperature ($\tau=4$ hours) of baked iron, a) After Chroming of XX3, b) $\gamma=95\%$ alloy ($T=1100\text{ }^{\circ}\text{C}$, $\tau=4$ hours) effect on mechanical properties: 1-hardness, 2-flexural strength limit, 3-impact viscosity

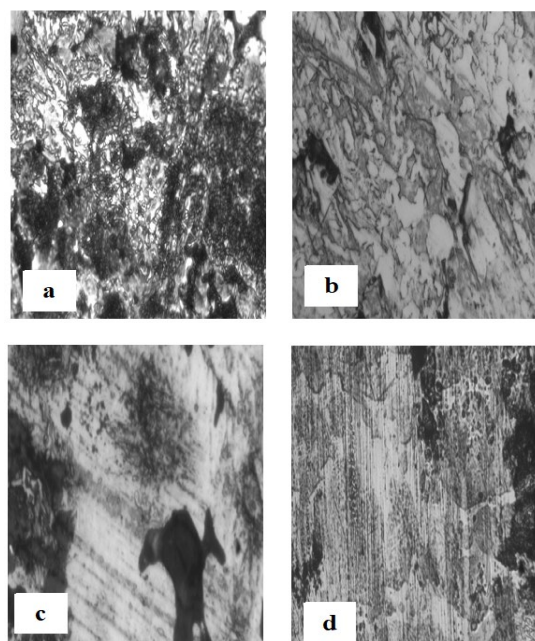


Figure 2. Wrought iron subjected to cementation and subsequent chroming ($\gamma=95\%$) microstructure; a) $T_{sem}=875\text{ }^{\circ}\text{C}$, b) $925\text{ }^{\circ}\text{C}$, c) $975\text{ }^{\circ}\text{C}$, d) $1025\text{ }^{\circ}\text{C}$, $\tau=4$ hours, $T_{chrom}=1100\text{ }^{\circ}\text{C}$, $\tau=4$ hours, x 300 times

In the first case, a change of chromium from 12-15 to 6-7% is observed with a higher concentration on the surface directly touching the carbide zone and having a depth of 20-25 mkm. Then, a bend is noted in the curve of chromium amount - layer depth, and a smooth decrease of its concentration from 6-7% to 0% occurs. A smooth change of chromium concentration from 6 to 0% occurs in the intermediate zone of carbonized samples at temperatures of 975-1025 °C. Most likely, the difference in the structure of the intermediate zone of the diffusion layer of iron cemented at different temperatures is determined by this. When increasing the initial carbonization temperature from 875-1025 °C, the depth of the intermediate zone increases from 40 to 45 mkm.

Under the intermediate zone, there is a sub-layer with a ferrite-pearlite structure. The concentration of carbon in on decreases from the intermediate zone to the core. The ratio of ferrite and pearlite is determined by the degree of carbonization of the material during the annual processing. In materials cemented at temperatures of 875 and 925 °C, the small initial depth of the carbonized zone and the high gradient of carbon concentration determine its small amount in the layer. Chemical analysis of layers shows that in this case the maximum concentration of carbon does not exceed 0.2-0.3%. At a depth of 2-2.8 mm, its amount decreases to 0.1% . In materials exposed to carbonization at temperatures of 975 and 1025 °C, the amount of carbon in the layer reaches 0.4-0.5%. The effect of the cementation temperature on the depth of the layer and the maximum concentration of carbon in it is given in Table 1.

Table 1. The influence of initial cementation temperature after chroming on the depth of the diffusion layer of wrought iron, its chemical composition and microhardness ($t_{\text{cement}}=4$ hours)

Cementation temperature, °C	Carbide zone			Folded	
	Carbide zone depth, mkm	Concentration of Cr on the surface, %	Micro-hardness, MPa	The depth of the fold, mkm	The maximum amount of C, %
875	16	71	13000-15000	2.1	0.25
925	18	74	13500-16000	2.8	0.30
975	21	80	14000-16500	3.1	0.40
1025	24	84	14500-17000	3.2	0.50

The distance from the intermediate zone to the zone containing up to 0.1% carbon is taken as the depth. A higher amount of carbon in the bottom layer can be obtained by increasing the initial depth of the cemented layer and reducing the carbon concentration gradient in it, which is achieved by applying longer modes of carbonization. Preliminary cementation of wrought iron at 975 °C for 8 hours allows to increase the maximum amount of carbon to 0.7%.

Both the significant effect of the cooked composition and the initial chemical effect of the cooked composition have a significant effect on the concentration of carbon in the cake. In the same mode of chemical-thermal processing, its amount in the lower layer of the XX3 brand chrome composition is much higher than in baked iron. In this case, the depth of the layers decreases by 10-15%. This is explained by the higher degree of carbonization of the surface layer of chromium-alloyed materials in the initial processing and the lower rate of its absorption in the final processing, because the diffusion coefficient of carbon in the iron-chromium composition is relatively low in iron.

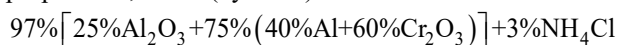
The t is to be expected that the properties of baked materials subjected to cementitization and chroming will be significantly determined by the amount of carbon in the substrate. Conducted studies show that in order to obtain a base with a sufficiently high concentration of carbon (more than 0.4%) in iron, the carbonization temperature should be within 975-1025 °C during the saturating process 4-8 for hours.

In the chemical-thermal processing of baked materials, which consists of cementitization and chrome-silicification, cementitization and chrome-titanization, the formation of the diffusion layer and its regularities are

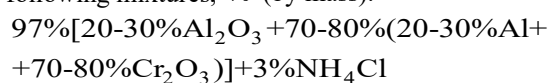
followed. At the next stage, the influence of the composition of the saturating mixture and the conditions of saturation on the processes of diffusion chroming, chromilication and chromititanization of the cooked materials subjected to primary carbonization was studied. Cementation of iron and XX3 composition was carried out in carburizers, and XX6 and XX9 compositions were carried out in special carburizers with the following composition: 85% charcoal +15% sodium bicor-banate. Cementation was carried out at a temperature of 975 °C for 4 hours. Chromation, chrome silicification and chrome titanation were carried out in the original recovered alumothermic alloys.

The predominant chromium impregnation process takes place in the amount of up to 30% aluminum in the initial mixture. In this case, carbide coatings are formed. X-ray structure analysis shows the presence of two phases in the carbide layer is $(Cr,Fe)_{23}C_6$ and $(Cr,Fe)_7C_3$ phases. When the amount of aluminum in the primary mixture is increased from 15 to 25%, the amount of chromium in the diffusion layer increases from 66 to 72%, which causes its hardness to increase from $H_{100} = 12500-14500$ to $H_{100} = 13500-16000$ MPa. If the initial alloy contains up to 30% Al, the concentration of chromium in the layer decreases to 64%, and that of aluminum increases 2.6%. Simultaneous saturation of the compositions with aluminum and chromium is determined by the presence of an excess of aluminum in the saturating mixture. Aluminum, which has a relatively large diffusion coefficient compared to chromium, diffuses faster. Diffusion of aluminum leads to the redistribution of carbon (due to the decrease of its solubility in the γ -phase and especially stronger γ - α -

recrystallization). This, in turn, facilitates the diffusion of chromium, increases the depth of the layer and changes its phase composition: for example, in saturation in a mixture containing primary components in the following proportions, in % (by mass):



layer at $T=1100\text{ }^\circ\text{C}$, $\tau=4$ hours is 26 and 17%, respectively. In this case, the diffusion layer consists of a Fe_3Al zone alloyed with chromium in a regular solid solution of aluminum in iron. In the diffusion layer of iron-chromium compositions there are carbide elements, the amount of which is determined by their initial amount in the carbonized zone. Thus, our research shows that the process of formation of carbide coatings on primary carbonized materials is more intensive when chroming in the following mixtures, % (by mass):



Chromization and silicification in primary regenerated aluminothermic mixtures lead to the formation of saturation carbide-type coatings, which indicate the predominant diffusion of chromium. The greatest depth of the carbide layer is observed in the ratio of $SiO_2:Cr_2O_3=15:85\%$ (by mass). The further increase of silicon oxide in the mixture provides a decrease in the depth of the diffusion layer. In the case of an optimal ratio of silicon oxide and chromium oxide, the chromium siliconized layer is formed in the amount of up to 30% of aluminum in the initial mixture. In this case, the diffusion layer consists of $Cr_{23}C_6$ and Cr_7C_3 phases alloyed with iron and silicon.

Aluminum, chromium and more than 30% of aluminum in the initial mixture simultaneous saturation with silicon takes place, which leads to a sharp increase in the depth of the diffusion layer and a sharp change in its phase composition. In the case of 40% aluminum saturation in the mixture, iron aluminide Fe_2Al_5 doped with chromium and silicon is formed on the surface, behind which complex alloyed solid solutions of variable concentration based on α -iron are located. The amount of saturating elements on the surface of the primary cemented iron was as follows, %: aluminum 43.0%, chromium 2.0%, silicon 1.3%.

4. RECOMMENDATION TO ENGINEERING PRACTICE

Most of the research conducted so far has been to provide recommendations for production using the new material. And by the method of chemical-thermal treatment, it is possible to make significant changes to the properties of existing materials without changing their shape. It should be noted that chemical heat treatment is also not a new method. However, the issues of improving the properties of lubricating composite materials using this method have not been sufficiently studied. This article addresses these issues. To do this, there must be active metallic and non-metallic atoms, and it is important to

ensure that these particles are absorbed by the surface and diffuse inward. However, this process is more effective in composite materials for polishing, unlike steel, cast iron and other alloys.

As a result of nitrocementation (gas cyanidation), an increase in complex mechanical properties has been achieved. Thanks to chromitization, it was possible to effectively increase corrosion resistance, as well as the ability to work in aggressive environments. Coatings obtained as a result of impregnation with carbon and boron increased the resistance to wear of the compositions. This property has not been observed in coatings on steels. This is also due to the fact that borides doped with chromium have a relatively high brittleness.

To compare the obtained result of this article, the results in [12], [13], which have the same direction in the solution, are selected. After comparison, it was found that the results of the works [12], [13] are much more expensive than the option proposed in our article. In [12], [13], the additional coating is enhanced by the chemical deposition method in the presence of carbon nanotubes in the hydrogen evolution reaction. This method is 40% more expensive, and the reliability of the protective coating is slightly more than 7% of the one proposed by our article. For serial application in practice, the method proposed in this article is more acceptable.

5. CONCLUSIONS

- 1) Chemical-thermal treatment of iron-based baked compositions with carburizing elements after cementation increases their mechanical properties and, in particular, resistance to corrosion.
- 2) In the chroming process, the highest concentration of chromium is observed on the surface, with an increased degree of material carbonization. It is established that, regardless of the initial cementation conditions, the carbide coatings exhibit the same phase composition; $(Cr,Fe)_{23}C_6$, $(Cr,Fe)_7C_3$. The amount of chromium in the intermediate zone of cemented materials is different.
- 3) Correspondences to the basic laws of the effect of porosity on the formation of boride coatings in iron are also typical for iron-carbon materials.
- 4) However, in iron-carbon compositions, the total depth of the boride layer changes less when the ratio changes, and the depth of the whole layer of borides is slightly less than that of iron.
- 5) Chemical-thermal treatment of iron-based baked compositions with carburizing elements after cementation increases their mechanical properties and, in particular, resistance to corrosion.
- 6) The effects of temperature, saturation time and content of saturation mixture on corrosion of wrought iron and iron-chromium composition subjected to cementation and subsequent chroming, chromosilicization and chromotitancing are expressed by appropriate regression equations.
- 7) Boride coatings on iron-chromium alloys have lower corrosion resistance than coatings on iron, which is probably due to the relatively higher brittleness of chromium-doped borides.

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