



REGULAR ARTICLE

Structure and Properties of Multilayer Coatings Obtained by Chromotitanizing

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This paper presents the results of studies of the structure, chemical composition, and microhardness of a complex chromium and titanium coating obtained by diffusion metallization of steel DIN C80W1. The coating was applied in a specially designed reaction chamber at a temperature of 1050 °C for 4 hours in a closed reaction space at a reduced pressure of the active gas phase. The starting components used were powder of chromium, titanium and carbon tetrachloride as activators. The resulting protective coating consists of three sequentially arranged carbide layers: a chromium carbide Cr₇C₃ layer adjoins the base, and above are a layers of Cr₂₃C₆ and TiC. This sequence of carbide layers provides a gradual increase in microhardness, which in turn has a positive effect on the material's wear resistance. The coatings proposed in this paper are recommended to protect products operating under high loads and wear conditions.

Keywords: Chromium, Titanium, Carbide, Multilayers coating.

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1. INTRODUCTION

The development of technology requires the search for new materials and the improvement of existing ones. That is especially true for the service life of machine parts and tools. Therefore, one of the main tasks of modern materials science is to study methods for improving the properties of surface layers of metals and alloys. One of the most effective methods of surface hardening of metals and alloys is chemical heat treatment (CHT). However, traditional CHT processes do not always satisfy the modern requirements for machine and tool parts [1].

Multilayer film materials (see, for example, [2-6]) and diffusion coatings based on transition metal carbides have a high range of physical and chemical properties, and their application to the surface of steels makes it possible to significantly improve the performance of machine and tool parts [5, 7, 8].

Recently, refractory compounds have been widely used as protective coatings. These coatings significantly increase the operational properties of mechanism parts and the tool's service life in conditions of sliding friction. Products with such coatings work in conditions of high temperatures and aggressive environments. The operating conditions of the product are decisive in choosing the optimal phase composition of the coating and the technology of its application. In addition, the properties and characteristics of the base and coating material, such as strength, hardness, coefficients of thermal expansion, heat resistance, etc., must be considered. Currently, there are many methods for applying various coatings to products. Each of them, having certain features, provides coatings that differ in

composition, structure, density, and other characteristics [9].

Various product sand tools' increasingly complex operating conditions for material processing require further improvement of coating properties. Therefore, one of the ways to improve the performance characteristics of coated products is to improve the physical, mechanical, and chemical properties of coatings by alloying them with various elements, i.e., creating multicomponent coatings of different structures – single and multilayer [10].

Given the above, this work aimed to study multilayer carbide coatings' structure and chemical composition. These coatings were obtained under different temperature and time conditions of saturation.

2. MATERIALS AND METHODS

The chromium titanium plating was carried out in one technological cycle in an installation based on a shaft electric resistance furnace [11].

Samples (15 × 10 × 5 mm) were made from steel DIN C80W1 with the following composition: 0.79% of C, 0.26 % of Si, 0.20 % of Mn, 0.20 % of Cr, not more than 0.018 % of S, not more than 0.025 % of P, not more than 0.20 % of Cu, and not more than 0.20 % of Ni.

The samples were degreased in one of the organic solvents (carbon tetrachloride or ethyl alcohol) before coating. Powders of technically pure titanium and chromium, activator (carbon tetrachloride) were used as starting reagents. The saturation process is implemented in several successive stages. The powder of the saturating element (chromium) is placed in the

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cup of a specially designed device (insert). After preparation, samples are fixed in the insert. Samples and powder do not come into contact.

Charcoal, inserted with samples and powder, are placed in the reaction chamber (retort). A vacuum seal is provided between the retort body and the lid to ensure the retort is airtight and has the required vacuum. The upper part of the chamber is cooled by water circulating in a sleeve welded to the body, which prevents the vacuum seal from burning at elevated temperatures and depressurizing the chamber. After sealing, the reaction chamber is vacuumed to 10-20 Pa using a vacuum pump. The pressure in the reaction chamber is measured using a thermocouple vacuum gauge. In parallel with this process, the retort is transferred to an oven heated to a temperature of 1050 °C. When the above pressure is reached, the vacuum pump is switched off. Carbon tetrachloride is injected in the required amount from a special container through a vacuum valve when the furnace is heated to the saturation temperature. As a result, chlorine interacts with metal powder and the formation of chlorides of saturating elements. Chlorides are suppliers of carbide-forming metals on the surface of samples.

After the saturation process with the first element (chromium) is completed, the powder of the second saturating element (titanium) and an additional portion of carbon tetrachloride are fed into the working space from the cone gate, and the surface is saturated with the second element. The furnace is switched off, and the retort is transferred to a cooling cup. Filters are provided in the system to prevent contamination of the environment and the vacuum pump by oil or chemical reaction products. It should be noted that the saturation process is implemented in one technological cycle without depressurization of the reaction chamber. The results of experimental studies have shown that the optimal saturation time for the first and second stages is 2 hours.

The phase composition and main characteristics of carbide coatings (thickness, microhardness, microbrittleness, etc.) are determined by the temperature and time conditions of the saturation process and the amount of the initial reagents.

Ultima-IV («Rigaku Corporation» Tokyo, Japan) using monochromatic CuK α radiation. Microhardness and coating thickness is determined according to the standard ASTM E92-82 (2003) by pressing on the device LHSV-1000Z (Chongqing Leeb Instrument Co., Ltd, Chongqing, China). Indenter is a quadrangular diamond pyramid with an angle at the top of 136°. X-ray spectral analysis was performed on a Jeol JSM-6490LV scanning electron microscope. Optimization elements Ti (10 kV), Co (20 kV), and other elements are set in the software database.

3. RESULTS AND DISCUSSION

Complex carbide coatings based on titanium and chromium have various properties determined by the type and composition of the phases and structure formed during the saturation process. Studying the phase and chemical composition allows us to establish

specific changes on the surface of the treated products and their core during the CHT process.

According to the X-ray diffraction analysis of coatings obtained at different temperature and time conditions of saturation, the main phases of the surface of chrome steels are chromium carbides Cr $_7$ C $_3$ and Cr $_{23}$ C $_6$, and titanium carbide TiC.

The complex saturation of two carbide-forming elements leads to the formation of a multilayer structure involving carbides of the original metals. When chromium titanium is applied to the surface of carbon steels, a two-layer coating is formed consisting of a layer based on chromium carbide (Cr $_7$ C $_3$ + Cr $_{23}$ C $_6$) and titanium carbide TiC, which is located on the outside of the coating.

The results of the XRD analysis of the resulting coating on steel DIN C80W1 are shown in Table 1.

Table 1 – Phase composition of the coating obtained by sequential chromotitanizing in one technological cycle*

Material	Phase composition	The period of crystalline lattice, nm
Steel DIN C80W1	TiC	$a = 0.4328$
	Cr $_{23}$ C $_6$	$a = 1.0663$
	Cr $_7$ C $_3$	$a = 0.6982$; $b = 1.2184$; $c = 0.4510$

*– total saturation time 4 hours, temperature 1050 °C

It is known that at the chrome plating stage, a coating based on Cr $_7$ C $_3$ is formed. The latter dissociates at the titanium stage, giving up its carbon to titanium to form Cr $_{23}$ C $_6$ carbide.

According to the results of metallographic analysis of coatings on steel DIN C80W1, after saturation with chromium for 2 hours and titanium for 2 hours at a temperature of 1050°C, a carbide coating with a total thickness of about 20 μ m is formed. Three zones are visually observed (Fig. 1).

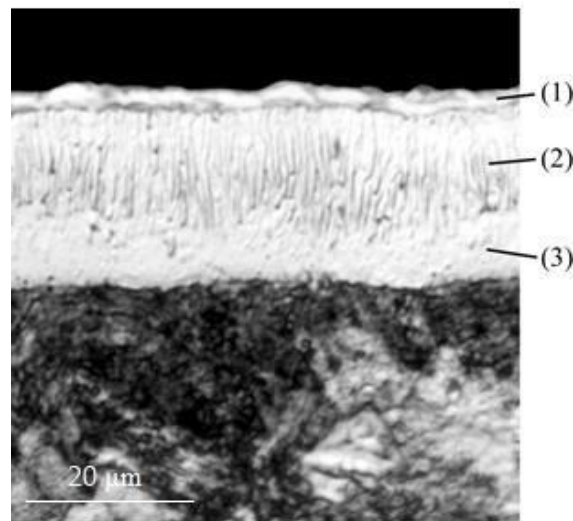


Fig. 1 – Microstructure of steel DIN C80W1 after chromotitanizing; (temperature – 1050 °C, time – 4 hours). 1 – titanium carbide TiC; 2 – chromium carbide Cr $_{23}$ C $_6$; 3 – chromium carbide Cr $_7$ C $_3$

The performance properties of carbide coatings depend on the phase composition and the content of carbon and alloying elements. The data on the distribution of elements in the coating thickness allows us to judge the diffusion processes of elements in the coating and is of some scientific interest.

According to the research results (Fig. 2), the surface contains a zone composed of titanium and carbon, with a carbon concentration of 20.6-22.3 % (wt %), corresponding to titanium carbide TiC. Iron (1.7-2.1 wt %) and chromium (1.3-1.9 wt %) are dissolve in carbide.

The chromium carbides layer consists of two zones: Upper Cr_{23}C_6 and lower Cr_7C_3 . The Cr_{23}C_6 carbide is alloyed with iron in 11.4-17.1 wt %, while the Cr_7C_3 carbide contains slightly more than 23.8-25.2 wt %. It indicates that, together with the base's carbon, the base's iron diffuses into the coating. At a distance of 5-6 microns from the carbide layer in the transition zone, the chromium content is 2.6-2.7 wt %.

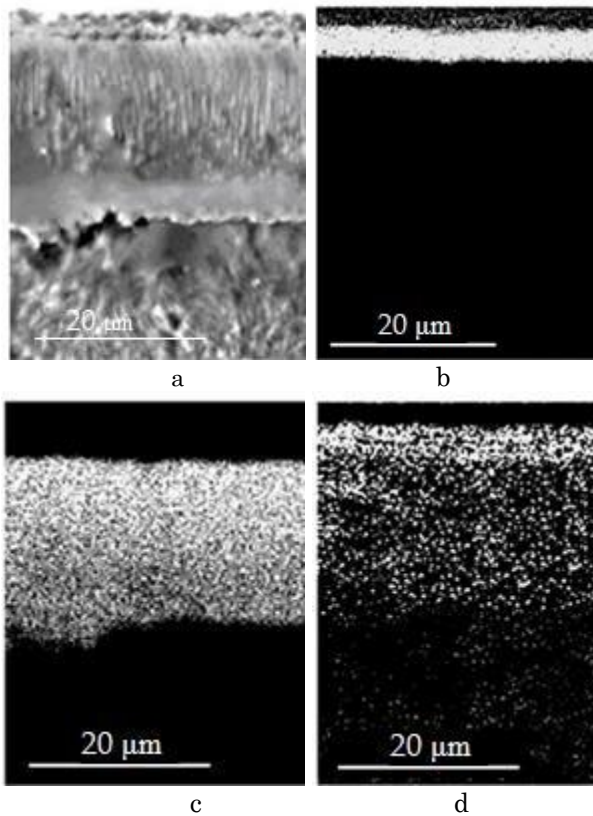


Fig. 2 – Microstructure of steel DIN C80W1 in reflected electrons (a); distribution of elements along the plane of the section in the characteristic X-ray radiation of titanium (b), chromium (c) and carbon (d) after chromotitanizing (temperature – 1050 °C, time – 4 hours)

The microhardness of the complex coating layers on steel DIN C80W1 during chromotitanizing is shown in Table 2.

Immediately adjacent to the base is a layer of chromium carbide C_7C_3 with a thickness of 5-6 μm and a microhardness of 16 GPa; above it is a layer with a pronounced dendritic structure Cr_{23}C_6 with a thickness of 9-10 μm and a microhardness of 17 GPa. Outside is a layer of TiC carbide with a thickness of 4-5 μm and a microhardness of 32 GPa.

Table 2 – Phase composition, thickness and microhardness of the protective coating on steel DIN C80W1 after chromotitanizing (temperature – 1050 °C, time – 4 hours)

Phases	Coating thickness, μm	Microhardness, GPa
TiC	4.0 – 5.0	32.0
Cr_{23}C_6	9.0 – 10.0	17.0
C_7C_3	5.0 – 6.0	16.0

The lower microhardness of TiC titanium carbide in complex coatings compared to known single-component coatings is obviously due to the lower carbon content in the carbide. In addition, substitution impurities have a significant impact on microhardness.

When applying carbide coatings, the pattern of change in their thickness with the process temperature follows an exponential law.

An increase in the process temperature is accompanied by an increase in the intensity of diffusion processes and the activity of the gas phase. As a result, under equal saturation conditions, the thickness of carbide coatings increases the higher the process temperature. However, too high temperatures can lead to overheating of the saturated products' material and the reaction chamber itself.

Therefore, the optimum recommended temperature range for saturating steels with carbide-forming elements (Ti and Cr) is 1000-1050 °C.

The dependence of the coating thickness on the saturation time is close to parabolic (Fig. 3).

The maximum growth rate of coatings is observed in the first hours of saturation. Over time, the speed gradually decreases somewhat. Such changes in growth kinetics are caused by several factors commensurate to the diffusion rate. The chemical reaction on the saturable surface is one such factor. Thus, during the first hours of saturation, carbon, which is part of the gas phase, plays a significant role in the formation of the coating.

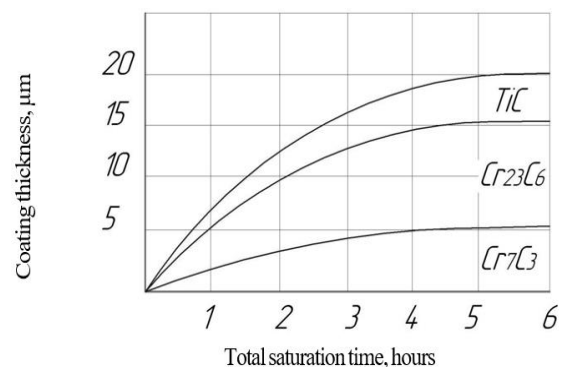


Fig. 3 – Effect of the duration of chromotitanizing of steel DIN C80W1 on the thickness of carbide coatings, $T = 1050$ °C

Analyzing the data obtained, it is advisable to carry out the rational saturation time with two components within 3-4 hours (2 + 1 and 2 + 2 hours, respectively), which makes it possible to obtain coatings with optimal thickness and microhardness. Further saturation leads to a relatively slight increase in coating thickness while overheating steels and irrational energy consumption occur.

4. CONCLUSIONS

The paper confirms the possibility of producing multicomponent coatings in one technological cycle, which undoubtedly has a positive effect on the operational properties of the coating and allows for increasing the process productivity compared to the sequential application of individual layers.

Metallographic analysis has shown that carbide coatings, after etching appear as a light zone with a straightforward interface with the substrate. Moreover, after chromotitanizing of steel DIN C80W1 should be carried out at a temperature of 1000-1050 °C, with a saturation time of 2 hours of chroming + 2 hours of titanizing, and a coating thickness of 18-20 microns, the coating consists of 3 separate zones with microhardness gradually increasing from the base to the surface.

The results of X-ray diffraction analysis showed that a layer of chromium carbide Cr₇C₃ is directly

adjacent to the base, above which is a layer of chromium carbide Cr₂₃C₆, and a layer of TiC is located outside.

The thickness of the Cr₇C₃ chromium carbide layer is approximately 5 μm and has a microhardness of 16 GPa; the Cr₂₃C₆ carbide layer reaches a thickness of 10 μm and has a microhardness of 17 GPa. The titanium carbide layer is 5 μm thick and has a microhardness of up to 32 GPa.

Based on the study of the phase and chemical composition and known results regarding the operational properties of coated steels, rational temperature and time parameters of the processes were proposed. Accordingly, chromotitanizing of steel DIN C80W1 should be carried out at a temperature of 1000-1050 °C, with a saturation time of 2 hours of chroming + 2 hours of titanizing, and a coating thickness of 18-20 microns.

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Структура та властивості багат шарових покриттів, отриманих хромотитануванням

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У роботі наведено результати досліджень структури, хімічного складу та мікротвердості комплексного хром-титанового покриття, отриманого методом дифузійної металізації сталі DIN C80W1. Покриття наносили у спеціально розробленій реакційній камері при температурі 1050 °C протягом 4 годин у закритому реакційному просторі при зниженому тиску активної газової фази. В якості вихідних компонентів використовували порошок хрому, титану і чотирихлористий вуглець. Отримане захисне покриття складається з трьох послідовно розташованих карбідних шарів: до основи прилягає шар карбіду хрому Cr₇C₃, а вище - шари Cr₂₃C₆ і TiC. Така послідовність карбідних шарів забезпечує поступове підвищення мікротвердості, що в свою чергу позитивно впливає на зносостійкість матеріалу. Покриття, запропоновані в цьому дослідженні, рекомендовані для захисту виробів, які працюють в умовах високих навантажень і зношування.

Ключові слова: Хром, Титан, Карбід, Багат шарові покриття.