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REGULAR ARTICLE

Structure and Properties of Diffusion Titanium Coatings Based on Hard Alloys

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This study presents the results of experimental investigations into the structure, phase composition, and microhardness of diffusion titanium coatings formed on the surface of hard alloys by diffusion metallization. The titanizing process was carried out in a specially designed reaction chamber at 1050°C for 2 – 3 hours under reduced pressure of the active gas phase in a closed system. Technically pure titanium powder, a carbon-containing additive, and carbon tetrachloride (CCl_4) as an activator were used as the initial components. The obtained coatings exhibited a multilayer structure consisting of titanium carbide (TiC) and intermetallic compounds of the CoTi type. The effects of temperature–time parameters and carbon content on the coating thickness, phase composition, and microhardness were systematically analyzed. It was found that under optimal titanizing conditions, a TiC layer 4.0 – 5.0 μm thick with a microhardness of up to 34.0 GPa is formed, resulting in a significant improvement in the wear resistance of hard alloy tools. The findings of this study can contribute to the advancement of diffusion carbide coating technologies for applications in mechanical engineering and tool manufacturing.

Keywords: Layer, Diffusion coating, Carbide, Microhardness

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1. INTRODUCTION

The development of modern mechanical engineering, aviation, energy, and tool industries is closely linked to improving the operational reliability and service life of components and assemblies that operate under conditions of intensive wear, elevated temperatures, and aggressive environments. One of the most effective approaches to addressing this challenge is the application of protective coatings [1, 2] and nanostructural films [3, 4] that significantly enhance the performance of tool materials.

Tool materials such as high-speed steels, hard alloys, ceramics, and superhard composites are widely used in the manufacture of cutting, forming, and measuring tools. The main factor limiting their efficiency is the rapid wear of the working surfaces during operation. In particular, cutting tools are susceptible to adhesive, abrasive, and diffusion wear resulting from severe thermomechanical loads in the cutting zone [5]. Conventional heat treatment and alloying methods do not always ensure the required combination of hardness, wear resistance, and thermal stability. In this context, diffusion coatings formed by saturating the surface layer with elements that create solid phases with high hardness and heat resistance are of particular significance [5, 6].

Diffusion saturation methods have been known for more than a century; however, in recent decades they have undergone significant advancement due to improvements in technological processes and the development of new chemical systems. Among these methods, cementation, nitriding, boriding, siliconizing, chromizing, and titanizing are the most widely used [7, 8]. These processes enable the formation of hard carbide, nitride, boride, or silicide phases on the surfaces of steels and alloys, thereby substantially increasing their hardness, wear resistance, and heat resistance.

Of particular importance are boride and carbide diffusion coatings, which provide exceptionally high hardness and wear resistance, greatly surpassing those of conventionally alloyed tool steels [9].

In addition, combining diffusion processes with physical and chemical vapor deposition method (PVD and CVD) enables the formation of multilayer coatings with gradient properties, providing an even higher level of operational reliability [10].

Of both scientific and practical interest is the study of the formation mechanisms, structure, and properties of diffusion coatings on tool materials, as well as the optimization of their application parameters. Such studies not only extend the service life of tools but also

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reduce production costs by minimizing downtime associated with the replacement of worn equipment [11].

Therefore, the relevance of investigating diffusion coatings on tool materials stems from the need to improve their operational performance, develop optimal processing technologies, and introduce new, highly efficient surface hardening methods into industrial practice.

2. MATERIALS AND METHODS

Diffusion titanizing was performed in a specially designed setup based on a shaft-type electric resistance furnace [12, 13]. Hard alloy plates of grades VK8 and T15K6 were used as substrates for the coating. Prior to processing, the samples were cleaned of surface contaminants by degreasing in ethyl alcohol. Technically pure titanium powder, a carbon-containing additive (charcoal), and an activator – carbon tetrachloride – were used as the initial reagents.

The mechanism of saturation with a single carbide-forming component proceeds as follows. Titanium powder was placed in a special container, and the prepared samples were fixed within it to prevent direct contact with the powder. Charcoal was loaded into the reaction chamber (retort), after which the insert containing the samples and powder was placed inside. To ensure tightness and maintain the required vacuum level between the chamber body and the retort lid, a vacuum seal was applied. The upper part of the chamber was water-cooled through a special jacket welded to the housing, which prevented overheating and degradation of the seal during high-temperature operation.

After sealing, the system was evacuated to a pressure of 10.0 – 20.0 Pa using a vacuum pump, and the pressure was monitored with a thermocouple vacuum gauge. Simultaneously with evacuation, the retort was inserted into a furnace preheated to 1050°C. Once the required pressure was reached, the pump was switched off. During heating, a controlled amount of carbon tetrachloride was introduced into the saturation zone from a special container through a vacuum valve. As a result, chlorine reacted with titanium powder to form titanium chlorides, which acted as the source of the carbide-forming metal for the surface of the samples.

After completion of the saturation process, the furnace was switched off, and the retort was transferred to a cooling vessel. To prevent contamination of the environment and the vacuum pump with reaction products or lubricants, additional filters were installed in the system.

The phase composition and main characteristics of the carbide coatings (thickness, microhardness, microbrittleness, etc.) were determined by the temperature – time parameters of the saturation process and the quantity of the starting reagents.

X-ray diffraction (XRD) analysis of the samples was performed using a DRON-UM-1 diffractometer in Cu Kα-radiation ($\lambda = 0.1541841$ nm). The X-ray diffraction patterns were interpreted, and the lattice periods of the obtained phases were determined using the PowderCell 2.4 software package according to the Rietveld method (complete profile analysis). The obtained diffractograms were compared with the reference diffractograms in the ICDD PDF-2 diffractogram database.

Microhardness and coating thickness is determined according to the standard GOST 9450-60 by pressing on the device "PMT-3". Indenter is a quadrangular diamond pyramid with an angle at the top of 136°. The characteristics of microhardness are determined as follows, kgf/mm²:

$$H_\mu = 1{,}854(P/d^2) \quad (1)$$

where P – load, g and d – imprint diagonal, μm.

3. RESULTS AND DISCUSSION

Titanium-based carbide coatings possess specific properties determined by the type and composition of the phases and the structure formed during the saturation process.

The study of the phase composition makes it possible to identify the changes that occur on the surface of treated samples and in their core during chemical heat treatment (CHT).

The maximum thickness of titanium carbide–based coatings on the surface of hard alloys is achieved at a carbon-containing additive concentration of 0.015 – 0.025 kg/m² (Fig. 1).

At lower charcoal contents in the initial reagent mixture, the formation of intermetallic compounds is observed in the coatings, which is attributed to an insufficient carbon supply for the formation of a carbide layer at the final stage of the process.

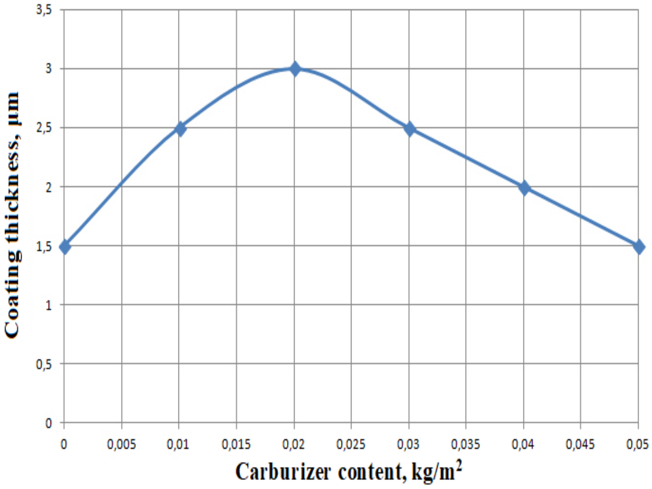

Fig. 1 – Dependence of the thickness of the titanium carbide coating on the VK8 hard alloy on the carbonaceous additive content in the starting reagent mixture (temperature – 1050 °C; time – 2 h; CCl_4 – 0.4 L/m³)

An excessive increase in the carburizer content leads to the formation of a layer of sooty carbon on the surface of the hard alloy, which in turn inhibits the saturation process.

The results of X-ray diffraction (XRD) analysis (Fig. 2) of the VK8 alloy after titanizing show that a coating based on titanium carbide (TiC) is formed on the surface of the hard alloy.

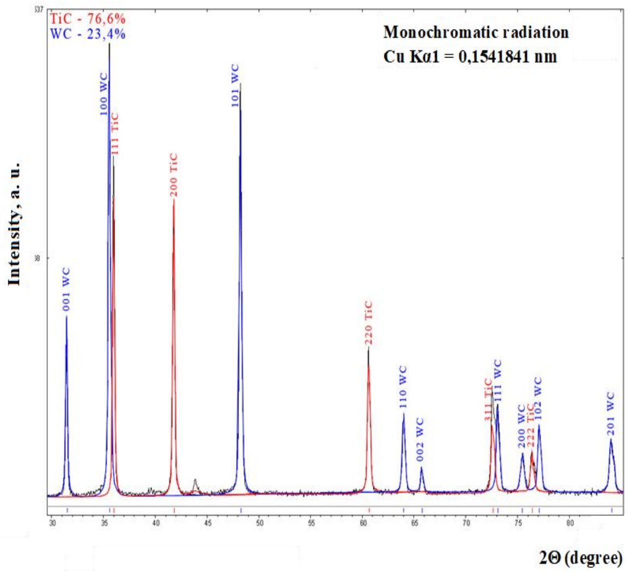

Fig. 2 – X-ray diffractogram of the surface of VK8 hard alloy after titanizing: temperature – 1050°C; time – 2 h; CuKα radiation, wavelength – 0,1541841 nm

The lattice parameters of TiC crystals are 0.4315 nm for VK8 and 0.4318 nm for T15K6. In some cases, with prolonged saturation (at a temperature of 1050°C and a duration of more than 3 h), a layer of the CoTi intermetallic compound is formed above the TiC layer. This phenomenon is apparently caused by insufficient carbon content at the final stage of carbide coating formation. As a result, cobalt from the substrate diffuses through the carbide layer to the surface, where it forms the intermetallic compound. The deficiency of carbon in this case is also confirmed by the presence of a Co_3W_3C zone located directly beneath the TiC layer.

The operational properties of carbide coatings depend not only on their phase composition but also on the carbon content and the concentration of alloying elements. Data on the elemental distribution across the coating thickness provide insight into the diffusion processes within the coating and are of considerable scientific interest. In this study, the chemical composition of carbide coatings on hard alloys was analyzed using micro–X-ray spectral analysis.

After titanizing, a coating containing Co and Ti is formed on the surface of the T15K6 hard alloy, which evidently corresponds to the CoTi intermetallic compound (Fig. 3).

The thickness of this intermetallic layer is insignificant and a titanium carbide zone is located directly below it, as evidenced by the intense peaks of the carbon and titanium lines. After titanizing, a light-colored TiC layer with a distinct boundary to the substrate is observed on polished cross-sections after etching. The formed layer, as noted earlier, corresponds to titanium carbide (TiC). Its thickness depends on the duration and temperature of the saturation process, as well as on the carbon content and alloying elements in the base material.

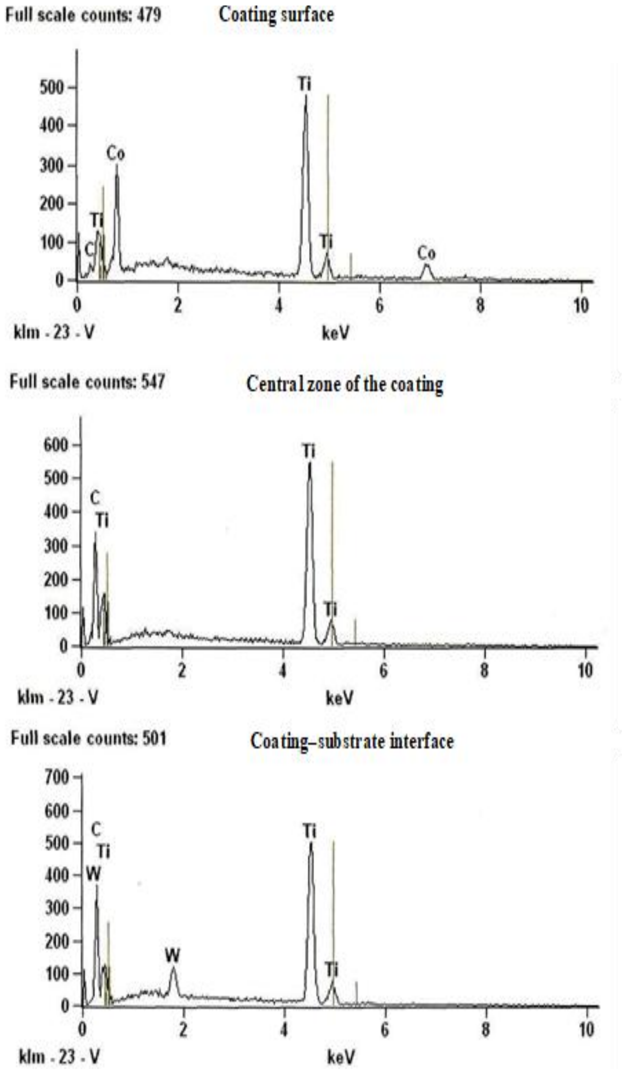

Fig. 3 – Spectral curves of the surface layer of the T15K6 alloy after titanizing (temperature – 1050°C; time – 3 h): (a) coating surface; (b) central zone of the coating; (c) coating–substrate interface

For the T15K6 hard alloy, the coating has a thickness of approximately 3.0 – 5.0 μm. When the saturation time is increased from 2 to 3 hours, the overall layer thickness increases; however, a CoTi intermetallic compound forms on the surface (Fig. 4).

As shown in the microstructure (Fig. 5), after titanizing for 2 hours, neither intermetallic phases nor a carbon-depleted sublayer are observed, which positively affects the coating's properties.

Table 1 presents the microhardness and thicknes of carbide coating layers on hard alloys during titanizing.

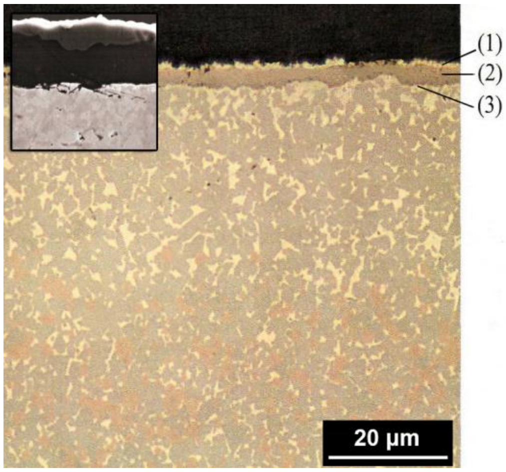

Fig. 4 – Microstructure of T15K6 hard alloy after titanizing (temperature – 1050°C; time – 3 h): 1– intermetallic CoTi; 2– titanium carbide TiC; 3 – carbide Co_3W_3C

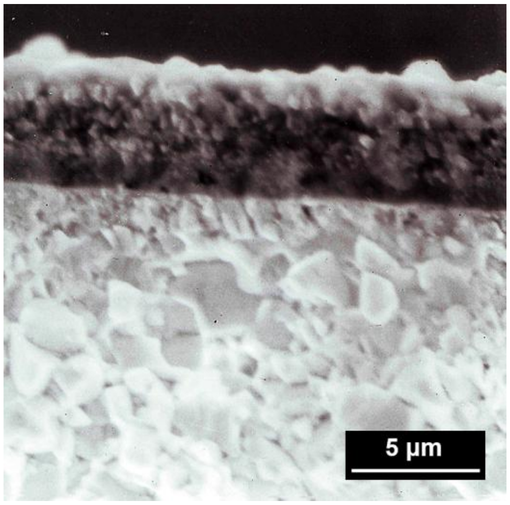

Fig. 5 – Microstructure of the fracture of T15K6 hard alloy after titanizing (temperature – 1050°C; time – 2 h)

When applying carbide coatings, the dependence of their thickness on the process temperature follows an exponential law.

Table 1 – Phase composition, microhardness and thickness of diffusion coatings

Type of processing	Alloy grade	T, °C; Saturation time, hours	Phases	Coating thickness, μm	Microhardness, GPa
Titanizing	VK8	1050; 2	TiC	4.0 – 5.0	33.0
	T15K6	1050; 2	TiC	4.5 – 5.0	34.0

An increase in process temperature enhances the intensity of diffusion processes and the activity of the gas phase. Consequently, under identical saturation conditions, the thickness of the carbide coatings increases with higher process temperatures. However, excessively high temperatures may lead to overheating of both the material being treated and the reaction chamber.

4. CONCLUSIONS

The conducted study confirmed the feasibility of forming carbide coatings, which significantly enhance the performance of tool materials and contribute to the optimization of their manufacturing processes.

Metallographic analysis revealed that, after etching the cross-section, the carbide coatings appear as a light zone with a well-defined boundary with the substrate. The temperature–time parameters of the process have a decisive effect on both the thickness of the formed layer and its phase composition.

X-ray structural analysis indicated that a layer of titanium carbide (TiC) is directly adjacent to the substrate. If the saturation time is increased to three hours or more, a CoTi intermetallic form above it, while a carbon-depleted zone containing the Co_3W_3C phase develops below it.

The average thickness of the TiC layer is 4 – 5 μm, with a microhardness of up to 34.0 GPa.

Based on the analysis of phase and chemical composition, and taking into account known data on the performance of coated hard alloys, rational temperature–time regimes for the saturation process were established.

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Структура та властивості дифузійних титанових покриттів на основі твердих сплавів

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У роботі представлено результати експериментальних досліджень структури, фазового складу та мікротвердості дифузійних титанових покриттів, сформованих на поверхні твердих сплавів методом дифузійної металізації. Процес титанування здійснювався у спеціально розробленій реакційній камері при температурі 1050 °C протягом 2 – 3 годин у замкненому реакційному просторі при зниженому тиску активної газової фази. Як вихідні компоненти використовували порошок технічно чистого титану, вуглецевмісну добавку та чотирихлористий вуглець як активатор. Встановлено, що отримані покриття мають багатошарову структуру, яка включає карбіди титану (TiC) та інтерметаліди типу CoTi. Показано вплив температурно-часових параметрів процесу та вмісту вуглецю на товщину, фазовий склад і мікротвердість покриттів. Визначено, що при оптимальних умовах титанування утворюється шар TiC товщиною 4.0 – 5.0 мкм із мікротвердістю до 34.0 ГПа, який забезпечує суттєве підвищення зносостійкості твердосплавного інструменту. Отримані результати можуть бути використані для вдосконалення технологій нанесення дифузійних карбідних покриттів у машинобудуванні та інструментальному виробництві.

Ключові слова: Титанування, Дифузійні шари, Карбідні покриття, Мікротвердість.