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FUNCTIONAL COATINGS AND SURFACE TREATMENT

Plasma Deposition of Ti–C–N Coatings in Air

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Abstract—The possibility of production of Ti-, N-, and C-containing superhard coatings on a metal substrate by a plasma-dynamic method in air is studied. The coating is deposited in the time of one short operating cycle of a magnetoplasma accelerator under the impact of a high speed electric discharge Ti-containing plasma jet on the substrate surface. Formation of TiN and TiCN nanostructured layers in the coating structure is ascertained with the help of the SEM and X-ray diffraction methods and it leads to the coating hardness increasing. Formation of a gradient layer of mixed material at the coating/substrate interface is found to occur under the action of a high-enthalpy plasma jet on a metal substrate. The value of hardness is not constant throughout the coating thickness, and ultrahigh nanohardness values >20 GPa were obtained for the subsurface layer and substrate/coating interface region. The mean value of hardness of the coating is 16.2 GPa. The coating produced has good adhesion with the substrate.

Keywords: coaxial magnetoplasma accelerator, titanium nitride, titanium carbonitride, superhard coatings

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INTRODUCTION

In [1], the possibility of the direct plasma-dynamic synthesis of nanodispersed titania in a hypervelocity jet of titanium-containing electric-discharge plasma flowing out to the air atmosphere was shown. The jet is generated using a pulse (up to 0.001 s) high-current (~100 kA) coaxial magnetoplasma accelerator (CMPA) [2] equipped with a titanium central electrode and electrode stem equipped with a cylindrical accelerator channel (AC). This method is considered direct, because titanium particles, which are formed during the surface erosion of AC, enter the current shell of discharge, where they are transformed into the plasma state and released from AC to the reactor chamber with the air atmosphere under normal pressure as a hypervelocity jet. The experiments showed that oxidative processes predominate even at low oxygen content in the gas medium, and a nanodisperse product consisting almost completely of polymorphous crystal phases of titania (40% anatase and 60% rutile) is synthesized.

PROCEDURE OF EXPERIMENT

When the planar metallic barrier is mounted on the surface of the target (substrate) along the plasma jet flow, a superhard titanium-containing coating with large thickness is deposited. The coatings were deposited using CMPA equipped with titanium electrodes; the parameters of the accelerator were the following: energy storage capacity C = 48 mF, charge voltage U_{ch} = 2.5 kV, accelerator channel length l_{AC} = 280 mm, diameter d_{AC} = 13 mm, distance from the chip of AC to the substrate s = 400 mm, and pressure in the reactor chamber P_0 = 1.0 atm.

The microstructure of the specimens with the deposited coating was investigated on a JEOL-840 scanning electron microscope; X-ray phase analysis (XPA) was carried out using a Shimadzu XRD 7000 diffractometer in Cu K_α radiation. The X-ray patterns were processed using the Powder Cell 2.4 program of full-profile analysis and the PDF4+ structural database.

The mechanical properties of the coatings were studied using a Nano-Hardness Tester nanohardness meter (CSEM instruments) at the load of 300 mN on indenter.

RESULTS AND DISCUSSION

In Fig. 1, surface micrographs of the cross section of a steel specimen with Ti-containing coating are given. It is clear that the coating thickness varies from ~300 to ~600 μm in the field of view. According to the change in the image contrast, one can distinguish three main layers of the coating (Fig. 1a).

In Fig. 2, the profile of the change in nanohardness $H(x)$ along the depth of the specimen is given. The data indicate a fairly high strength of the material of the coating. Ultrahigh values of nanohardness exceed-

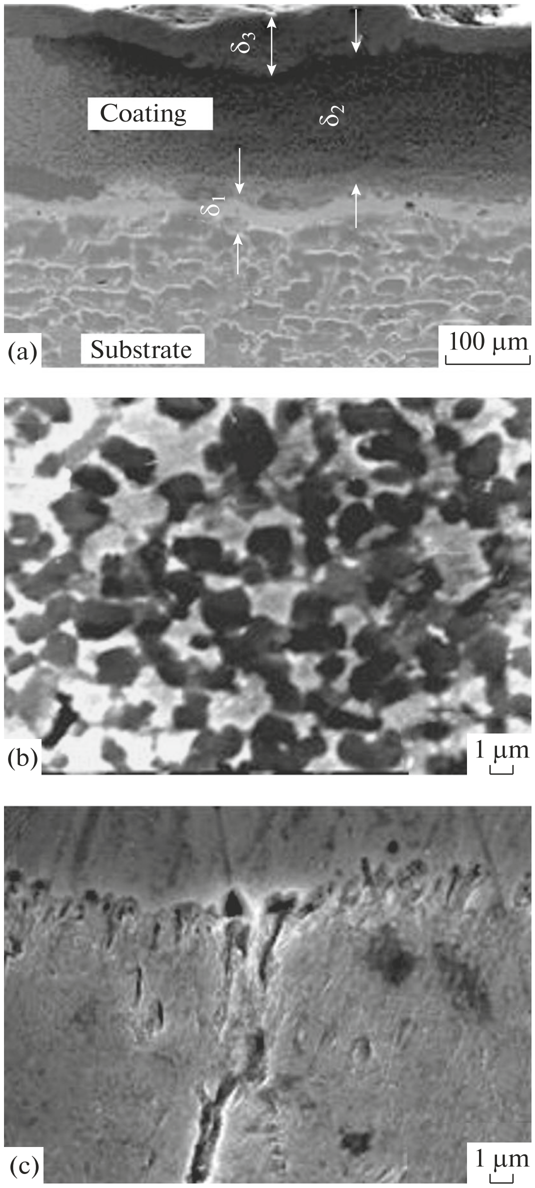

Fig. 1. SEM images of cross section of steel substrate with Ti-containing coating: (a) overall image, (b) microstructure of the intermediate coating layer, and (c) channels of superdeep penetration of microcumulative plasma jets.

ing 20 GPa were obtained on the surface layers of the coating with the thickness δ_1 and in the regions with the thickness of δ_3 near the substrate (Fig. 1a). The main layer of the coatings with the thickness δ_2 has an intermediate hardness value H = 16.2 GPa, which agrees with the data from [3, 4].

Analysis of the X-ray patterns (Fig. 3) obtained from the surface of the coating and the boundary layer between the coating and the substrate (surface of the chip of coating from the substrate) showed that the composition material of the titanium-containing coating contains four crystal phases (Table 1).

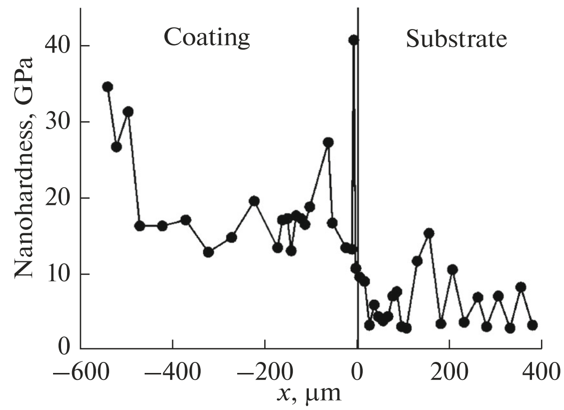

Fig. 2. Nanohardness H depth distribution for specimen with Ti-containing coating.

High hardness of the surface and boundary layers of the coating is caused by the formation of superhard crystal phases based on titanium, nitrogen, and carbon during deposition. In the surface layer of the coating with the thickness δ_3, the content of nitride phases with the predomination of c-TiN is slightly higher than in the boundary layer δ_1, where an elevated concentration of superhard c-Ti_2CN is recorded though, which leads to the "burst" of hardness values with the penetration of the indenter into the grains of this phase [5]. Carbon, which is necessary for the formation of the c-Ti_2CN phase, was used as a conducting material for the initiation of the discharge in the plasma structure formation channel of CMPA, from where it entered the plasma jet.

Judging by the mean size of the coherent scattering regions (CSR), the formation of the nanostructure in the layers of the coating occurs owing to the fast cooling of the melt due to the heat withdrawal upon the contact with the substrate and the gas medium. The presence of crystal iron c-Fe in the material of the coating and, in particular, in the near-boundary layer is caused by the mutual hydrodynamic mixing of the materials of the coating and the substrate upon high-energy exposure of the plasma jet on the surface of the substrate [6]. A slight decrease in the hardness of the main intermediate layer of the coating δ_2 can be rationalized by the decrease in the total content of nitride phases and agglomeration of grains in this layer [7], which occurs because of relatively slow cooling (Fig. 1b).

Thus, during the exposure of the high-enthalpy plasma jet on the metal substrate, a boundary layer is formed, in which the materials of the coating and the substrate mix with each other. The concentration of Ti in the boundary layer from the substrate gradually decreases, which results in the decrease in its hardness (Fig. 4); in this case, there is no clear boundary between the coating and the substrate (Fig. 1a).

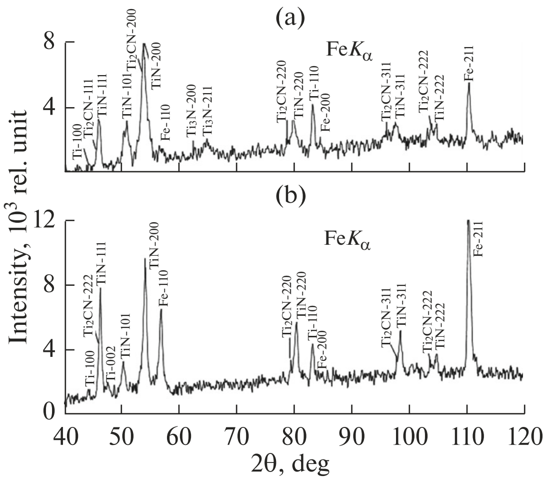

Fig. 3. XRD patterns of Ti-containing coating on steel substrate: (a) the surface layer of coating and (b) coating/substrate interface layer.

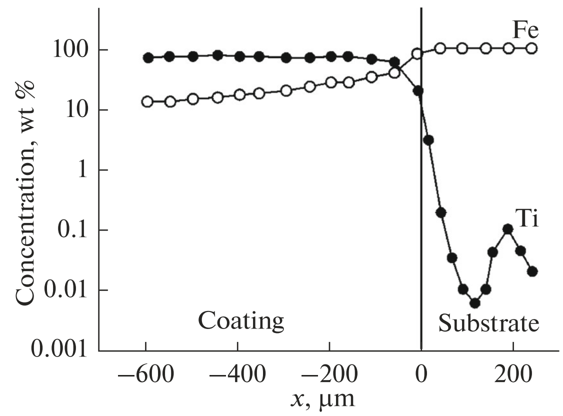

Fig. 4. Concentration depth distribution of the main elements (Fe, Ti) in coating and steel substrate boundary layer.

The hardness of the transient layer approaches the hardness of the starting material of the substrate only at the depth of several hundred microns. The form of the change in nanohardness and the microstructural features of this transient layer indicate that the reason for its formation is impact-wave processes which arise during hypervelocity exposure of the plasma jet on the surface of the substrate. High local values of nanohardness of this layer are achieved owing to the impact layer-by-layer thickening of the materials, as well as the incorporation of superhard particles, which are included in the plasma jet, into the structure of the material of the substrate along grain boundaries (Fig. 4) or their superdeep penetration according to the cumulative mechanism [6]. This is indicated by the form of the boundary between the coating and the substrate (Fig. 1c), where multiple traces of microcumulative jets and superdeep penetration channels, which are filled with superhard material, are present. The penetration of the indenter into the region of this material gives high nanohardness values.

CONCLUSIONS

The possibility for the preparation of plasma coatings based on titanium, nitrogen, and carbon on a metal substrate in the air atmosphere has been shown. The coating is deposited in one short-period cycle of operation of the magnetoplasma accelerator as a result of the exposure of a hypervelocity jet of erosion titanium-containing plasma on the substrate. The methods of scanning electron microscopy and X-ray phase analysis have shown that, in the coating deposited using this method, nanostructural layers of titanium nitride and carbonitride are formed, which provides its

Table 1. Results of full-profile XRD analysis of Ti-containing coatings

	Crystal phase	Content, %	Size of CSR, nm	$\Delta d/d$, 10^{-3}	Lattice parameters: experiment/PDF4 + data	
					a	*c*
Coating surface	*c*-TiN	84.5	16.8	1.2	4.2637/4.2440	–
	c-Ti_2CN	6.8	9.2	4.1	4.2051/4.2860	–
	h-Ti	5.1	20.0	1.8	2.9139/2.9440	4.7633/4.6780
	c-Fe	3.6	11.4	2.2	2.8792/2.8702	–
Coating–substrate interface	*c*-TiN	40.9	34.7	0.5	4.2372/4.2440	–
	c-Ti_2CN	42.6	18.4	3.4	4.2498/4.2860	–
	h-Ti	Traces	22.1	1.7	2.9135/2.9440	4.7633/4.6780
	c-Fe	16.5	17.3	2.0	2.8882/2.8702	–

high hardness. The coating possesses high adhesion to the substrate.

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