

## PROPERTIES OF HYBRID TiN/Al<sub>2</sub>O<sub>3</sub> COATINGS USING ELECTRON BEAM MELTING

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New experimental results on studies of the structure, element and phase composition of hybrid coatings deposited on a substrate of stainless steel AISI 321 are presented using combined application of several methods of coating deposition (plasma-detonation and vacuum arc ones) with subsequent surface treatment by a high-current electron beam (HCEB). We found that an increase in the energy density enhanced the processes of mass-transfer and allowed one to produce denser powder coatings. We demonstrated the results of corrosion tests for TiN/Al<sub>2</sub>O<sub>3</sub> coatings in their initial state and after electron-beam modification of their surfaces. We obtained an essential increase in the hybrid coating resistance to corrosion in 0.5 M solution of H<sub>2</sub>SO<sub>4</sub> after electron beam treatment.

### INTRODUCTION

Servicing characteristics of plasma-detonation produced powder coatings are mainly determined by the state of their surfaces (porosity and roughness) as by well as the physical and mechanical characteristics of deposited materials. It is known that an oxide aluminum ceramic has good physical, mechanical and as servicing properties [1]. One of the ways to harden the ceramic coatings is to deposit TiN films to them and subsequently melt them by electron beams, high-powder ion beams and plasma jets. This way intensifies the processes of mass transfer and diffusion due to intensive heating and melting. Duration and intensity of heating affects the relief of the formed surface and the mechanisms of phase transformations in the deposited materials. Therefore, to produce hard and simultaneously ductile coatings with a high corrosion resistance and a good adhesion, one needs a detailed selection of deposition regimes and subsequent melting taking into account individual features of deposited materials.

### EXPERIMENTAL METHODS

Protecting hybrid coatings TiN/Al<sub>2</sub>O<sub>3</sub> were manufactured on a substrate of austenitic stainless steel AISI 321 (composition: 18wt.% Cr, 9 wt.% Ni, 1 wt.% Ti, 0.3wt.%Cr, Fe the rest, 1.1mm thick). Powder coatings of aluminum oxide (45 to 60 μm thick) were deposited using a high-rate pulsed plasma jet by the facility "Impulse-5"

(the regimes (conditions) and techniques for deposition are presented in [2]). To increase the corrosion resistance of the protecting ceramic coating and to eliminate defects of the plasma-detonated deposited powder coating in the vacuum-arc source of "Bulat-3T" type, we additionally deposited films of titanium nitride of 1.5 to 2.0 μm thick. To smooth the surface structure non-uniformities, to outgas coating bulk and to enhance diffusion and mass transfer processes in the "coating-substrate", we melted the surfaces of hybrid coatings using a high-current electron beam. Thermal activation was realized by an electron-beam accelerator "U-212".

Mechanical properties of coatings based on of oxide aluminum depend on the phase composition of this material [1]. For example, an increase of the content of metastable phases in the near surface region of Al<sub>2</sub>O<sub>3</sub> essentially decreases the surface hardness and its resistance to the action of aggressive media. However, at the same time, we observed good adhesion of the coatings with the surface of steel substrates unlike the coatings content 100% of α-phase. The application of high-energy beams for selected substrate thickness was impossible due to intensive substrate deformation. Therefore to pack (seal) the powder coatings, we performed two-time melting of the surfaces under the following HCEB parameters: first the coatings were melted by an electron beam of 760 W/cm<sup>2</sup> power density ( $U = 30$  kV,  $I_B = 20$  mA,  $v_B = 60$  m/hour,  $d_B = 0.1$  m); then

the coatings were cooled in the accelerator chamber down to room temperature. After above treatments a part of the samples was used for studies, the other part was HCEB melted ( $U = 30$  kV,  $v_B = 60$  m,  $I_n = 10, 15, 20, 25$  and  $35$  mA).

The element composition of TiN/Al<sub>2</sub>O<sub>3</sub> and TiN/Cr/Al<sub>2</sub>O<sub>3</sub> coatings was studied using the Rutherford back-scattering (RBS) by the accelerating facility UPK-2-1 (Nuclear Physics Institute, Almaty, Kazakstan) having 0.8 and 1.5 MeV proton beam energy and raster electron microscopy with micro-analysis (REMMA-102 microscope with WDS-2 adapter (Selmi, Sumy, Ukraine)).

An analysis of the coating microstructure and of the transition zone was performed using a method of selective chemical etching of cross-sections with a metallographic microscope Neophot 30. To study the non-uniformities of powder coatings we performed an etching of various inclusions by a solution of hydrofluoric acid (50 ml HF, 50 ml H<sub>2</sub>O) for 10 minutes. The steel structure at the transition steel part was determined after subsequent grinding and etching ( $t = 5$  min) in hydrochloric acid. The corrosion resistance of the prepared coatings was studied using electrochemical techniques. A saturated calomel electrode was used as a reference electrode and a graphite one was used as an auxiliary electrode for all measurements. The tests in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution were performed in the potential region  $-1000$  to  $+1500$  mV at ambient temperature. Five rapid scans (scan rate = 25 mV/s) followed by one slow scan (scan rate = 0.25 mV/s) were performed on each specimen.

## EXPERIMENTAL RESULTS AND DISCUSSION

As a result of electron beam surface bombardment the coatings are melted and a subsequent hardening due to heat removal from surface bulk occurs. The efficiency of these processes depends on the electron beam energy parameters and on the physical properties of melted materials. As a result of high-rate electron deceleration occurring in the coating material their interaction with material atoms and electrons is initiated. A source is formed in the material bulk and it has a characteristic maximum at some depth. A degree

of surface heating was determined by solution of a problem about body heating [3].

According to performed calculations, the temperature in the coating near surface region rose to about 890 K ( $I_n = 10$  mA,  $q = 380$  W/cm<sup>2</sup>); about 1340 K ( $I_n = 15$  mA,  $q = 570$  W/cm<sup>2</sup>); about 1730 K ( $I_n = 20$  mA,  $q = 760$  W/cm<sup>2</sup>); about 2230 K ( $I_n = 25$  mA,  $q = 960$  W/cm<sup>2</sup>); about 3100 K ( $I_n = 35$  mA,  $q = 1340$  W/cm<sup>2</sup>).

Fig. 1 shows the morphology of hybrid coating surfaces depending on the value of energy introduced to an area unit. Since aluminum oxide and titanium nitride are refractory materials, and their melting temperatures are respectively  $T(\alpha\text{-Al}_2\text{O}_3) = 2323$  K [4] and  $T(\text{TiN}) = 3478$  K, a (non-essential) decrease in surface roughness (Fig. 1b-d) is realized due to partial and full melting, as well as to the action of shock waves. Basing on obtained photos for coatings and performed calculations, one can say that the decrease in surface roughness in the case of fig. 1c is a consequence of a complex action of temperature and deformation-wave mechanisms. Near the melting point the surface relief began to change significantly (fig. 1c).

One can see non-uniformly formless regions with an obvious melting distributed over the surface. We consider that these non-uniformities are themselves the centers of formation of formless regions. But heating of the powder sublayer is not enough, since one does not observe an evident melting of the upper layer of titanium nitride. The coating surface in the region of valleys has dark inclusions, in which, according to the performed element analysis, the basic component is aluminum. Distribution of components over the surface (as it was the case of one-time melting) was not uniform (tabl. 1). We should also like to note that carbon starts to appear in some local surface regions. This fact can be explained by a diffusion of this element from the powder sublayer towards the surface at the moment of melting.

Action of HCEB with 1340 W/cm<sup>2</sup> power density on the coating surfaces allows heating of the near surface region to the temperature of titanium nitride melting. Such regimes of treatment are accompanied by an intensive change in the geometry of the surface layer of the alumi-

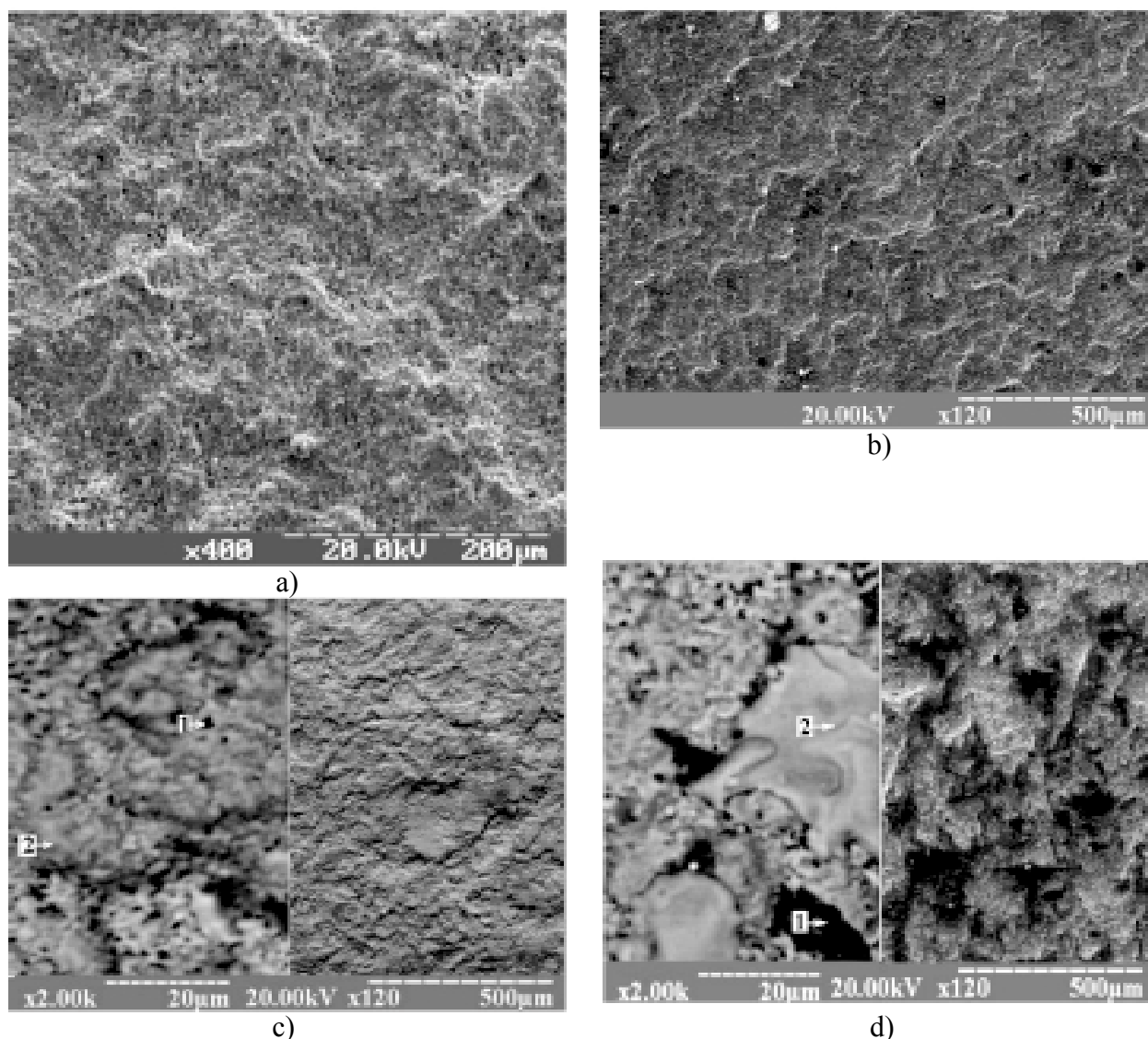


Fig. 1. Surface morphology of hybrid coatings after electron – beam treatment: a) – an initial state; b) – one cycle melting ( $q = 760 \text{ Wt/cm}^2$ ); c), d) – second cycle melting ( $q = 960 \text{ Wt/cm}^2$  and  $1340 \text{ Wt/cm}^2$ ); 1, 2 – points of local element analysis.

Table 1

Chemical composition of the surface of hybrid coatings  $\text{TiN/Al}_2\text{O}_3$  (mas. %)

Region of analysis	N	O	Al	Ti	C	Si	Fe	Other elements
$U = 30 \text{ kV}, I_B = 25 \text{ mA}, v_B = 60 \text{ m/hour}, \text{fig. 1c}$								
p. № 1	0.69	39.93	56.04	3.34	–	–	–	–
p. № 2	26.67	73.33	–	–	–	–	–	–
Integral element compos.	0.05	21.42	1.71	75.62	–	1.20	–	–
$U = 30 \text{ kV}, I_B = 35 \text{ mA}, v_B = 60 \text{ m/hour}, \text{fig. 1d}$								
p. № 1	19.01	–	10.35	70.21	–	–	0.43	–
p. № 2	4.70	2.29	1.58	20.33	67.69	0.51	0.26	Na, S, Cl, K, Ca
Integral element compos.	2.75	5.23	6.73	62.82	–	1.75	15.11	Cr, Ni

num oxide surface, which occurs in the zone where direct thermal action of HCEB leads to a transition towards an overheated state. The material in the near surface region is refined. As a consequence, the coating roughness decreases. Near the melting point titanium nitride becomes more ductile. The coating becomes practically uniform in its chemical composition. Taking into account the data on a quantitative element content, one should note that more intensive material melting resulted in increased aluminum and carbon concentration in the surface region together with a simultaneous decrease in titanium and nitrogen content.

According to RBS results, a repeated action of the high-current electron beam on the surface under the regime of melting provides an intensive

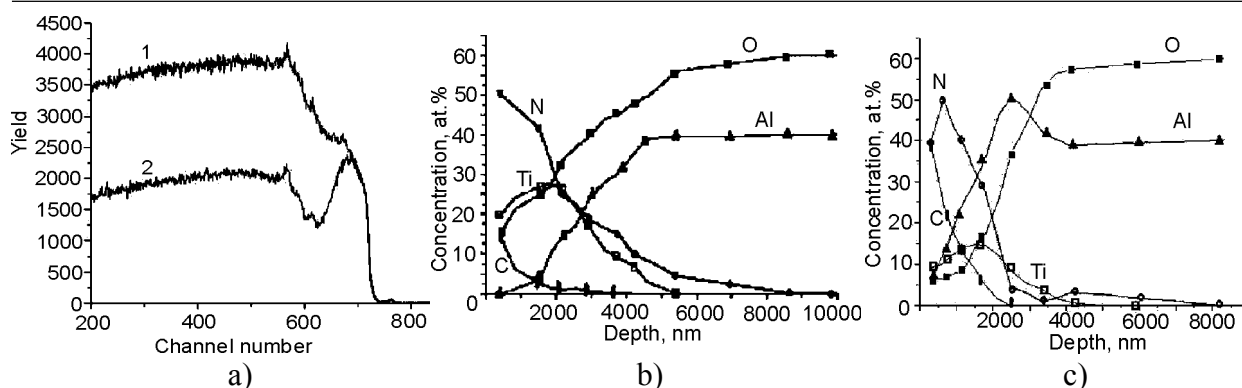


Fig. 2. a) Energy spectra of ion back-scattering measured for hybrid coatings (TiN/Al<sub>2</sub>O<sub>3</sub>/steel) taken in HCEB-irradiated region. The energy of incident ions was respectively: 1.5 MeV (a top curve, irradiation density of the electron beam was (760 + 1340) Wt/cm<sup>2</sup>), 0.8 MeV (a lower curve, HCEB irradiation density was 760 Wt/cm<sup>2</sup>); Element profiles taken from RBS spectra with ion energy 1.5 MeV for the hybrid coating after HCEB irradiation (b) – powder density of 760 Wt/cm<sup>2</sup>, c) – powder density of (760 + 1340) Wt/cm<sup>2</sup>.

activation of mass transfer processes for elements composing the surface coating layer (Ti, N, C). Fig. 2a shows RBS energy spectra measured for TiN/Al<sub>2</sub>O<sub>3</sub>/steel samples for two various energies (the initial energy being 0.8 MeV and 1.5 MeV). As one can see from these spectra, in the case of low energy an analyzing ion beam did not allow us to divide the contributions from TiN and Al<sub>2</sub>O<sub>3</sub> spectra due to essentially thick Al<sub>2</sub>O<sub>3</sub> layer. Using RBS spectra and the Simnra program we calculated the element distribution profiles for the coatings which were irradiated with 760 W/cm<sup>2</sup> power density (fig. 2b) and (760 + 1340) W/cm<sup>2</sup> (fig. 2c). The obtained experimental results show that high current electron beam irradiation without visible melting of the coating and subsequent increase in the power density to 35 J/cm<sup>2</sup> resulted in a smoothing of the titanium concentration profile almost to 5 μm. This feature is related to titanium diffusion to the sample bulk (as well as to the limits of RBS sensitivity – the least concentration boundary) The spectra show that aluminum penetrated into the TiN film and formation of a AlTi compound was possible, as is confirmed by the same behavior of Al and Ti at the depth 2.5 to 4 μm. It was not the case when the energy density was significantly lower.

Additionally, if one applies the known ratio in count intensities (when a step was apparent in the spectra), one can evaluate the stoichiometry of the assumed compound, which was close to Al<sub>50</sub>Ti<sub>50</sub>. To determine the degree of uniformity of the material chemical composition, we prepared cross-sections of TiN/Al<sub>2</sub>O<sub>3</sub> coatings. According to [5] a solution of HCl acid etched va-

rious inclusions for 5 minutes remaining the aluminum oxide stable.

The photo of the cross-section presented in fig. 3a shows non-uniformly distributed dark inclusions. We relate these inclusions in the near surface and central parts to pores occurring in the coating structure. The α-phase of aluminum oxide has a high hardness and a low ability to deformation under normal conditions and therefore was badly polished.

Closer to the contact region with the substrate the concentration of those dark inclusions increased. We consider that the changes in the reflexive ability of this region were a consequence of etching off the substrate elements in the steel contact region with the aluminum oxide powder. The conclusion that most of dark inclusions are pores is confirmed by results of etching of TiN/Al<sub>2</sub>O<sub>3</sub> coatings, which were melted by HCEB at 1340 W/cm<sup>2</sup> power density. Fig. 3b shows the cross-section of one of the regions of such coatings. Dark inclusions are practically absent in the near surface and the central part of this region. It follows that the action of heat field of the electron beam allows one to seal the powder coatings. Strong etching of the transition region confirms the formation of strong bonds between the corundum powder and the metallic base. Results of X-ray structure analysis show a variety of coating phase composition after melting by the electron beam [2]. Aluminum oxide is a unique material in its physical and chemical properties and standard agents do not affect it [5]. Therefore under usual conditions we set a problem non to etch some concrete phases Al<sub>2</sub>O<sub>3</sub> in

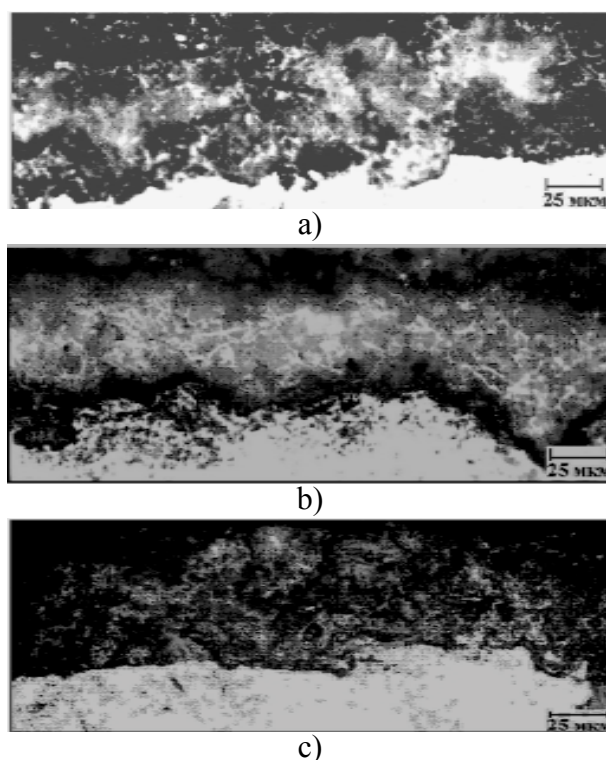


Fig. 3. Optical photos of transversal cross-sections of TiN/Al<sub>2</sub>O<sub>3</sub> coatings, which were melted by HCEB with the following power densities: a) – 180 Wt/cm<sup>2</sup>; b) – (760 + 1340) Wt/cm<sup>2</sup>; c) – (760 + 960) Wt/cm<sup>2</sup>.

the given sublayer, but tried to change their color. Photos obtained after cross sectioning of these coatings were similar (fig. 3c).

Taking into account the reference data [5] and the obtained photos, we now can say that the matrix of the sublayer of aluminum oxide powder is formed by  $\alpha$ -phase (domination of grey and dark grey colors) and a mixture of metastable modification of the given material. We would like to note that a trigonal structure of aluminum oxide is composed in most cases of small grains, which are evidently seen on photos with 4000 magnification. So it is difficult to see the grain structure on these photos, and the biggest inclusions which we relate to Al<sub>2</sub>O<sub>3</sub>  $\alpha$ -phase are marked by arrows.

Corresponding data on the sample corrosion after their treatment in sulphuric acid solution 0.5 M under temperature of environment are presented in tabl. 2.

The corrosion potential in the case of steel samples without coating was – 445 mV. It essentially decreased in the case of samples with coatings. The decrease in corrosion potential and

Table 2

## Results of Electrochemical Studies

Sample	$E_{\text{corr}}^{\circ}$ (mV)	$i_{\text{corr}}^{\circ}$ (mA)	$i_{\text{pass}}^{\circ}$ (mA)	$E_{\text{pass}}^{\circ}$ (mV)	$E_{\text{rep}}^{\circ}$ (mV)
TiN/Al <sub>2</sub> O <sub>3</sub> +HCEB	-410	2.5	0.7	1022	1066
TiN/Al <sub>2</sub> O <sub>3</sub>	-330	11.9	-5.0	860	870
Steel	-445	4.5	1.3	1022	1023

passivation current density in the case of samples with coatings indicates an increase in their corrosion resistance due to a protecting effect of the deposited layer. Improvements were more evident in the case of samples which were subjected to HCEB treatment because of an inner diffusion of the titanium nitride layer. The behavior of samples with coating in HCl solution was almost the same in the sulphuric acid solution – samples demonstrated lower corrosion resistance. Qualitative evaluation of SEM data for the samples which were subjected to strong corrosion demonstrated that the electrochemical treatment did not induce essential deviations in samples.

## CONCLUSIONS

The studies of element composition of TiN/Al<sub>2</sub>O<sub>3</sub> coatings demonstrated that titanium, nitrogen, carbon, oxygen and aluminum are their basic composing elements. Melting of the surface by concentrated energy flows stimulated mass transfer processes. We observed a saturation of near surface regions by aluminum and oxygen ions and a simultaneous penetration of titanium and nitrogen ions in to the coating bulk. Electron beam annealing of the surface provided a uniform redistribution of titanium ions and a partial melting of non-uniformities in the surface morphology.

Plasma detonation techniques can be successfully utilized for deposition of a composite and hybrid coatings on metallic surfaces. A high current electron beam treatment enhanced the corrosion resistance of TiN/Al<sub>2</sub>O<sub>3</sub> coatings.

## ACKNOWLEDGMENTS

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**МОДИФІКАЦІЯ ВЛАСТИВОСТЕЙ  
ГІБРИДНИХ ПОКРИТТІВ  
НА ОСНОВІ TiN/Al<sub>2</sub>O<sub>3</sub>  
М.К. Килишканов**

Представлено нові експериментальні результати досліджень фазового складу гібридних покриттів TiN/Al<sub>2</sub>O<sub>3</sub>, осаджених на підкладку з нержавіючої сталі типу AISI 321 комбінованим способом. Показано, що в процесі кристалізації порошку Al<sub>2</sub>O<sub>3</sub> на підкладці формуються зародки його γ-фази і метастабільних модифікацій. Вакуумно-дугове осадження нітриду титана на підшар Cr або порошку корунду дозволяє сформувати плівку, матриця якої складається з ГЦК-TiN з домішкою його тетрагональної модифікації ε-TiN. Знайдено режими оплавлення поверхні низькоенергетичним потужнострумним електронним пучком (НСЕП), що дозволяють активувати ряд поліморфних перетворень типу γ-, β-, δ-, θ → α-Al<sub>2</sub>O<sub>3</sub> і ε-TiN → TiN і сформувати покриття з α-фази корунду і кубічної модифікації TiN.

**МОДИФІКАЦІЯ СВОЙСТВ  
ГИБРИДНЫХ ПОКРЫТИЙ  
НА ОСНОВЕ TiN/Al<sub>2</sub>O<sub>3</sub>  
М.К. Кылышканов**

Представлены новые экспериментальные результаты исследований фазового состава гибридных покрытий TiN/Al<sub>2</sub>O<sub>3</sub>, осажденных на подложку из нержавеющей стали типа AISI 321 комбинированным способом. Показано, что в процессе кристаллизации порошка Al<sub>2</sub>O<sub>3</sub> на подложке формируются зародыши его γ-фаза и метастабильных модификаций. Вакуумно-дуговое осаждение нитрида титана на подслое Cr или порошка корунда позволяет сформировать пленку, матрица которой состоит из ГЦК-TiN с примесью его тетрагональной модификации ε-TiN. Найдены режимы оплавления поверхности низкоэнергетическим сильноточным электронным пучком (НСЭП), позволяющие активировать ряд полиморфных превращений типа γ-, β-, δ-, θ → α-Al<sub>2</sub>O<sub>3</sub> и ε-TiN → TiN и сформировать покрытие из α-фаза корунда и кубической модификации TiN.