

# Modification of Properties of Hybrid TiN/Al<sub>2</sub>O<sub>3</sub> Coatings Using Electron Beam Melting

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**Abstract** – New experimental results on studies of a structure, element and phase composition of the hybrid coatings, which were deposited on a substrate of stainless steel AISI 321 using combined application of several methods of coating deposition ( a plasma-detonation and a 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 the 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 the electron beam treatment.

## 1. Introduction

Servicing characteristics of plasma-detonation produced powder coatings are mainly determined by the state of their surfaces (porosity and roughness) as well as the physical and mechanical characteristics of deposited materials. It is known that an oxide aluminum ceramic has the high physical and mechanical as well 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 the 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 mechanisms of phase transformations in the deposited materials. Therefore, to produce hard and simultaneously ductile coatings with the high corrosion resistance and good adhesion, one needs a detailed selection of deposition regimes and subsequent melting taking into account individual features of the deposited materials.

## 2. Experimental Methods

The protecting hybrid coatings TiN/Al<sub>2</sub>O<sub>3</sub> were manufactured on the substrate of austenite stainless steel AISI 321 (the composition: 18 wt.% Cr, 9 wt.% Ni, 1 wt.% Ti, 0.3 wt.% Cr, Fe the rest, 1.1 mm 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

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 coatings 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 coatings bulk and to enhance diffusion and mass transfer processes in the region "coating-substrate", we melted the surfaces of hybrid coatings using the high-current electron beam. Thermal activation was realized by the electron-beam accelerator "U-212".

Mechanical properties of the coatings on the base of oxide aluminum depended on the phase composition of this material [1]. For example, the increased content of metastable phases in a near surface region Al<sub>2</sub>O<sub>3</sub> essentially decreased the surface hardness and its resistance to action of aggressive media. However, at the same time, we observed good adhesion of the coatings with the surfaces of steel substrates unlike the coatings having 100 % content of α-phase. Application of high-energy beams for selected substrate thickness was impossible due to intensive substrate deformation. Therefore to pack the powder coatings, we performed melting of the surfaces twice under the following HCEB parameters: first the coatings were melted by the 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 to room temperature. After this a part of these samples was used for studies, other part was HCEB melted ( $U=30$  kV,  $v_b=60$  m,  $I_b=10, 15, 20, 25$  and  $35$  mA).

The element composition of TiN/Al<sub>2</sub>O<sub>3</sub> coatings was studied by Rutherford back scattering (RBS), using the accelerating complex UPK-2-1 and scanning electron microscopy with microanalysis (SEM-103-01 with WDS attachment). An analysis of the coating microstructure and that of the transition zone was performed using a method of selective chemical etching of the cross-sections using a metallographic microscope Neophot 30. To study the non-uniformities of powder coatings and find various inclusions into the substrate matrix, for 10 minutes in

the contact region we performed etching of various inclusions by a solution of a hydrofluoric acid (50 ml HF, 50 ml H<sub>2</sub>O). The steel structure at the transition steel part was determined after subsequent grinding and etching ( $t=5$  min) in a hydrochloric acid. The corrosion resistance of the prepared coatings was studied using electrochemical techniques. A saturated calomel electrode used as a reference electrode and a graphite one as an auxiliary electrode for all measurements. The tests in 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.

### 3. Experimental Results and Discussion

As a result of electron beam surface bombardment the coatings are melted and their subsequent hardening due to heat removal to the surface bulk occurs. An efficiency of these processes depends on the electron beam energy parameters and physical properties of the melted materials. As a result of high-rate electron deceleration occurring in the coating material their interaction with the material atoms and electrons is initiated. A heat 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 the performed calculations, the temperature in the coating near surface region rose to about 890K ( $I_n=10$  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 2230K ( $I_n=25$  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 a stage by stage in the morphology of hybrid coating surfaces depending on the value of energy introduced to an area unit. Since the 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, then a non-essential decrease in surface roughness (Fig. 1, *a–b*) is realized due to a partial melting and material full melting, as well as due to an action of shock waves. Basing on the obtained photos for the coatings and the performed calculations, one can say that the decrease in surface roughness in the case of Fig. 1, *b* 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. 1, *b*). One can see non-uniformly distributed over the surface formless regions with an obvious melting. We consider that these intensive non-uniformities are themselves the centers of formation of these formless regions. But namely heating of this powder sublayer is not enough, since one do 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 per-

formed element analysis, the basic component is aluminum. Distribution of components over the surface (as it was in the case of one-time melting) was not uniform (Table 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.

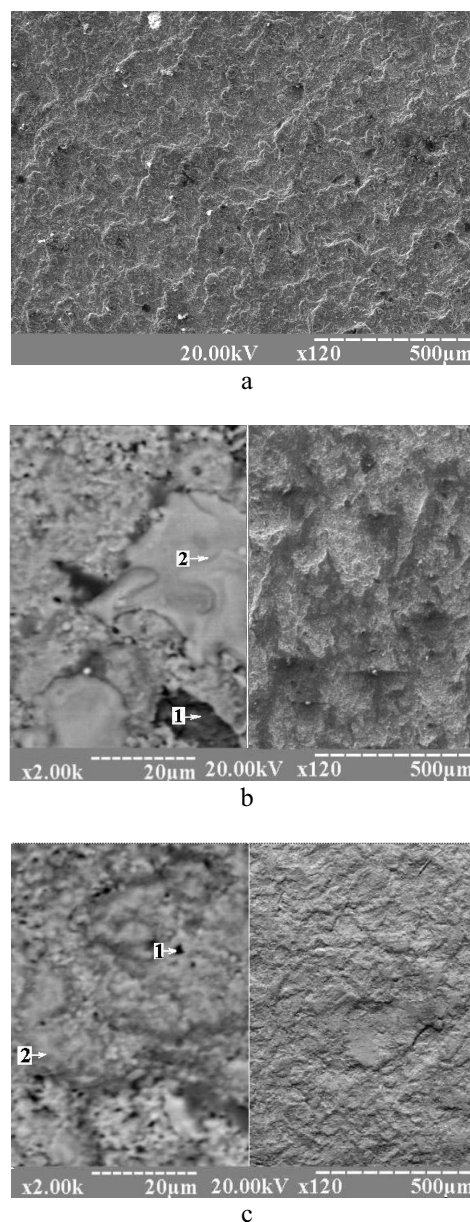


Fig. 1. Surface morphology of hybrid coatings after electron-beam treatment: a – one cycle melting ( $q=760$  W/cm<sup>2</sup>); b – second cycle melting ( $q=960$  and  $1340$  W/cm<sup>2</sup>); 1,2 – points of local element analysis

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 geometry of the surface layer the aluminum oxide surface, which occurs in the zone of

direct thermal action of the HCEB must transit to an overheated state. The material in the near surface region is refined. As a consequence, the coating roughness decreases essentially. 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 together with simultaneous decrease in titanium and nitrogen content.

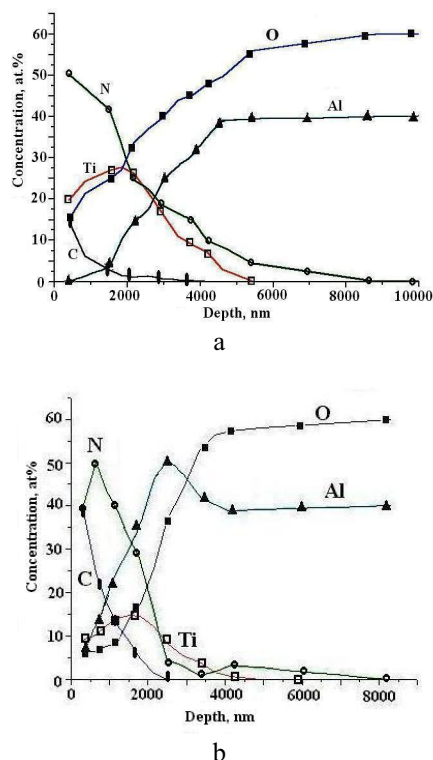


Fig. 2. Element profiles taken from energy spectra with ion energy 1.5 MeV for the hybrid coating after HCEB irradiation (a – the powder density was 760 W/cm<sup>2</sup>, b – the powder density was (760+1340) W/cm<sup>2</sup>)

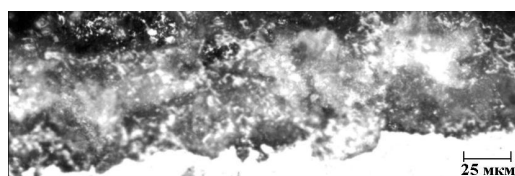
Table. I. Chemical composition of surface of hybrid coatings TiN/Al<sub>2</sub>O<sub>3</sub> (mas.%)

Region of analysis	N	O	Al	Ti	C	Si	Fe	Other elements
<i>U=30 kV, I<sub>b</sub>=25 mA; v<sub>b</sub>=60 m/hour, fig. 1</i>								
p. № 1, fig. 1, b	0.69	39.93	56.04	3.34	–	–	–	–
p. № 2, fig. 1, b	26.67	73.33	–	–	–	–	–	–
Integral element compos.	0.05	21.42	1.71	75.62	–	1.20	–	–
<i>U=30 kV, I<sub>b</sub>=35 mA; v<sub>b</sub>=60 m/hour, fig. 1c</i>								
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

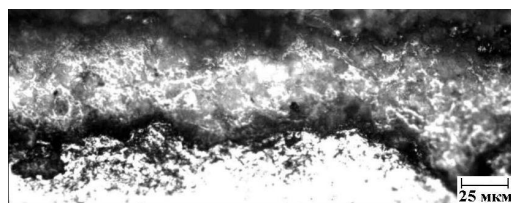
According to RBS results, a repeated action of the high-current electron beam on the surface under the regime of melting provides an intensive activation of mass transfer processes for elements composing the surface coating layer (Ti, N, C). Using the RBS energy spectra and the Sinnra program we calculated that the element distribution profiles for the coatings which were irradiated with 760 W/cm<sup>2</sup> power density (Fig. 2, a) and (760+1340) W/cm<sup>2</sup> (Fig. 2, b).

The obtained experimental results show that high current electron beam irradiation without visible melting of the coating and the subsequent increase in the power density to 35 J/cm<sup>2</sup> resulted in smoothing of the titanium concentration profile almost to 5 μm. First of all it is related to the 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 to the TiN film bulk and formation of a compound on the basis of AlTi was possible that 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 will apply the known ratio in count intensities (when a step was appeared 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 a degree of uniformity of the material chemical composition, we etched the cross-sections of the TiN/Al<sub>2</sub>O<sub>3</sub> coatings. According to [5] the solution of HCl acid etched various inclusions for 5 minutes remaining the aluminum oxide stable. The photo of the cross-section presented in Fig. 3, a shows non-uniformly distributed dark inclusions. We relate these inclusions in the near surface and central parts to the pores occurring in the coating structure. α-phase of aluminum oxide had high hardness and 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 reflexive ability of this region were a consequence of etching off of the substrate elements in the steel contact region with the aluminum oxide powder. A conclusion that the most part of dark inclusions are pores is confirmed by results of etching of the TiN/Al<sub>2</sub>O<sub>3</sub> coatings, which were melted by the HCEB of 1340 W/cm<sup>2</sup> power density. Fig. 3, b shows the cross-section of one of the regions of such coatings. Dark inclusions are practically absent in near surface and central part of this region. It follows, in such a way, 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 speak about a variety of the coating phase composition after melting by the electron beam [2]. To Wee tried to use metallography for controlling these results. Aluminum oxide is a unique ma-

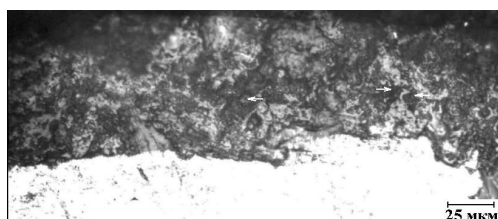
terial in its physical and chemical properties and standard agents do not affect it [5]. Therefore under usual conditions we set a problem non to etch some concrete phases  $\text{Al}_2\text{O}_3$  in the given sublayer, but tried to change their color. Photos obtained after cross sectioning of these coatings were similar, Fig. 3, *c* demonstrating one of these photos. Taking into account the reference data [5] and the obtained photos, we can say that the matrix of the sublayer of aluminum oxide powder is formed by  $\alpha$ -phase (domination of a grey and dark grey colors) and a mixture of metastable modification of the given material. We should like to note that a trigonal structure of aluminum oxide in most cases is composed of small grains, which are evidently seen at photos with 4000 magnification. So it is difficult to see the grain structure at these photos, and the biggest inclusions, which we relate to  $\text{Al}_2\text{O}_3$   $\alpha$ -phase are marked in this figure by arrows.



a



b



c

Fig. 3. Optical photos transversal cross-sections for  $\text{TiN}/\text{Al}_2\text{O}_3$  coatings, which were melted by a HCEB with the following power densities: a –  $180 \text{ W}/\text{cm}^2$ ; b –  $(760+1340) \text{ W}/\text{cm}^2$ ; c –  $(760+960) \text{ W}/\text{cm}^2$

Corresponding data on the samples corrosion after their treatment in sulphuric acid solution 0.5 M under temperature of environment are presented in Table 2. The corrosion potential in the case of steel samples without coating was  $-445 \text{ mV}$ . It essentially decreased in the case of samples with coatings. The decrease in corrosion potential and passivation cur-

rent density in the case of samples with coatings indicates an increase in their corrosion resistance due to protecting effect of the deposited layer. Improvements were more evident in the case of samples, which were subjected to the 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 the SEM data for the samples which were subjected to strong corrosion, demonstrated that electrochemical treatment did not induce essential deviations in samples.

Table 2. Results of Electrochemical Studies

Sample	$E_{\text{corr}}$ (mV)	$i_{\text{corr}}$ (mA)	$i_{\text{pass}}$ (mA)	$E_{\text{pas}}$ (mV)	$E_{\text{rep}}$ (mV)
$\text{TiN}/\text{Al}_2\text{O}_3 + \text{HCEB}$	-410	2.5	0.7	1022	1066
$\text{TiN}/\text{Al}_2\text{O}_3$	-330	11.9	5.0	860	870
Steel	-445	4.5	1.3	1022	1023

#### 4. Conclusions

In such a way the studies of element composition of  $\text{TiN}/\text{Al}_2\text{O}_3$  coatings demonstrated that titanium, nitrogen, carbon, oxygen and aluminum are their basic composing elements. Melting of the surface by concentrated energy flows stimulated the mass transfer processes. In the process of this we observed essential saturation of near surface regions by aluminum and oxygen ions and simultaneous penetration of titanium and nitrogen ions to the coating bulk. It was set that the electron beam annealing of the surface provided a uniform redistribution of titanium ions and partial melting of non-uniformities in the surface morphology.

Plasma detonation techniques can be successfully utilized for deposition of the composite and hybrid coatings on metallic surfaces. The high current electron beam treatment enhanced the corrosion resistance of  $\text{TiN}/\text{Al}_2\text{O}_3$  coatings.

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