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TiN/Cr/Al_2O_3 AND TiN/Al_2O_3 HYBRID COATINGS STRUCTURE FEATURES AND PROPERTIES RESULTING FROM COMBINED TREATMENT

Abstract: New experimental results on the structure and the element and phase composition of hybrid coatings, which were deposited on a substrate of AISI 321 stainless steel using a combination of plasma detonation, vacuum arc and subsequent high-current electron beam treatment (HCEB), are presented. We found that an increase in energy density intensified mass-transfer processes and resulted in changes in aluminum oxide phase composition (γ→α and β→α). Also we observed formation of a nano-crystal structure in Al_2O_3 coating.

Keywords: hybrid protecting coatings, plasma jet, vacuum-arc deposition, electron beam treatment, adhesion, nano- and micro-hardness, wear and corrosion resistance.

1.Introduction

Traditional methods of surface modification, which are applied now in practice (physical, chemical, electro-chemical and mechanical ones [1]) as well

as more advanced methods such as ion implantation, ion-assisted deposition of thin films, plasma technologies and electron-beam treatment [1 - 4] in some cases cannot result directly in a desired effect. In this connection, solving the concrete industrial problems arising in sheep building and chemistry, for instance [1, 5, 6], one has to combine such methods of surface modification, which allow the production of hybrid coatings possessing the definite operation properties [1, 7]. An oxide-aluminum ceramics and the coatings on titanium and tungsten carbides and nitrides [1, 8 - 10] base possess a number of unique properties, which are able to provide corrosion protection, high hardness and mechanical strength, low wear, and good electro-isolation properties. Additional treatment of these coatings by high current electron beams (HCEB) in the regime of partial melting results in ablation of surface impurities (e.g. carbon-, oxygen- and nitrogen-compounds) and activation of the coating surfaces. Melting of the surfaces and their high-rate cooling result in the formation of nano- dispersed and metastable phases, as well as amorphous layers. Deposition of a TiN-layer, also showing high-melting temperature, hardness and corrosion resistance, additionally allows the decrease of the surface porosity of the oxide coatings and the enhancement of the protective action.

2. Experimental

2.1. Preparation of samples

The protecting hybrid coatings TiN/Cr/Al_2O_3 and TiN/Al_2O_3 were formed on the substrate of austenite stainless steel AISI 321 (18wt.% Cr; 9wt.%Ni; 1wt.%Ti; 0.3wt.% Cr; Fe the rest; 0.3mm and 2 mm thickness). The aluminum oxide coating (45 to 60μm thick) was formed using a high-velocity pulsed-plasma jet from the facility “Impulse-5”.

This technology applied for production of the protecting coatings is relatively new and based on electromagnetic acceleration of burning products from gas mixtures (propane, oxygen and air). Approaching such an electric conducting layer the aluminum oxide powder is quickly heated and accelerated

in the flow of pulsed plasma. At the moment when the pulsed plasma jet is ejected from the plasmatron the electric circuit is shorted between an eroding electrode and the substrate surface. In this shorted system a pulsed magnetic field in which temperature of the plasma-powder flow was increased for the second time, was formed. Evaluation of the pulsed plasma flow technological characteristics (temperature, velocity and power density) for the opted operation plasmatron regimes was performed using the method described in [13] by solution of a two-dimensional non-stationary problem of detonation wave distribution in an electric field between two coaxial electrodes.

2.2. **The characterization of the coatings**

The element composition of TiN/Al_2O_3 and $TiN/Cr/Al_2O_3$ coatings was studied by back-scattering (BS) using the accelerating facility UPK-2-1 (Nuclear Physics Institute, Almaty, Kazakstan) under 0.8 and 1.5MeV proton beam energy and by scanning electron microscopy with micro-analysis (REMMA-102 microscope with WDS-2 and EDS adapters (Selmi, Sumy, Ukraine).

Detailed studies of the detonation-produced aluminum oxide coating micro-structure were performed by the transmission electron microscope PEM-125 with 125kV accelerating voltage (Selmi, Sumy, Ukraine). Very thin foils of various coating thicknesses were manufactured from the samples. Then one their edge was polished electro-chemically. Using ion etching, we reached that thickness which allowed us to study micro-diffraction of various regions.

X-ray analysis of the hybrid coatings was performed by the DRON-2.0 facility (S-Peterbourg, Russia) with Cu k_α emission. Additional studies of the hybrid coating surface phase composition were performed by a low-angle scattering using the X-ray diffraction meter D8 Advance (Bruker AXS, Germany) in Cu k_α emission. To decode and interpret the obtained diffraction patterns, we applied the licensed data base PCDFWIN containing information about more than 150 000 compounds, and a package of programs for data treatment Diffrac. Plus 80000 compounds. Microhardness measurements were

performed by the PMT-3 (St-Peterbourg, Russia) facility by the Vickers's diamond pyramid under 0.1 to 0.15kg indentation loads to the transversal cross-sections.

2.3. Investigation of Corrosion Behavior Using Electrochemical Techniques

The corrosion resistance of the prepared coatings was investigated using electrochemical techniques. An AUTOLAB Potentio-Galvanostat (ECO CHEMIE, Netherlands) and Princeton Applied Research corrosion testing cell were used for the electrochemical measurements. 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_2SO_4 solution were carried out 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. The rapid scans allow investigations under constant conditions of the material surface and corroding medium, whereas slow scans lead to predictions of the general corrosion behavior of the material. In all cases the sample surface exposed to the corroding medium was $1cm^2$ [22 - 24]. The above-mentioned experimental conditions were also applied for the corrosion tests in HCl and NaCl solutions, whereas the scanning region was from -300 to +1700 and from -1000 to + 1000 mV, respectively [25].

3. Results and Discussion

Application of the combined technology for protecting coating deposition was accompanied by a number of features of the produced surface structure. Plasma-detonation deposition of the aluminum oxide powder included the coating formation by a successive placement of fully or partially melted powder particles of Al_2O_3 [1]. Studies of morphology features of the AISI 321/Al_2O_3 surface (Fig.1) demonstrated that the ceramic coating represented an

alternation of non-uniformly distributed hills and valleys. It seems to be due to the fact that in the process of gas-thermal coating deposition the heavier powder fractions (of 44 to 56μm diameter) of various melting states, mass, and motion rate in the plasma flow formed the coating matrix. The powder with 27 to 44μm particle size was melted most strongly and impacting the surface particles filled the valleys or was splashed depending on their velocity. As a result of high-rate solidification a surface with a highly developed relief was formed. 2000 times magnification failed to demonstrate the regions with in-melted powder particles.

Plasma detonation deposition of an aluminum oxide powder layer provided formation of surfaces with higher wear resistance. As one can see in the Figure TiN/Cr/Al_2O_3/steel321 coating had essentially lower wear, but the lowest one was found in TiN/Al_2O_3/steel321 after electron beam treatment with double surface melting under 35J/cm^2 current density.

We assume that decreased roughness of the hybrid coating after electron beam treatment resulted in wear decreasing together with grain grinding occurring in the protecting coating. Taking into account the fact that destruction character and wear intensity were mainly determined by mechanical properties of a contact surface [10, 16], in the coatings we performed studies of nano-hardness. Figure 13 shows results of measurements by nano-indenter. As one can see in this Figure, the coating had essentially higher hardness – about 9GPa. This hardness value is closer to γ – Al_2O_3, which was mixed with TiN film.

4.Conclusions

In such a way, the performed studies of surface phase composition in the process of plasma detonation deposition of metal ceramics (α – Al_2O_3). We observed a number of phase transformations in aluminum oxide (like α→γ and α→β). Restoration of α – phase (corundum) was realized by thermal annealing of the surface by an electron beam. Element analysis of TiN/Cr/Al_2O_3 and TiN/Al_2O_3 coatings demonstrated that basic composing elements were titanium, nitrogen, carbon, oxygen and aluminum. Surface melting by a concentrated

energy flow stimulated mass transfer processes. We observed essential saturation of near surface region by aluminum and oxygen ions with simultaneous motion of titanium and nitrogen ions towards the coating bulk. We stated that electron beam annealing of a surface provided uniform distribution of titanium ions and partial sealing of inhomogeneities of the surface morphology.

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Table.1

Sample series	Deposited coatings	Additional treatment
I	Al_2O_3+Cr(0.1-0.2 μm)+TiN(0.5-1.2 μm)	-
IB	Al_2O_3+Cr(0.1-0.2 μm)+TiN(0.5-1.2 μm)	HCEB
II	Al_2O_3+Cr(0.1-0.2 μm)+TiN(2-3 μm)	-
IIB	Al_2O_3+Cr(0.1-0.2 μm)+TiN(2-3 μm)	HCEB
III	Al_2O_3+TiN(0.5-1.2 μm)	-
IIIB	Al_2O_3+TiN(0.5-1.2 μm)	HCEB
IV	Al_2O_3+TiN(2-3 μm	-
Uncoated steel		