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Structure and Properties of Nanocomposite Coatings Based on Titanium, Oxygen, Carbon and Hydrogen Obtained by the Cumulative-Detonation Device

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Nanocomposite coatings based on Ti, O, C and H thickness of 70-200 microns with hardness of 1015 ± 250 HV0.05 and porosity $\sim 2-5\%$ were deposited on aluminium samples by using the cumulative-detonation equipment. The nanocomposite coatings were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM) with diffraction, X-ray phase analysis, hardness measurements. It is shown that the area of the coating that adjoins to the substrate contains a transition layer of intermetallic TiAl and the nanocomposite coatings based on Ti, O, C and H are characterized by the presence of titanium nanocrystalline grains with face-centered close-packed lattice, amorphous phases and nanoamorphous oxide of titanium. It was found that the main phases of the composite coatings are Ti, TiO, rutile, anatase, Ti2O3. In the composite coatings formed from the hydrogenated powder was recorded the presence of δ -TiH phase and TiH₂.

Keywords: cumulative-detonation technology, aluminium alloys, nanostructured composite coatings, lamellas.

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1. INTRODUCTION

One of the priorities of science and technology is the creation of new materials, in particular, multi-, nanocomposite coatings with a typical grain size of less than 100 nm [1,2].

One of the new technologies for applying protective coatings, composites and other functions is the cumulative-detonation technology of coatings. Multifunctional nanocrystalline material on the surface of products with a wide range of controlled composition, structure and properties can be used to protect them from wear and corrosion, as well as to improve the thermal stability [3]. For example, to protect from wear and corrosion of aluminum products have a fairly thin layer of composite coatings based on Ti, O, C and H, which does not affect significantly the weight of the structure [4].

Taking into account high physical-mechanical properties of titanium and titanium ability to form stable solid solutions and a series of compounds with different types of chemical bonds with the combustion products, which contain oxygen, nitrogen, hydrogen and carbon, is of interest to the creation and study of multicomponent composite materials based on titanium surface production of light alloys [5]. The combination of such diverse components leads to the formation of a new material whose properties are quantitatively and qualitatively different from the properties of each of its components, and superior to traditional materials for their mechanical properties [6].

At present the titanium coatings are produced by plasma spraying of wire VT1-0. The coatings are porous and have low adhesion. The maximal values of adhesion (up to 80 MPa) are achieved at a substrate temperature of 500° C. The substrates are made from alloys VT6 and

VT20 [7]. Much work is underway now on using upgraded HVOF [8,9], as well as a helium jet under a pressure of 24 atm. and temperature of $450 - 550^{\circ}$ C [11], or a nitrogen jet under a pressure of 30 atm. and temperature of up to 600° C [12]. The titanium coatings are produced by using plasmatrons [10]. It can be noted that all the coatings are porous, their adhesion strength is not in excess of 30 - 50 MPa, and they comprise local phases with hardness of HV 700 - 1500. These phases contain nitrogen, oxygen and carbon.

The purpose of this study is to investigate the interaction of titanium powder obtained from titanium sponge, with the components of the combustion products in the shaped-charge cumulative-detonation device and its effect on the structure of protective nanocomposite coatings based on Ti, O, C and H.

2. EXPERIMENTAL PROCEDURE

2.1 Feedstock material, deposition process, and conditions

An essential difference of the cumulative-detonation device from the detonation one is that it combines the energy from several, specially profiled detonation chambers. This provides an efficient energy transfer to the powder materials. In addition, it is characterized by a wide possibility of controlling the velocity and temperature of the powder materials. The device operates at a frequency of up to 30 Hz, this allowing the use of standard powder and gas control devices, simplification of the equipment, reduction of its price, and improvement of its operational reliability.

The cumulative-detonation technology has of a pulse character. This makes it possible to form the composite coatings from a small distance (10 - 60 mm) in a shield-

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ing gas atmosphere. As a result, oxidation and losses of spraying materials are reduced. The titanium powder utilization factor in deposition of the composite coatings is 85 - 90 %. The velocity of the powder material is 800 - 900 m/s.

In this work, coatings were deposited on the surface of samples by the cumulative-detonation device [4]. The samples of aluminum alloy 1545 K of the system Al-Mg-Sc were used as a substrate.

Composite coatings of titanium powder were deposited (the results of fragmentation of titanium sponge) in the environment of the combustion products, which contain oxygen, nitrogen, hydrogen and carbon. Titanium sponge was saturated with hydrogen before the dispersion. Obtained powder filter out and held in a vacuum oven at 900° C for 4 hours.

Four types of powder were used: 1 – titanium (Ti), 2 – hydrogenated titanium (Ti/H), 3 – a mechanical mixture

Tab	le 1 –	The	morpho	ology	and	composition	of t	he	powd	lers
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of powders of titanium and boron amorphous (Ti/B), 4 - a hydrogenated mechanical mixture of powders of titanium and boron amorphous (Ti/B/H) (see. Table 1 and, for example, Fig. 1). The particle size was measured by the laser scattering method and confirmed by electron microscopy.

Since a mechanical mixture of such materials during the deposition of the coatings is easily splits, powder feeder with a rotating bunker and a dynamic mixer of powders was used. Composite coatings were deposited with a frequency of 20 Hz of the snake with a transverse displacement 4 mm and a three-time repetition. Speed of moving was 3000 mm/min, distance from the sample – 65 - 70 mm. The powders of Ti and Ti/H are sprayed by a two-chamber device with an output nozzle of 16 mm. Powders from a mechanical mixture of Ti/B and Ti/B/H were deposited on a single chamber device with an output nozzle of 20 mm.

Describerta		W			
Powders	Ti	0	В	Zr	Size of powder particles
Ti	99.40	-	-	0.60	6 - 70
Ti/H	97.09	2.91	-	-	1 - 50
Ti/B	77.40	1.09	21.51		0.6 - 60
Ti/B/H	81.91	3.88	14.21	-	0.7 - 19

Table 2 - The elemental composition of nanocomposite coatings

Continga	Wt%								
Coatings	Ti	Al	0	С	Ca	Si	В	Zr	Fe
Ti	83.23	0.49	14.17	0.61	1.50	-	-	-	-
Ti/H	61.34	0.48	33.63	1.31	-	3.23	-	-	-
Ti/B	60.16	0.54	22.51	3.21	-	1.73	10.63	0.57	0.64
Ti/B/H	61.23	0.42	22.28	1.94	0.29	1.84	10.95	0.40	0.64





Fig. $1-\mathop{\rm SEM}\nolimits$ (a) and TEM image (b) of the hydrogenated titanium powder

2.2 Microstructure Observation

Examinations of microstructure and elemental composition of the titanium powders and the nanocomposite coatings based on Ti, O, C, and H were carried out by using electron ion microscope Quanta 600 equipped with integrated microanalysis system Pegasus 2000. Local phase and diffraction analysis of the titanium powder and the nanocomposite coatings was conducted by using transmission electron field emission microscope Tecnai G2 20F S-T (FEI) with microdiffraction and X-ray powder diffractometer ARL X'TRA, providing integrated information on a layer of several microns thick.

3. RESULTS AND DISCUSSION

3.1 SEM observation of the system «nanocomposite coatings - substrate»

The study of the microstructure and elemental composition of the transverse sections of samples with composite coatings showed that were obtained uniform coatings with thickness of 70 - 200 microns and good adhesion to the substrate, the bulk of the coating material is deformed and tightly packed (see, for example, Fig. 2a). Porosity of the coatings was determined by metallographic method was 2 - 5%. STRUCTURE AND PROPERTIES OF NANOCOMPOSITE COATINGS BASED ...

The visible boundary of the coating-substrate interface has no defects. Fig. 2 shows that in the contact area of coating and substrate is mixed structure consisting of islands covering the substrate a very different shapes and sizes. Part of the powder material penetrated deeply and firmly connected to the substrate material (see. Fig. 2). At impact a large powder particles, it corrects and deforms the surface layer of the substrate. There are "splashes" of the substrate material, which are located in surface (see. Table 2). Area of the coating that adjoins to the substrate contains a transition layer of intermetallic TiAl (see. Fig. 2b). Total this layer has a high density of dislocations caused by the shock effect of plasmadetonation wave.





Fig. 2-SEM image of cross section of the nanocomposite Ti/H coating layer and substrate (a), TEM image of the coating-substrate interface (b), diffraction TEM photographs of a transition layer of intermetallic TiAl

Furthermore, it was established that the hardness of nanocomposite coatings is 1015 ± 250 HV_{0.05}, which is 15 times higher than the hardness of the substrate material $85\pm5\;HV_{0.05}.$ A wide range of hardness values of the composite coatings caused by their different phase composition and porosity. According to the theory [13] during the deposition, the small fraction of the powder is almost completely melted, while larger particles of the nucleus remain in the solid state. In practice, this leads to the formation of material with local differences in mechanical properties. The maximum hardness of the coating is associated with the formation of regions containing TiO and TiO₂ [14]. It is known [15], oxygen forms a large number of compounds with titanium, and their compositions are located within the lower and higher valence oxides, titanium dioxide (TiO up on TiO₂). Titanium is oxidized with greater speed compared to its interaction with other gases. The formation of solid solution of oxygen in titanium related to the strong distortion of the crystal lattice and, therefore, related to significant changes in the mechanical properties of titanium. Increasing the oxygen content leads to a sharp increase in strength, hardness and lower ductility of titanium.

Hydrogen is also absorbed by the titanium in extremely large quantities that can be explained by the formation, along with the introduction of solid solution, hydrogen compounds hydrides of titanium. Even at very low concentrations of hydrogen in titanium can be formed hydride of titanium. The increase of the concentration of hydrogen could lead to a sharp decrease in ductility. Further increase of the content of hydrogen could lead to a catastrophic decrease in ductility at room temperature [16]. Carbon dissolves in titanium in small quantities. Due to the low solubility of carbon in titanium content in the metal fraction of a percent of carbon causes a selection of metal carbide and fragile. A marked decrease in ductility and increase of strength and hardness of the metal take place at content of more than 0.1 -0.2%°C [17]. On further increase of the content of carbon due to the appearance of the carbide phase, the mechanical properties of titanium are more or less stabilized.

3.2 TEM observation of the system «nanocomposite coatings - substrate»

Local phase and structure analysis of the composite coatings based on Ti, O, C and H showed that lamellas in the coatings consisted of the mixture of titanium nanocrystalline grains with face-centered close-packed lattice and amorphous phases, and nanoamorphous oxide of titanium (see. Fig. 3). This is confirmed by results of diffraction analysis of the nanocomposite coatings (see. Fig. 4). This structure could be caused by a hightemperature cycle in formation of composite coatings [18,19].

Therefore, it can be assumed that the values of hardness in fine lamellae of the nanocomposite coatings are attributable to the absence of dislocations inside the crystalline grains and ratio of the volume contents of nanocrystalline to amorphous phases of metallic and non-metallic titanium compounds.

Strength of intermediate and near-interface layers leads to increase of deformation resistance of nanocomposite coatings. The absence of dislocations inside the crystalline grains leads to increase in elasticity and, at the same time, in plasticity of nanocomposite coatings. It was detected for the first time ever [19], as far back as 20-25 years ago, that ceramic materials of titanium oxides acquire superplastic properties at room temperature at the characteristic sizes of crystals equal to several nanometers.

3.3 XRD analysis of the nanocomposite coatings

Carried out phase analysis showed that the main phase of the coating layer, which is located at a distance of about 1-2 mm from the free surface was Ti with a face-centered close-packed lattice (a = 2.965 Å) (see. Fig. 4). The calculated interplanar distances reflections suggest the presence in the coatings and the following phases: TiO with a cubic lattice (a = 4.197 Å), rutile TiO₂ with tetragonal lattice (a = b = 4.585 Å, c = 2.972 Å), anatase TiO₂ with tetragonal lattice (a = b = 3.775 Å, c = 9.492 Å), Ti₂O₃ with a hexagonal lattice (a = b = 5.129 Å, c = 13.815 Å). In the nanocomposite coatings formed from the hydrogenated powder, M.G. KOVALEVA, M.Y. ARSEENKO, M.S. PROZOROVA, ET AL.

recorded the presence of δ -TiH phase with a cubic lattice (a = 4.415 Å) and TiH₂ with tetragonal lattice (a = b = 3.148 Å, c = 4.140 Å). The studies did not report the presence of boron in the coatings. Apparently this is due to the fact that micron particles of amorphous boron overheat and evaporate in the environment of the combustion products.



Fig. 3 - TEM image and diffraction photographs of material of nanocomposite coating of TiH powder: mixture of titanium nanocrystalline grains with face-centered close-packed lattice and amorphous phases (1), amorphous phases (C, Ti, Al, O) (2), nanoamorphous oxide of titanium (3)



Fig. 4 – XRD analysis of the nanocomposite coatings: 1 – Ti/H, 2 – Ti, 3 – Ti/B, 4 – Ti/B/H

4. CONCLUSIONS

Cumulative-detonation technology provides formation of dense composite coatings based on Ti, O, C, H thickness of 70-200 microns with hardness of 1015 ± 250 HV0.05. The porosity of coatings was $\sim 2-5\%$, which correlates

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with the technological requirements of industrial coatings. The apparent limit of adhesion of the coating to the substrate is free of defects. It was found a transition region coating/substrate consisting of a nanocrystalline TiAl. The main phases of the composite coatings are Ti, TiO, rutile, anatase, Ti₂O₃. In the composite coatings formed from the hydrogenated powder was recorded the presence of δ -TiH phase and TiH₂.

Based on the results of the study could be offered energy-saving technology for deposition of composite coatings based on Ti, O, C, H on substrates of aluminum alloy.

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