The study of the modes of Ta-Zr powder mixture non-vacuum electron-beam cladding on the surface of the cp-titanium plates

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Abstract. The effect of the modes of non-vacuum electron-beam cladding of Ta-Zr powder mixtures on the structure and properties of the layers formed on the surface of cp-titanium were studied. The mode of the electron-beam alloying of titanium with zirconium and tantalum, which ensured the formation of a defect-free layer with a high content of alloying elements was selected. Metallographic examination indicated the presence of a dendritic- and plate-type structure of cladded layers. The microhardness of the layers, formed at the optimum mode, was not changed in the cross section and was equal to 450 HV.

1. Introduction
Modern development of industry puts high demands on the materials, working in particularly aggressive environments, such as boiling solutions of acids. These materials should provide high mechanical properties combined with high chemical resistance to corrosion. Stainless steel is one of the most common corrosion resistant materials. However, despite the favorable combination of mechanical properties the use of stainless steels is limited by the reduced level of corrosion resistance in boiling acids. Titanium alloys have higher corrosion resistance [1-3]. Titanium is almost not subjected to corrosion in oxidizing acid solutions over a wide range of concentrations and temperatures, as its mediums promote its passivation [3]. However, titanium strongly interacts with boiling solutions of reducing acids such as hydrochloric, phosphoric and sulfuric [1, 4, 5]. High resistance is observed only in dilute solutions [5].

One way to reduce the corrosion rate in boiling acids is alloying with the elements that contribute to passivation in these solutions (tantalum). The corrosion resistance of this alloy is increased due to the formation of a dense and stable passive film Ta₂O₅ [6]. It is indicated in the sources [6-8] that a significant effect is achieved upon alloying titanium with tantalum in an amount of 40% or higher. However, a significant drawback is the high density of tantalum, which is equal to 16.6 g/cm³. Also this element is expensive as a consequence of its low prevalence in the crust. [7] The materials operation features should be also taken into account, since in some cases it’s enough to protect only the surface of the item, which is subjected to aggressive action. In this regard, obtaining the workpieces sparingly alloyed with tantalum on the surface of less scarce material (titanium) is an
important task. Such a solution can not only increase the corrosion resistance of the surface, provide savings of expensive element but significantly reduce contribution of the high density of tantalum into the total weight of the workpiece.

As the technology of production of tantalum-containing layers a method based on the partial melting of the alloying powder mixture by electron beams, injected in the air atmosphere is offered in the paper. This technology is implemented using an industrial electron accelerator ELV-6 at the Institute of Nuclear Physics SB RAS, which important advantage is the absence of a vacuum chamber. By doing so the remelted metal bath is protected from the atmosphere by means of the introduction of welding fluxes in the cladding mixture. It should be noted that in prior experiments powder mixture contained titanium powder in addition to tantalum and fluxes, which is added to wet the alloying component [9-11]. However, the melting point of tantalum and boiling temperature of titanium are close that may lead to evaporation of the wetting component and losses of alloying elements. To reduce the loss of tantalum it is rationally to replace the titanium powder to a refractory material with similar properties (zirconium). Experiments devoted to the cladding of Ta-Zr powder mixture were conducted earlier [12, 13]. Nevertheless, optimization of the non-vacuum electron-beam treatment modes was not carried out.

In this regard, the aim of this study is to investigate the influence of the modes of cladding of the Ta-Zr powder mixture on the surface of titanium VT1-0 by electron beams, outputted in an air atmosphere.

2. Materials and methods

Cladding of the tantalum-zirconium layers was carried out on the plates made of commercially pure titanium VT1-0. Plates dimensions were 50x50x12 mm. Powder mixture for cladding consisted of the tantalum powder, the zirconium powder and the flux in an amount of 11.5 g of Ta, 4.7 g of Zr and 6.3 g of flux. Flux was the mixture of LiF and CaF₂ salts in the ratio 3:1 by weight.

The technological experiment in creation of the surface-alloyed layers consisted of several stages. At the preparatory stage, the alloying powder mixture was thoroughly mixed and applied to the greater face of a titanium plate. Then, the plate was placed on a table-manipulator so that the distance from the outlet window of the accelerator to the surface of the formed powder layer was 90 mm. The table progressively moved longitudinally with respect to the window with the rate of 10 mm/s. Thus the plate surface was scanned in the transverse direction by the electron beam with the peak-to-peak value of 50 mm. At the final stage, the mechanical removal of the slag crust from the surface of the cladded layer was performed. In order to study the effect of electron-beam cladding conditions on the structure and properties of the layers the beam current value varied in the range of 21 to 24 mA.

The structural features of cladded layers were studied by optical and scanning electron microscopy using Carl Zeiss Axio Observer A1m and Carl Zeiss EVO 50 XVP microscopes respectively. Microsections for metallographic studies were prepared by the standard method. The samples were cut in the transverse direction of the surface-alloyed plates using a Struers Exotom-150 machine. Then cut samples were pressed into the polymeric material using a Buehler Simpli Met 1000 press. Further formed samples were ground and polished using a Buehler Ecomet 250/300 machine. The structure of the material was detected by chemical etching in a solution of 40% KOH, 30% H₂O₂ and H₂O in the reactant ratio of 2:1:4 by volume. The solution was heated up to the temperature 70-80 °C. The microsections were immersed in the etchant for 60 seconds.

The chemical composition of the surface-alloyed layers was determined using an INCA X-ACT (Oxford Instruments) energy-dispersive analyser. To evaluate the level of mechanical properties microhardness tests were conducted using Wolpert Group Hardness 402 MVD. The measurements were carried out on polished thin sections. Indenter impressions were directed from the surface area of the cladded layer to the titanium base. The number of indenter impressions was 20. The distance between indenter impressions was 200 microns. The load on the diamond indenter corresponded to the value of 0.98 N.
3. Results and discussion
The structure of the layers cladded at different currents is shown in Figure 1. It can be seen that with an increase in electron beam current the thickness of the surface-alloyed layer increases. Thus, the electron-beam treatment of the tantalum-zirconium powder mixture at a current of 21 mA leads to the formation of a layer with the thickness of 1.1 mm (Figure 1 a). The thickness of the cladded material on the samples obtained at a current of 22 mA and 23 mA was 1.5 and 1.9 mm, respectively (Figure 1 b, c). Maximum thickness (2.1 mm) was fixed in the experiments for the layer formed at a current of 24 mA. (Figure 1 d).

The structure of the layers formed at a current of 21 mA, has defects. The pores and the insoluble tantalum particles present in the material (Figure 2 a, b). Increasing the beam current by 1 mA helps eliminating pores in the cladded layer, but there is still a certain amount of insoluble particles of alloying components in cross section (Figure 2 c). Samples that were formed at a current of 23 mA and 24 mA are characterized by a homogeneous and defect-free structure (Figure 2 d, e). However, in the photomicrographs there is a significant contrast between the layers, obtained at the currents, which indirectly indicates the difference in the chemical composition. The sample that was cladded at a current of 23 mA is more alloyed with Ta and Zr due to less depth of the titanium fusion penetration compared to the sample formed at a current of 24 mA. This assumption was confirmed in [14] on the system of Ti-Ta. Thus, to obtain a defect-free surface layer with the highest concentration of alloying components electron beam treatment should be carried out at the beam current of 23 mA.

The structure of a layer formed at a current of 23 mA has a dendritic structure (Figure 2 d). Dendritic crystals grow preferentially in the direction from the surface layer to the melting zone of the base material that corresponds to the direction of the heat removal. At high magnifications thin-plate material structure can be seen (Figure 2 f).
Figure 2. The structure of the surface-alloyed layers formed at the beam current of: a, b – 21 mA; c – 22 mA; d, f – 23 mA; e – 24 mA

The concentration of alloying elements in the layer formed on the optimal current amounts is 31.4 % (wt.) Ta and 11.74 % (wt.) Zr. Using EDX analysis it was established that there is a difference in chemical composition between the surface area and the central portion of the deposited layer (see Figure 3). The near-surface zone is less alloyed with tantalum and zirconium (spectrum 1), compared with the central part of the layer (spectrum 2). This is due to a large difference in the densities of alloying elements and the base material. Since during the electron beam treatment heavier components settle on the bottom of the molten metal bath, displacing the lighter.

Figure 3. EDX analysis of the Ti-Ta-Zr layer: a – the spectrum accumulation region; b – the chemical composition

To evaluate the mechanical properties, the microhardness tests were conducted. Distribution of the microhardness over the surface of the sample prepared at a current of 23 mA is shown in Figure 4. The average microhardness of the Ti-Ta-Zr layer does not vary throughout the thickness, and is about 450 HV. In the transition to the base metal is an abrupt drop in the level of microhardness up to 130 HV, which corresponds to the hardness of commercially pure titanium.
4. Conclusions
The optimal mode of electron-beam cladding of the tantalum-zirconium powder mixture was selected by the work. The layers, formed at the optimal mode, had a homogeneous structure in which no defects such as pores and insoluble particles of alloying components were observed. It was found that the structure of cladded layers and the plate is presented a dendritic structure. The concentration of alloying elements in the surface layer according to the EDX analysis was 31.4 % (wt.) Ta and 11.74 % (wt.) Zr. The microhardness of the cladded material was 450 HV. The value of the microhardness did not change for the whole cross section of the formed layer, which indicated the homogeneity of mechanical properties in different parts.

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References
[1] Leyens C and Peters M 2003 Titanium and Titanium Alloys Fundamentals and Applications (Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA) p 532
[2] Matthea J and Donachie Jr 2000 Titanium: A Technical Guide (ASM International, Materials Park, Ohio) p 381
[3] Shreir L L, Jarman R A and Burstein G T 1976 Corrosion Metal/Environment Reactions (London: Newnes-Butterworths)
[4] Uhlig’s Corrosion Handbook 2011 ed Winston Revie R (Hoboken: John Wiley & Sons, Inc.) p 1288
[5] Corrosion resistance of titanium. TIMET Corporation Brochure 1997 (Denver: Titanium Metals Corporation)
[6] De Souza K A and Robin A 2007 Mater. Chem. Phys. 103 351-60
[7] De Souza K A and Robin A 2003 Mater. Lett. 57 3010-16
[8] Lyons L R 13 December 1960 Tantalum-titanium corrosion resistance alloy U.S. Patent No 2,964,399
[9] Golkovski M G, Bataev I A, Bataev A A, Ruktuev A A, Zhuravina T V, Kuksanov N K, Salimov R A and Bataev V A 2013 Mater. Sci. Eng., A 578 310-17
[10] Ruktuev A, Golkovski M, Samoylenko V, Komarov P, Bataev I and Bataev A 2014 Adv. Mater. Res. 1040 759-63
[11] Ruktuev A A, Samoylenko V V and Golkovski M G 2014 Adv. Mater. Res. 682 100-103
[12] Samoylenko V V, Lazuenko D V, Lenivtsiva O G and Polyakov I A 2014 IOP Conf. Series: Materials Science and Engineering 66 012026
[13] Samoylenko V V, Lazuenko D V, Lenivtsiva O G and Lozhkin V S 2015 Appl. Mech. Mater. 698 424-29
[14] Samoylenko V V, Lenivtsiva O G, Polyakov I A, Laptev I S and Martyushev N V 2016 IOP Conf. Series: Materials Science and Engineering 124 012117