Study of the effect of heat treatment on the structure of surface alloys formed on cp-titanium plates by electron beam cladding in the air atmosphere

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Abstract. The effect of different heat treatment on the structure of Ti-Ta-Zr layers formed by electron beam cladding in the air atmosphere on titanium substrates was investigated. It was established that annealing of surface alloys at the temperature of 900 °C promoted the formation of an equilibrium coarse-plate structure regardless of the concentration of the alloying elements. No complete annealing occurred at temperatures below 800 °C. Quenching of the layer with 26 % Ta, 15 % Zr from 900 °C made it possible to obtain a more homogeneous structure of the material. Significant changes in the morphology of alloys were also observed for layers with a lower concentration of tantalum after quenching from 600...900 °C.

1. Introduction
The current level of the chemical industry development puts forward new requirements for the materials operating under conditions of constant chemical aggression of the various types of corrosive media. Materials of this type should have a high complex of mechanical and anticorrosion properties. Titanium is one of the materials that can provide the listed properties. Titanium is characterized by high specific strength, ductility and corrosion resistance while the metal has low density [1-3]. The disadvantage of the metal is its low resistance to hot acids. The impact of these media contributes to the dissolution of the surface at high speed, which does not allow using it under similar conditions. Since only areas contacting with the medium are subjected to corrosion, the formation of protective layers with a high level of corrosion resistance on the surface of the metal will solve this problem. In addition, this approach will preserve the complex of mechanical properties of the titanium substrate.

The investigations carried out earlier have shown that an increase in the resistance of titanium to corrosion in boiling acid solutions is possible due to combining tantalum and zirconium powders over electron beam cladding on the surface of metal substrate [4, 5]. This solution makes it possible to increase titanium resistance to corrosion, both in boiling nitric acid and hydrochloric acid solutions. It should be noted that in the above papers the structure of the cladded layer is presented by a finely dispersed plates. From the standpoint of corrosion resistance, this structure is unfavorable, since it is
possible to form galvanic pairs between the plates and the space between it. In addition, each boundary of the plate will serve as an additional stress concentrator in the emerging film, due to a violation of coherence at the junction between the phases.

For this reason, the formation of a single-phase structure is one of the ways to increase the corrosion resistance of the alloy without changing the chemical composition. Another possible way to increase durability is to form a coarser structure of the plates. Such a solution will reduce the number of interface boundaries that will lead to the formation of a film with fewer defects on the alloy surface. Quenching allows the formation of single-phase structures for alloys containing β-stabilizers (tantalum). Reducing the dispersion of the plates is achieved by performing such a heat treatment as annealing.

In this regard, the structure of surface layers obtained by combined tantalum and zirconium electron-beam cladding on titanium alloys after various types of heat treatment was studied in this paper.

2. Materials and methods

The preparation of surface-alloyed titanium substrate was carried out at the ELV-6 electron accelerator at the Institute of Nuclear Physics of the SB RAS. In the course of the experiment, cladding of two compositions with a different ratio of tantalum to zirconium in the initial powder mixture (Table 1) was realized. The total weight of the powder mixture in both cases was 22.5 g. The plates of commercially pure titanium with a thickness of 12 mm and a size of 100x50 mm were used as the substrate. Before melting, the alloy powder mixture was applied evenly to the substrate surface. Electron-beam treatment was carried out according to the operating conditions given in [6]. After cladding the layers, the formed workpiece was machined to remove the flux residues.

The obtained materials were annealed in the temperature range 600 ... 900 °C during 1 hour. Heat treatment at the temperature above 900 °C was not conducted because of the propensity of technically pure titanium to a strong grain growth in the β-region. Quenching of the samples was carried out in water from similar temperatures.

The structure of the materials before and after heat treatment was studied using a Carl Zeiss Axio Observer Z1m optical microscope and a Carl Zeiss EVO 50 XVP scanning electron microscope. The content of the alloying elements in the cladded layers was determined using INCA X-ACT.

3. Results and discussion

The chemical composition of the samples after cladding is presented in Table 2. Melting of the powder mixture No. 1 (Table 1) with an electron beam makes it possible to form a layer with a concentration of 12 % Ta and 23 % Zr. The change in the ratio of alloying components in the initial powder mixture to the higher tantalum concentrations promotes the formation of a layer in which the tantalum content is 26 %, and zirconium content is 15 %.

| Sample number | Ta  | Zr  | CaF₂ | LiF  |
|---------------|-----|-----|------|------|
| No. 1         | 4.9 | 9.6 | 6.0  | 2.0  |
| No. 2         | 9.8 | 6.0 | 5.0  | 1.7  |

The content of the subjected alloying elements in the cladded layers was determined using INCA X-ACT.

| Sample number | Elements composition (wt. %) |
|---------------|-------------------------------|
|               | Ta   | Zr   | Ti   |
| No. 1         | 12.0 | 23.0 | 65.0 |
The morphology of surface alloys without thermal treatment is characterized by a dendritic structure (Figure 1 a). At large magnifications, a plate-like structure is revealed (Figure 1 b). Annealing of these layers at the temperature of 600 °C does not lead to the changes in the structure of the material. Increasing the heat treatment temperature to 700 °C promotes the appearance of the first indications of a change in the structure of alloys. For a layer with 26 % Ta, 15 % Zr, it is expressed in the local growth of α-plates (Figure 1 c). Presumably, the plates grow in regions enriched in tantalum, since this surface alloying method is characterized by the presence of dendritic liquation [6, 7]. The layer with 12 % Ta, 23 % Zr at the temperature of 700 °C has no significant changes in the structure of the alloy. However, when the annealing temperature increases to 800 °C, the first indications of the plate growth appear on the sample (Figure 1 d), and the structure of the alloy has a similar morphology with a 26 % Ta layer, 15 % Zr after annealing at 700 °C. This difference in the beginning of the diffusion processes is explained by the difference in the chemical composition of the cladded layers. So for an alloy with a higher concentration of tantalum, phase transformations will begin at a lower temperature due to stabilization of the high-temperature β-phase of titanium with tantalum.

![Figure 1. The structure of the layers after cladding (a, b), annealing at 700 °C (c) and 800 °C (d).](image-url)

Annealing of the workpiece with 26 % Ta, 15 % Zr at 800 °C promotes an increase in the proportion of growing plates (Figure 2 a). There is no complete annealing of the material, since small interlayers with a finely dispersed lamellar structure are observed between regions of different chemical composition (Figure 2 b). Heating the layers to 900 °C with subsequent slow cooling promotes the formation of the layers with a completely annealed structure. This is evidenced by the formation of a typical α+β structure having a characteristic lamellar packets structure of the α-phase with interlayers of the β-phase (Figure 2 c, d). In addition, with this annealing, the dimensions of the plates are much larger than that of the alloy without heat treatment.
The structure of the layers after cladding (a, b), annealing at 800 ºC (c) and 900 ºC (d). The structure of surface alloys after quenching is shown in Figure 3. Heating the layers to the temperature of 600, 700 and 800 ºC followed by quenching in water does not lead to a significant change in the structure of the cladded materials compared to the material without heat treatment. The morphology of the alloys is represented by a dendritic structure against which a plate-like structure is revealed during etching (Figure 3 a, b). An increase in the heating temperature to 900 ºC does not lead to the significant changes in the structure of the layer with 12 % Ta, 23 % Zr, but it contributes to the formation of a more homogeneous structure on the 26 % Ta alloy, 15 % Zr (Figure 4 a). Nevertheless, prolonged etching of the material still helps to identify the lamellar structure. It should be noted that the plates are etched significantly worse than the surrounding space (Figure 4 b). This is attested to by a large number of holes, chaotically located in the body of grain. This fact suggests that quenching in water from 900 ºC of the layers with 26 % Ta, 15 % Zr can positively affect the corrosion resistance of this material.

Figure 2. The structure of the layers after cladding (a, b), annealing at 800 ºC (c) and 900 ºC (d).

Figure 3. The structure of the layers after cladding.
4. Conclusion
Temperatures for the heat treatment of surface alloys formed by the method of electron-beam cladding of tantalum and zirconium powders were determined. It was established that annealing at the temperature of 900 °C promotes the formation of an equilibrium structure having the coarse-plate morphology, compared to the material without thermal treatment. Quenching of the cladded layers from temperatures of 600 .. 900 °C does not allow obtaining a single-phase structure. The only exception is the layer with 26 % Ta, 15 % Zr after quenching from 900 °C, which is characterized by the formation of a more homogeneous structure. Long-term etching of this alloy promotes the identification of lamellar morphology. However, the structural components are etched out worse than the surrounding space, which can indirectly indicate an increase in corrosion resistance compared to layers without heat treatment.

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References
[1] Leyens C and Peters M 2003 Titanium and Titanium Alloys Fundamentals and Applications (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) p 532
[2] Matthew J and Donachie Jr 2000 Titanium: A Technical Guide (ASM International, Materials Park, Ohio) p 381
[3] Lütjering G and Williams J C 2007 Titanium (Engineering Materials and Processes) (Springer, Berlin) p 442
[4] Samoylenko V V, Ogneva T S, Polyakov I A, Ivanchik I S, Lenivtseva O G and Matts O E 2016 Structure and Properties of Surface Alloyed Layers Formed by Non-vacuum Electron Beam Cladding of Ta and Zr Powders on Commercially Pure Titanium Plates AIP Conference Proceedings 1785 040057
[5] Samoylenko V V Polyakov I A Golkovski M G Bataev I A Ruktuev A A 2014 Poverhnostnoe legirovanie titana tantalom i cirkoniem metodom vnevakuumnoj ehletronno-luchevoj naplavki poroshkovyh materialov Proceedings of the XXIV International Conference Radiation Solid State Physics 345-51 [in Russian]
[6] Samoylenko V V Lozhkina E A Polyakov I A Lenivtseva O G Ivanchik I S and Matts O E 2016 The study of the modes of Ta-Zr powder mixture non-vacuum electron-beam cladding on the surface of the cp-titanium plates IOP Conf. Series: Materials Science and Engineering 156 012024
[7] Bataev I A Zhuravina T V Ruktuev A A Lenivtseva O G Romashova Y N 2012 Structural investigation of “titanium-tantalum” coatings obtained by non-vacuum electron beam cladding Obrabotka metallov 56 56-59 [in Russian]