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Corrosion resistance of Ti-Ta-Zr coatings in the Boiling Acid Solutions

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Abstract. In this study corrosion resistance of Ti-Ta-Zr coatings fabricated on VT14 titanium alloy workpieces using a high-energy electron beam injected in the atmosphere was investigated. Estimation of corrosion resistance of surface alloyed layers was carried out by the weight-change method. Boiling solution of 65 % nitric acid in water and 5 % of sulfuric acid in water were used as the corrosive environments. Investigation of samples after corrosion tests was carried out using a Carl Zeiss EVO 50 XVP scanning electron microscope.

Keywords: Titanium alloy, Zirconium, Tantalum, Electron beam cladding, Corrosion resistance.

1. Introduction

Titanium and its alloys possess a number of unique properties such as high specific strength, biocompatibility, heat resistance and excellent corrosion resistance [1, 2]. However, production of the constructions for critical applications in nuclear and chemical industries requires a higher corrosion resistance. Thus, tantalum-, zirconium- and niobium-based alloys are often used as structural materials in these areas. Meanwhile, the literature data give evidence of increase of titanium corrosion resistance by alloying it with tantalum and zirconium [3-5]. Taking into account a high price of aforementioned materials, it is more appropriate to fabricate the layers alloyed with tantalum and zirconium on the surfaces of titanium workpieces. Non-vacuum electron beam cladding can be considered as the efficient technology for fabrication of such materials [6-9].

In papers [6, 8-10] result of investigations of surface alloyed layers obtained on commercially pure (CP) titanium substrates are presented. Ultimate tensile strength of CP-titanium is about 300 MPa. Increase of strength of surface alloyed materials can be achieved by substitution of CP-titanium substrate by VT14 titanium alloy. Ultimate tensile strength of this material is 3-fold higher than that of CP-Titanium (VT1-0 grade) and equal to 980 MPa.

2. Materials and methods

VT14 titanium plates with dimensions of 12x50x100 mm were used as a base material in this study. A powder mixture used for cladding consisted of alloying elements and protective fluxes (Table 1).

Fluxes kept a molten bath from saturation with atmosphere gases and contributed in uniform distribution of alloying elements in the depth of cladded layers.

Table 1. Compositions of the powder mixtures and percentage of alloying components in the coating determined by EDX analysis, wt. %.

Sample label	Percentage of the components in the powder mixtures					Percentage of alloying components in the coating			
	Ta	Zr	Ti	CaF_2	LiF	Ta	Zr	Al	Mo
3Ta-4Zr	8.2	8.2	40	32.7	10.9	3.3	3.9	4.5	3.2
9Ta-3Zr	17	8.5	35	29.62	9.88	8.6	3.3	3.8	3.3

Before cladding, a powder mixture was homogeneously distributed on a surface of a treated workpiece. A surface density of the alloying powder placed to the workpiece surface before cladding was 0.3 g/cm^2 on the average; the total surface density of a powder mixture with flux was 0.45 g/cm^2.

Cladding was carried out in Budker Institute of Nuclear Physics SB RAS (Novosibirsk) using an ELV-6 electron accelerator. A beam current was 24 mA; a sample movement respectively to the electron beam was 10 mm per s; a scanning amplitude was 25 mm; a scanning frequency was 50 Hz.

An INCA X-ACT (Oxford Instruments) energy dispersive X-ray (EDX) analyzer was used for determining concentrations of alloying components in the surface alloyed layers.

Samples for corrosion tests were cut out of the cladded layers; their dimensions were 1x15x20 mm. These plates were hung on fluoroplastic filaments and immersed in 65 % nitric acid in water and 5 % of sulfuric acid in water. Diluted solution of sulfuric acid was chosen due to the aggressive action of this acid to titanium alloys. The temperatures of nitric and sulfuric acids were about 125° C and 100 °C respectively. At equal time intervals samples were removed, washed, dried and weighed. After that the experiment was continued. Summarized testing duration in nitric and sulfuric acids was 120 h and 50 min respectively. During the experiment a corrosion rate of cladded layers and a reference material (VT14 titanium alloy) was determined. Surfaces of samples after corrosion tests were analyzed by a Carl Zeiss EVO 50 XVP scanning electron microscope.

3. Results and discussion

Results of corrosion tests are presented in Table 2 and in Figure 1. It was found that the VT14 titanium substrate possessed the maximum dissolution velocity in both acids. Electron beam cladding of Ta-Zr powder mixtures lead to significant increase of corrosion resistance (Table 1, Figure 1 and Figure 2). The lowest corrosion rate (0.296 mm per year in nitric acid and 19.3 mm per year in sulfuric acid) was typical for samples alloyed with 9 % Ta and 3 % Zr. Corrosion rate of the alloys doped with 3 % Ta and 4 % Zr was 0.392 mm per year and 49.8 mm per year in nitric and sulfuric acids respectively.

Table 2. Corrosion rate of VT14 titanium alloy and Ti-Ta-Zr alloyed layers.

Sample label	Corrosion rate in the boiling concentrated solution of nitric acid in water, mm per year	Corrosion rate in the boiling concentrated solution of sulfur acids, mm per year
VT14	0.4768±0.016	53.7±3.6
3Ta-4Zr	0.392±0.036	49.8±6.4
9Ta-3Zr	0.296±0.008	19.3±2.5

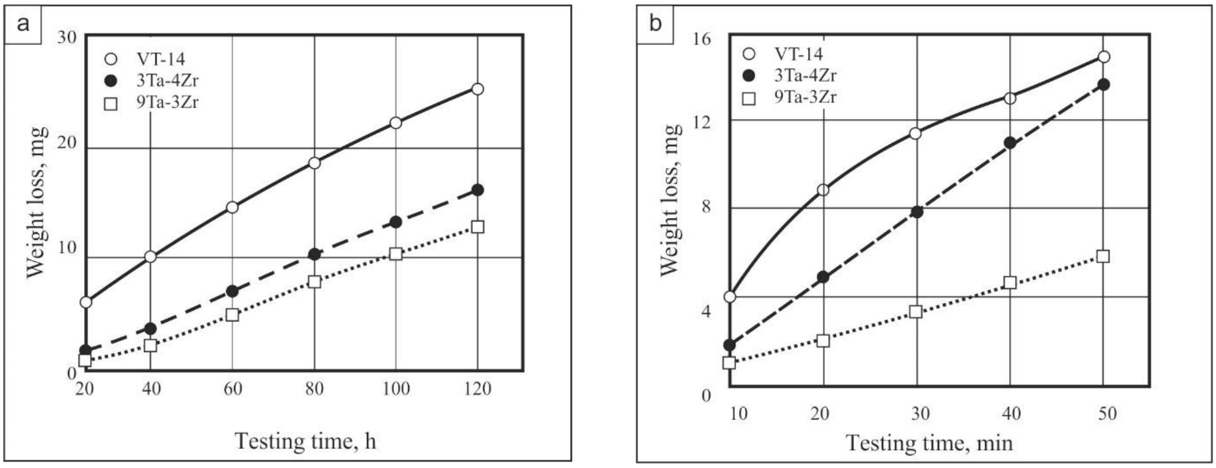

Figure 1. Relation between mass loss and test duration of samples in concentrated solutions of nitric (a) and sulfuric (b) acids.

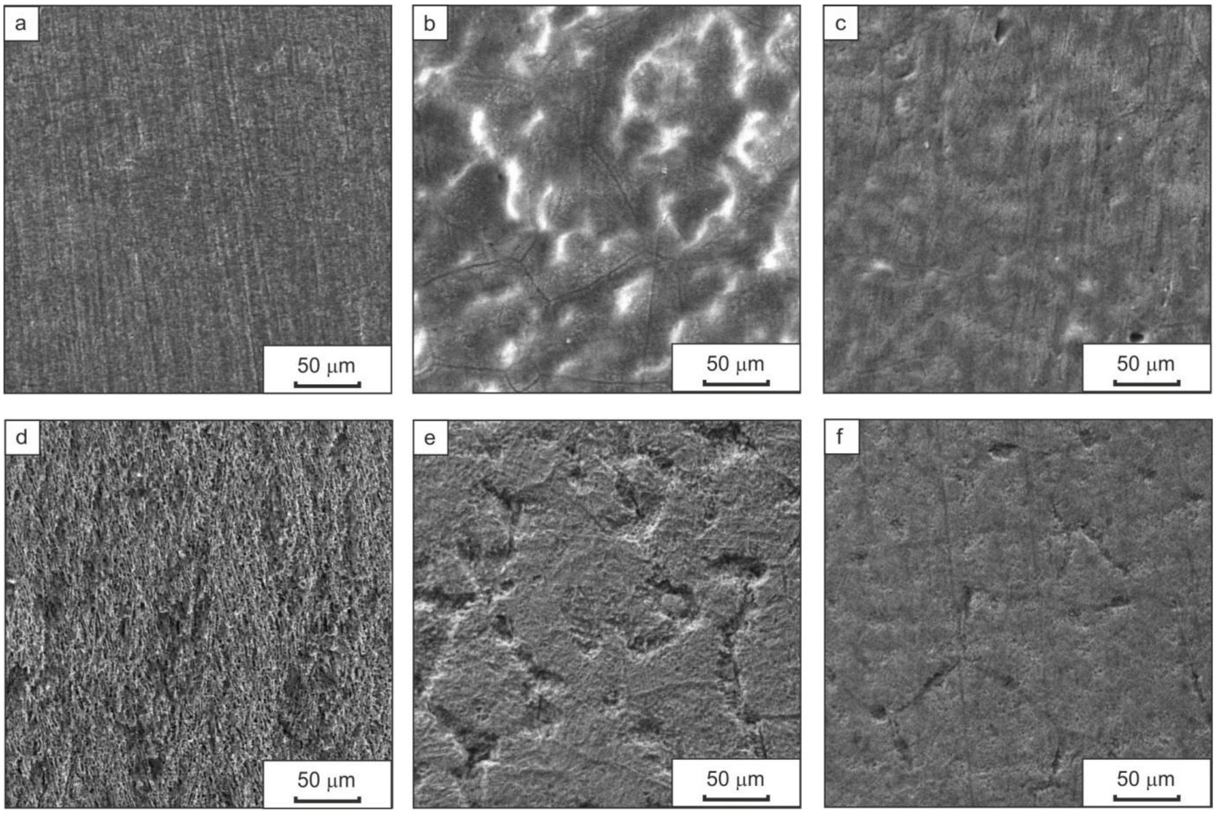

Figure 2. Surfaces of the samples after corrosion tests in the boiling concentrated solution of nitric acid (a-c) and sulfur acids (d-f): a, d – VT14 titanium alloy; b, e - 3Ta-4Z alloy; c, f –9Ta-3Zr alloy.

Surfaces of samples after corrosion tests in boiling solutions of acids were analyzed using a scanning electron microscope. Traces of preliminary mechanical treatment were observed on the surfaces of samples after testing in nitric acid (Figure 2, a-c). Damage of 3Ta-4Zr alloy exposed by boiling nitric acid occurred predominantly in the areas corresponding to the interdendritic space with formation of apparent relief which was not observed on the surfaces of other samples (Figure 2 a, c). The higher was a percentage of alloying components in the coatings the fewer interdendritic space was exposed to etching by a corrosive solution. Figure 2 c shows the contrast between dendritic axes and the interdendritic space.

In the boiling solution of 5 % sulfuric acid in water VT14 titanium alloy was demonstrated a tendency to general corrosion (Figure 2 d). Cladding of the Ti-Ta-Zr powder mixture led to transformation of the corrosion character. Thus, 3Ta-4Zr alloy fractured in the aggressive environment with formation of corrosion pits (Figure 2, e). It can be supposed that pits appeared in the area corresponded to the interdendritic space due to the lower percentage of alloying elements in them. Increase of Ta content in the cladded layer up to 9 % led to decrease of number of pits and their depth (Figure 2, f). There were no any corrosive pits on the surface of this alloy comparing to 3Ta-4Zr (Figure 2 e, f).

4. Conclusions

Coatings fabricated on the titanium substrate by non-vacuum electron beam cladding possessed a high corrosion resistance in the boiling solutions of nitric and sulfuric acids. Alloying titanium with 9 % Ta and 3 % Zr led to 1.6-fold and 2.78-fold increase of corrosion resistance in solutions of nitric and sulfuric acids respectively comparing to VT14 titanium alloy.

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