The technology of forming Ti-Nb layers on the surface of titanium alloy plates using a high-voltage electron beam output into a protective argon medium

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Abstract. The structure and properties of layers obtained by electron-beam melting of titanium-niobium powder mixtures in a protective argon medium are studied in the work. The method allows cladding traces 16.5 ... 17.5 mm wide with a maximum thickness of 3.5 ... 4.5 mm. The concentration of niobium in the formed surface layers is 6.6 and 13.8%. The cladded material has a predominantly lamellar structure. The production of layers in the protective medium of argon makes it possible to increase the microhardness level, as well as the corrosion resistance of titanium in boiling solutions of nitric and sulfuric acid.

1. Introduction

Titanium alloys have recently become more widely used in industry [1, 2]. Titanium possesses a high complex of mechanical and anticorrosive properties that draws the attention of researchers and engineers working in directions where the listed properties are necessary. For this reason, titanium and its alloys have proven themselves in the chemical and nuclear industries. However, in some cases, the use of metal is limited to particularly aggressive conditions of operation and, generally, titanium alloys are not chemically resistant in such mediums as boiling solutions of strong acids.

Addition of alloying elements with higher corrosion resistance under the similar conditions, but not forming chemical compounds and mechanical mixtures, improves the metal chemical resistance. These requirements are met by elements located next to the titanium in the periodic table: Zr, Hf, Nb, Ta, Mo. Zirconium and hafnium are analogues of titanium because these elements have completely isomorphic correspondence. However, a significant increase in chemical resistance is achieved at high alloying component concentrations: 50% and more [3]. Alloying with molybdenum makes it possible to protect titanium in boiling solutions of sulfuric and hydrochloric acid [4, 5]. Nevertheless, an increase in the molybdenum content leads to a decrease in the chemical resistance of the alloy in boiling nitric acid due to its re-passivation. One of the elements possessing high resistance both in boiling solutions of HCl, H_2SO_4, and in HNO_3 is tantalum. However, the addition of this component leads to a significant increase in the cost and weight of the alloy (density 16.6 g/cm^3). The cheaper analogue of tantalum is niobium. The element is less chemically resistant than tantalum, but has similar corrosive characteristics. In addition, the addition of niobium does not lead to a significant

increase in the weight of the alloy (density 8.57 g/cm^3). For this reason, its use as the main alloying component for the purpose of complex increase in the corrosion resistance of titanium in various acids is the most rational.

Obtaining titanium products niobium-alloyed through all the volume is expedient in those cases when its introduction makes it possible to provide the necessary mechanical properties. From the standpoint of increasing the corrosion resistance, the presence of niobium throughout the material has practically no effect on corrosion resistance, since only the surface layer steps into the interaction. In this regard, it is sufficient to protect only the surface exposed to corrosion.

Previous studies on the creation of niobium-containing layers on the surface of titanium alloys have shown a high efficiency of the electron-beam cladding. The method allows applying homogeneous layers a few millimeters thick. Experiments on the formation of surface alloys, as a general rule, are conducted in air that leads to a slight saturation of the deposited material with gases of the air medium by a depth of ~ 30…60 μm [6], despite the presence of fluxes. In order to eliminate the influence of gases, electron-beam treatment is rationally to be carried out in a protective medium. For this reason, a new approach to the creation of niobium-containing layers in a protective medium of argon is implemented in the work.

2. Materials and methods

The layers were cladded on the basis of the industrial ELV-6 electron accelerator at the Institute of Nuclear Physics of the SB RAS. In order to implement the method in a protective medium, a sealed chamber was specially designed and created, in which a movable table was placed. Before treatment, the chamber was filled with protective gas (argon). The workpieces were titanium plates 12 mm thick and 100x25 mm in size with a previously applied trace of the powder layer. The trace was applied along the center of a large side plane. Since the electron-beam treatment was carried out in a protective medium, the flux was completely eliminated from powder portion, which was used to protect the melted metal when the method was performed in air [7]. The composition of the initial powder portion is shown in Table 1.

Table 1. Chemical composition of the powder portion and the cladded layer**.**

Specimen designation	Powder portion composition, wt. %		Cladded layer composition, wt. %	
	Nb	Ti	Nb	Ti
6.6 % Nb	27.2	72.8	6.6	93.4
13.8 % Nb	66.0	34.0	13.8	86.2

Electron-beam treatment was carried out at a beam current of 11 mA; electron energy 1.4 MeV; conveying speed 10 mm/s. The distance from the outlet to the surface of the workpiece was 136 mm. In the works carried out earlier, this distance was 90 mm [7]. This difference is explained by the availability of special technological equipment connecting the outlet of the accelerator with a protective chamber.

The structural study was carried out using the Carl Zeiss microscopes Axio Observer Z1m and EVO 50 XVP. The content of niobium in the formed layer was determined by micro-X-ray analysis using INCAX-Act (Oxford Instruments).

To determine the level of mechanical properties, the microhardness was measured. The microhardness was determined on the cross-sections using a WolpertGroup 402 MVD hardness tester.

The level of corrosion resistance of the cladded layers was estimated by the weight method. As an aggressive medium, a boiling solution of concentrated nitric acid (65 %) and dilute solution of boiling sulfuric acid (5%) were chosen. For the study, specimen with the size of 10x10x1 mm were prepared from a cladded layer. The plates of technically pure components of similar dimensions were used as materials of comparison. The total time of immersion in boiling solutions of nitric and sulfuric acid

was 120 hours and 50 minutes, respectively. The weight loss was monitored every 24 hours when tested in HNO_3 and 10 minutes when tested in H_2SO_4 solution. Changes in the mass of materials were recorded on the analytical balance AND GR-300 with an accuracy of 10^{-4} g.

3. Results and discussion

The cross-section of the layer with 6.6 % Nb is shown in Figure 1. The formed layer is characterized by a practically defect-free structure. A small amount of pores is detected in the fusion zone of the layer with a titanium base on the edge of the applied trace. The layer thickness in the central part is ~ 4.5 mm. The width of the trace is 16.5 mm. The cross section of the layer with 13.8 % Nb has a similar structure. A small difference is observed in the width and thickness of the formed material. The thickness of the surface alloy with 13.8 % Nb in the central part is 3.5 mm, and the width of the trace is ~ 17.5 mm.

Figure 1. The cross-section of the Ti-Nb layer cladded by an electron beam in a protective media of argon.

At the micro level, the structure of the cladded layers is mainly represented by lamellar morphology (Figure 2 a, b). In a specimen with 6.6 % Nb, this morphology is characterized by two types of structures: fine- and coarse-lamellar. The finely dispersed lamellar structure is identified only at high magnifications and forms the background of the cladded layer (Figure 2 a). The coarse-grained structure is fixed only in individual grains (Figure 2 b). The direction of growth of such plates coincides with the orientation of finely dispersed plates. For a surface alloy with 13.8 % Nb, a coarse-plate structure is not observed in the grain volume (Figure 3 a). However, there are small light areas that are poorly identified by chemical etching (Figure 3 b). Presumably, these areas are regions with a higher content of niobium. According to the works [8] when electron-beam cladding of niobium-containing mixtures on the surface of titanium workpieces, the formation of a structure with an apparent chemical heterogeneity is typical. Since only small local microvolumes are found in the layer with 13.8 % Nb, it can be assumed that a further increase in the concentration of niobium in the alloy will lead to an increase in aliquation.
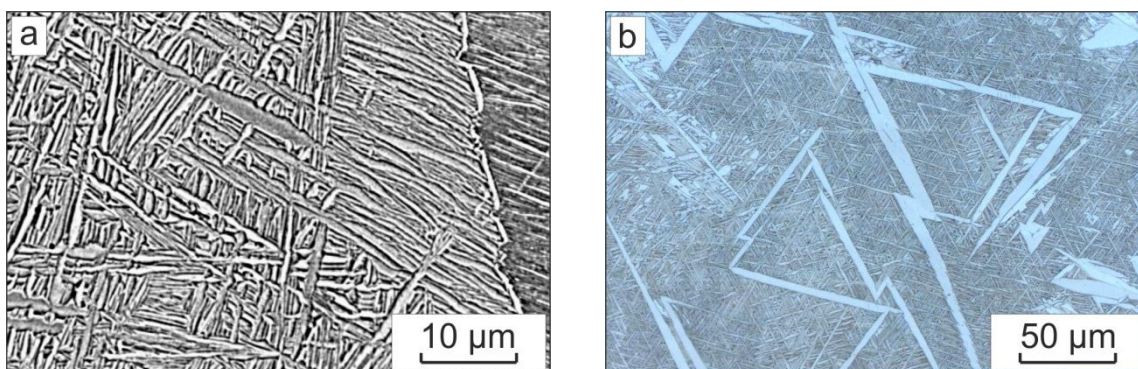

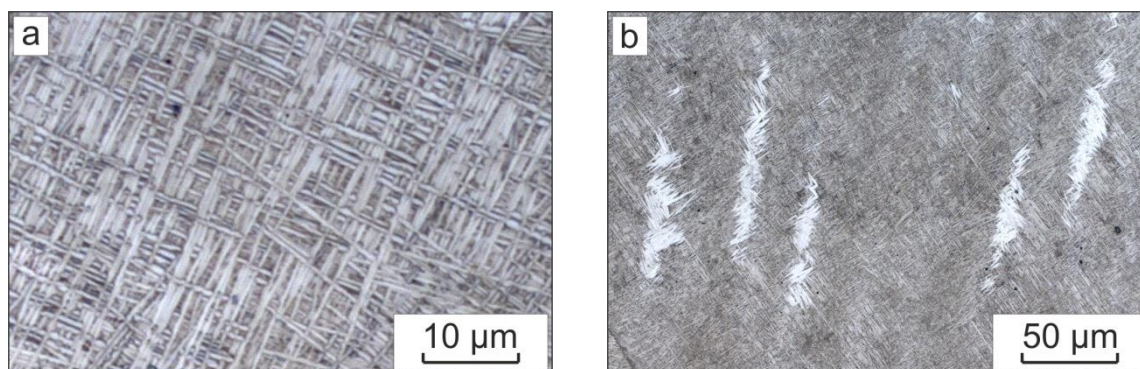**Figure 2.** The structure of the layers with 6.6 % Nb.

Figure 3. The structure of the layers with 13.8 % Nb.

To determine the level of mechanical properties, durometric tests were carried out. The results of the experiment are shown in Figure 3. The lowest value of the microhardness level was recorded for a cp-titanium base, which is ~ 185 HV. Electron-beam cladding of niobium in argon allows increasing this index by 1.4 ... 1.6 times. The HV value for the 6.6 % Nb layer was 255. The sample with the highest concentration of niobium in the experiment showed 295 HV.
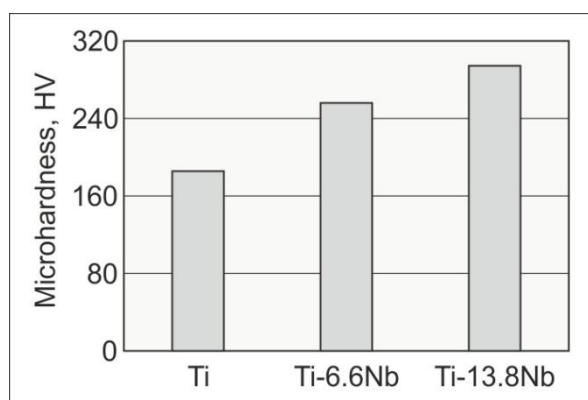

Figure 4. Microhardness of cp-titanium and layers with 6.6 % Nb and 13.8 % Nb.

Corrosion resistance of layers with different concentrations of niobium was estimated in boiling solutions of nitric and sulfuric acids. The results of the tests conducted in boiling concentrated HNO_3 are shown in Figure 5 a. The highest value of corrosion rate was recorded on a titanium specimen, and it was 0.158 mm/year. Surface alloying of titanium with niobium in an argon media promotes an increase in the level of corrosion resistance of the protected material. Forming a layer with 6.6 % Nb allows to reduce the corrosion rate to 0.037 mm/year, which is 4.3 times lower compared to titanium. A higher effect of surfacing is achieved when forming an alloy with 13.8 % Nb. The corrosion rate of this layer is 0.019 mm/year, and the anticorrosive effect of this type of protection reaches 8.3 times. Cp- niobium under the influence of aggressive solution for a year would lose a layer of metal equal to 1.2 microns.

Boiling solution of dilute (5 %) sulfuric acid has a more aggressive effect on the materials under study. This is evidenced by high values of corrosion rate (Figure 5 b). The lowest level of corrosion resistance in the experiment was shown by a sample made of cp-titanium. The corrosion rate of this material in the sulfuric acid solution was 64.3 mm/year. Electron-beam cladding of niobium-containing layers in the protective media of argon makes it possible to reduce the dissolution rate of the material by 2.3 ... 12.8 times. So for a sample with 6.6 % Nb, the corrosion rate is 28.4 mm/year. While for a surface alloy with 13.8 % Nb, dissolution of the material under the action of an aggressive

medium proceeds at a rate of 5 mm/year. For samples prepared from cp- niobium, no changes in the sample mass were observed during the experiment.
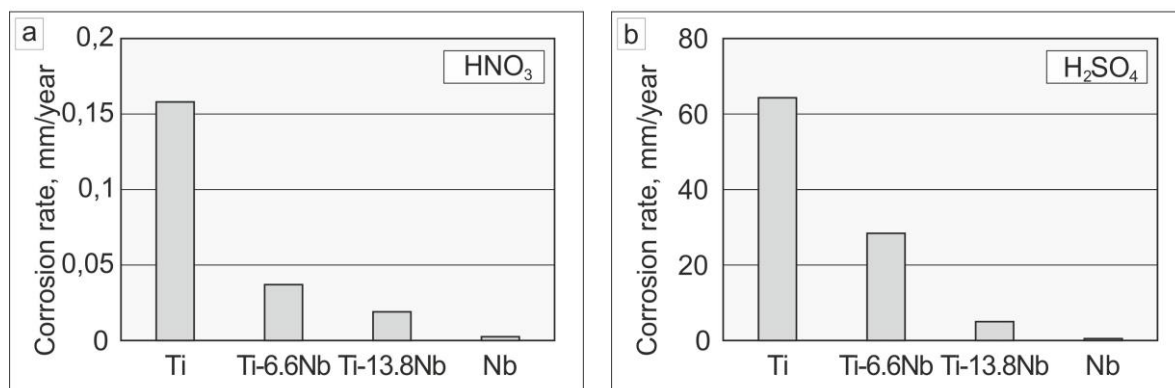

Figure 5. The corrosion rate of titanium, niobium and Ti-Nb layers in a boiling solution of 65 % nitric acid (a) and 5 % sulfuric acid solution (b).

4. Conclusion

Electron-beam cladding of niobium-containing powder mixtures allows the formation of layers with a maximum thickness of 3.5 ... 4.5 mm on the surface of titanium base. In the zone of fusion of the layers with the base, defects are practically not observed, except for single pores. Surface alloys are characterized by a lamellar structure throughout the cross-section of the cladded material. Fusing a surface with a previously applied powder layer helps to increase the microhardness level by 1.4 ... 1.6 times to 255 ... 295 HV compared to the cp- titanium. Electron-beam alloying with niobium makes it possible to obtain an alloy characterized by a higher resistance to corrosion in boiling acid solutions than the base material.

References
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