

## Composite material of the Ti-Ta-Zr system intended to work in boiling sulfuric and hydrochloric acids

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**Abstract.** The paper presents the results of a study of relatively thick corrosion-resistant coatings of the Ti-Ta-Zr system. The coatings are obtained by surfacing powder mixtures on a titanium base using a focused electron beam emitted into the air atmosphere. It was shown in previous works that the coatings of the Ti-Ta-Nb system obtained in this way are resistant to boiling concentrated nitric acid, but not sufficiently resistant to two other boiling strong acids: sulfuric and hydrochloric. The purpose of this work is to overcome this shortcoming by forming a fused deposited layer of the Ti-Ta-Zr system with a high degree of alloying, resulting in a coating that is resistant to all three of the mentioned strong acids at their boiling temperatures.

### 1. Introduction

Strong acids, in particular nitrogenic, sulfur and hydrochloric at elevated temperatures up to boiling one are used in a number of chemical processes. There are only a small number of metallic materials suitable for use in such severe conditions. The most resistant to boiling strong acids are tantalum, to a lesser extent zirconium, niobium and special nickel-based alloys – hastelloys. The listed materials are expensive, especially tantalum. In addition, tantalum is in some cases inconvenient for use due to its high specific gravity. The resistance of cheaper, traditionally used corrosion-resistant materials: titanium and stainless steels drops sharply with increasing media temperature. They are not suitable for boiling acids. As one of the options to overcome the difficulties associated with the search for corrosion-resistant materials, a composite material was proposed based on a titanium sheet with a coating of about 2 mm thick, consisting of alloys of the Ti-Ta and Ti-Ta-Nb systems [1, 2]. This material is produced by surfacing mixtures of initial powders onto a titanium substrate using extracted into atmosphere a focused electron beam as an energy source. An industrial electron accelerator generates the beam. The work was carried out at the “UNU Stand ELV-6” facilities at the Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences. The resulting composite material has a very high (about 0.01 mm/g) resistance to boiling nitric acid up to a concentration of 68%. Its cost is relatively low compared to the cost of the alloying components included in the protective layer. However, the resulting material is not resistant to two other boiling strong acids: sulfuric and hydrochloric.

To overcome this shortcoming, in the present study, Zr is introduced into the surfacing mixture instead of Nb. The reasons for this substitution are as follows. On Fig.1 shows the so-called isocorrosion curves in the concentration-temperature coordinates for sulfuric (a) and hydrochloric (b) acids. In accordance with the name of the curves, all points lying on them refer to the same level of corrosion resistance, namely, a corrosion rate of 0.1 mm/g. Graphs are taken from [3–5]. The authors as well placed on graphs the curve of the boiling point of acids depending on their concentration. Points lying above these curves were obtained at pressures above atmospheric. It can be seen the resistance of Zr significantly exceeds the resistance of Nb, and the resistance of stainless steels and titanium is still incomparably lower.

There is another consideration in favor of choosing Zr as the alloying element. During the formation of the deposited Ti-Ta-Nb layer, titanium is added to the initial powder mixture as a component, which can be called a wetting agent. Of the metals included in the powder, it melts first, wets the refractory components of powder, filling the voids between them.

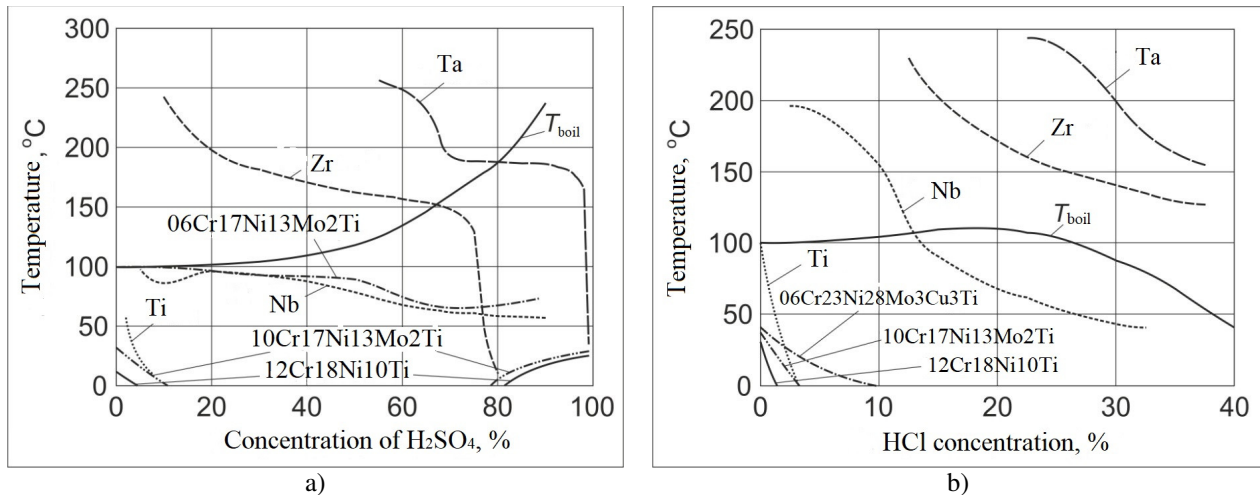


Fig.1. Isocorrosion curves corresponding of 0.1 mm/g in sulfuric (a) and hydrochloric (b) acids.

Next, the refractory components are dissolved in a common titanium bath, which is formed both from titanium from the powder and from the substrate. Because of the melting point of zirconium is not much higher than the melting point of titanium, it can itself serve as a wetting agent in the formation of a coating of the Ti-Ta-Zr system, which makes it possible to exclude titanium from the initial powder mixture. Since the mass thickness of the initial powder layer (in g/cm<sup>2</sup>) in this technology is fixed and determined by the energy of the beam electrons, the exclusion of the titanium component makes it possible to increase the degree of alloying of the deposited layer.

Along with the two noted positive properties of zirconium, its negative feature is the larger size of the atom compared to the atoms of titanium and tantalum. This leads to additional, in comparison with the Ti-Ta-Nb system, stresses in the lattice and its greater imperfection. High stresses and lattice defects contribute to a decrease in the corrosion resistance of the material. As measurements show [6, 7], the Ti-Ta-Zr system in boiling nitric acid is noticeably less resistant than the Ti-Ta-Nb system with a comparable degree of alloying with corrosion-resistant elements. High stresses and lattice defects contribute to a decrease in the corrosion resistance of the material. An increase in resistance of the Ti-Ta-Zr system also in nitric acid can be expected due to a significant increase in the concentration of alloying components in the protective layer.

## 2. Materials and Methods

The description of the method of surfacing powder mixtures on titanium bases, the process parameters and the characteristics of the electron accelerator are given in previous works, for example, [1, 2, 7]. Briefly the main features of the process are as follow. Before surfacing, a layer of powder mixture is placed on a plate made of commercially pure titanium VT1-0. The mixture consisted of powders of tantalum, zirconium and flux, the latter consisted of fluorides CaF<sub>2</sub> and LiF taken in a ratio of 3:1 by weight. The flux serves as protection against atmospheric action. The plate had dimensions of 12×50×100 mm, the powder was placed on its large side. Technical grades of powders of tantalum, zirconium and fluxes were used. The chemical composition of the metal components of the powder is given in Table 1. The ratio of components in the powder is given in Table 2. A plate with a layer of powder moved along its length under a scanning electron beam with a frequency of 50 Hz at a speed of 1 cm/s. The scanning direction was perpendicular to the direction of movement of the plate, the span of scanning coincided with the width of the plate.

**Table 1.** Chemical composition of the components of the surfacing powder, wt.%.

| Ta    | Ba   | Mg   | Mo   | Cl   | Fe   | K    | Ca             | Other elements |
|-------|------|------|------|------|------|------|----------------|----------------|
| 98.11 | 0.82 | 0.32 | 0.27 | 0.23 | 0.08 | 0.05 | 0.04           | 0.08           |
| Zr    | Hf   | Mg   | P    | W    | In   | Ti   | Other elements |                |
| 97.54 | 1.45 | 0.2  | 0.11 | 0.1  | 0.1  | 0.09 | 0.41           |                |

The electron energy in the beam was 1.4 MeV. The mass thickness of the powder layer (surface density) was  $0.45 \text{ g/cm}^2$ , which is comparable with the effective penetration depth of the electron beam into various materials [1, 7]. The beam current was 23 mA, which corresponds to its power of 32.2 kW.

The paper investigates two types of coatings: obtained by a single surfacing of a powder mixture and a double surfacing of a mixture of the same composition to increase the degree of alloying of the surface layer. The increase in concentration during double surfacing is achieved due to the remelting during processing of the powder placed on the first layer with an already formed layer. In this case, the content of alloying elements in the deposited material increases. The chemical composition of the deposited layer was determined by the EDS method during the study of samples on a Carl Zeiss EVO50 XVP scanning electron microscope using an X-ACT analyzer (Oxford Instruments). In the course of metallographic studies, the structure and mechanical properties of the resulting composite material were determined.

The authors evaluated the corrosion resistance of the material by the weight method in accordance with Russian GOST R 9.907-2007. To determine the corrosion resistance, plates 1 mm thick and  $20 \times 30 \text{ mm}$  in size were cut out from the applied coatings. The plates were cut by the method of electric spark cutting from the middle part of the deposited layer. Fig.2 shows cross sections of the alloyed layers obtained with an optical microscope at low magnification. On Fig.2b, a layer with a high content of alloying elements, obtained by surfacing the second coating layer, is clearly distinguished. Under it is the unaffected part of the first layer. The corrosion test plate was cut from the second doubly alloyed coating layer.

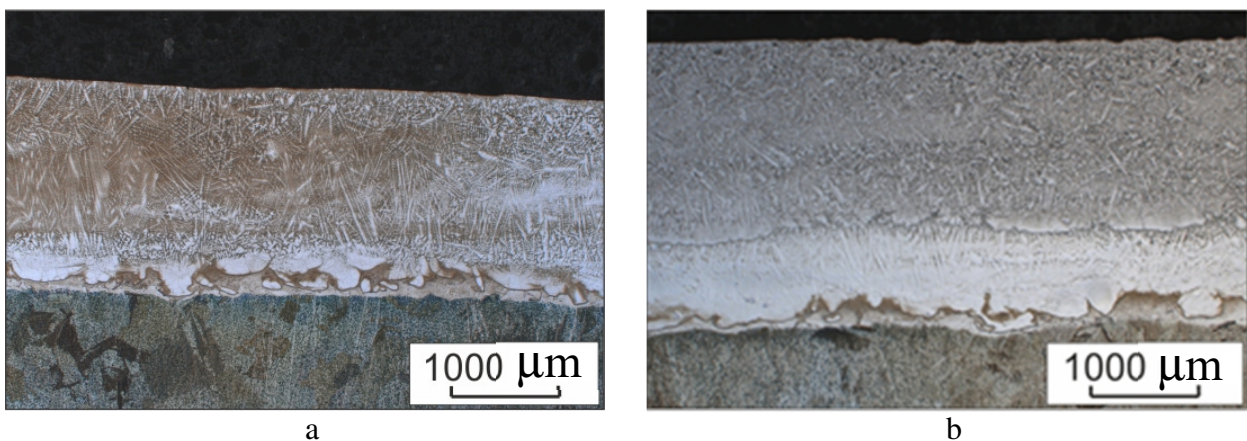


Fig.2. Cross-section of layers surface-alloyed with tantalum and zirconium at low magnification: a – single surfacing; b – double surfacing with an electron beam.

Plates suspended on fluoroplastic threads were immersed in flasks with acid of a given concentration. To equalize the temperature of the acid inside the flasks and establish the equality of temperatures between the flasks, they were immersed in a metal reservoir with mineral oil, which was installed on an electric heating plate (Fig.3). The oil temperature was controlled.



Fig. 3. Corrosion testing equipment.

Vapors of boiling acid rose from the flasks into a water-cooled reflux condenser hermetically attached to the flasks, where they condensed and flowed into the flask. The tests were carried out in concentrated 65% nitric, 5, 10, 20, 30% sulfuric and 5, 10, 20, 30% hydrochloric acids. The test time depended on the degree of aggressiveness of the medium. It was divided into 5 stages of equal duration. Before the start of the tests, as well as after each stage, the samples were taken out, washed in distilled water, then in acetone, dried in a stream of hot air, and weighed on an analytical balance AND GR-300 with an accuracy of 0.0001 g. The acid after each stage was replaced with a fresh one.

### 3. Composition and structure of the deposited layer

The proportion of titanium in the deposited layer is determined of the degree of its penetration from the top layer of the base into the melt bath during the formation of the coating. In Table 2 shows the concentration of the components of the powder mixture before surfacing and the average concentration of alloying elements in the deposited layer. In the marking of samples in the left column of the table, weight percentage concentrations of elements in the deposited layer are used, rounded to integer values.

Previous studies on Ti-Ta and Ti-Ta-Nb systems indicate the presence of dendritic segregation in layers formed by an electron beam [8]. The difference in the crystallization temperatures of the chemical elements entering the melt explain it. This phenomenon is also typical for layers obtained by surfacing Ta-Zr powder mixture. The presence of a clear contrast in the images obtained from the surface of unetched thin sections in the backscattered electron mode (Fig.4) indicated it. Measurement of the chemical composition of local microvolumes showed that the light areas corresponding to the branches of the dendrites are more enriched in tantalum, and an increased content of titanium and zirconium is observed in the interdendritic space. Table 3 shows the values of the measured concentrations at the indicated in Fig.4 microsites.



**Table 2.** The concentration of alloying elements in the initial powder layer and the surfaced alloyed layer

| Samples marking         | Concentration of alloying elements in the initial powder layer, weight % |    |      | Chemical composition in the surfaced alloyed layer |      |      |       |     |      |
|-------------------------|--------------------------------------------------------------------------|----|------|----------------------------------------------------|------|------|-------|-----|------|
|                         | Ta                                                                       | Zr | Flux | wt. %                                              |      |      | at. % |     |      |
|                         |                                                                          |    |      | Ta                                                 | Zr   | Ti   | Ta    | Zr  | Ti   |
| 31Ta-12Zr               | 51                                                                       | 21 | 28   | 31.4                                               | 11.7 | 56.9 | 11.5  | 8.8 | 79.9 |
| 48Ta-20Zr<br>(2 layers) | 51                                                                       | 21 | 28   | 48.4                                               | 19.8 | 31.8 | 23    | 19  | 58   |

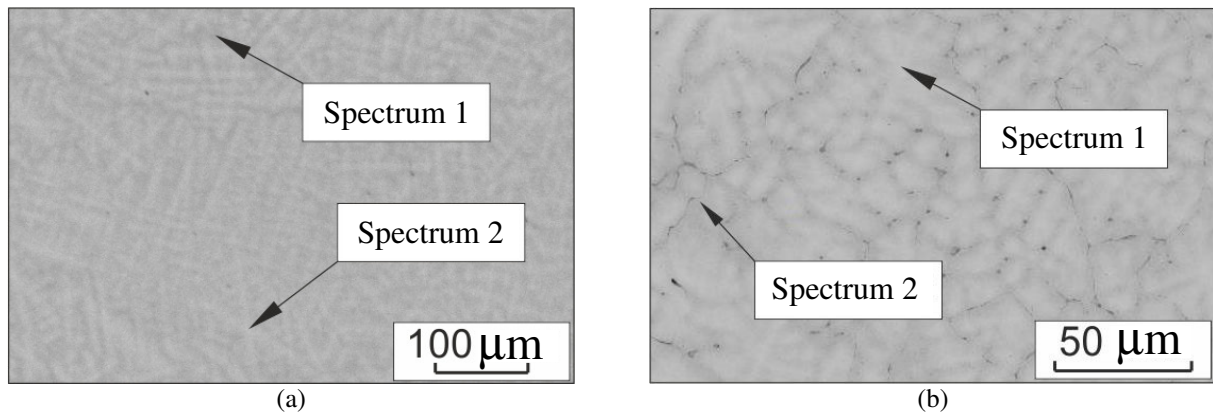


Fig.4. Scanning electron microscope images of alloyed layers: a – 31Ta-12Zr, b – 48Ta-20Zr.

**Table 3.** Local chemical composition of layers alloyed with tantalum and zirconium

| 31Ta-12Zr  | Composition, wt. % |    |    | 48Ta-20Zr  | Composition, wt. % |    |    |
|------------|--------------------|----|----|------------|--------------------|----|----|
|            | Ta                 | Zr | Ti |            | Ta                 | Zr | Ti |
| Spectrum 1 | 26                 | 12 | 62 | Spectrum 1 | 57                 | 15 | 28 |
| Spectrum 2 | 32                 | 10 | 58 | Spectrum 2 | 41                 | 24 | 35 |

The average distribution of alloying elements over the depth of the deposited layer is sufficiently uniform, as can be seen in Fig.5, which shows the distribution of elements in selected rectangular areas located at different depths in the 31Ta-12Zr sample (Table 4). The black wavy zone at the bottom of the figure is the bottom of the weld pool.

**Table 4.** Depth distribution of alloying elements at sample 31Ta-12Zr

| #          | Concentration, wt. % |    |    |
|------------|----------------------|----|----|
|            | Ta                   | Zr | Ti |
| Spectrum 1 | 29                   | 11 | 60 |
| Spectrum 2 | 33                   | 13 | 54 |
| Spectrum 3 | 34                   | 13 | 53 |

According to the results of X-ray diffraction (Fig.7), the coating in a single deposited sample consists of three phases: martensitic  $\alpha'$ ,  $\alpha''$  and an equilibrium  $\beta$ -phase. In the double-deposited layer, only the  $\beta$ -phase is present. The complete transition to the  $\beta$ -phase can be facilitated by 2 conditions: the combined  $\beta$ -stabilizing effect of Ta and Zr at their high concentration and accelerated cooling of the deposited layer from the high-temperature region. Let's analyze them separately. According to the equilibrium double phase diagram of Ti-Ta, the formation of the  $\beta$ -phase at room temperature requires a concentration of tantalum equal to 85%. Zirconium, according to the Ti-Zr diagram, is a very weak  $\beta$ -stabilizer and, it would seem, its presence can be ignored. Consider the second condition – rapid cooling.

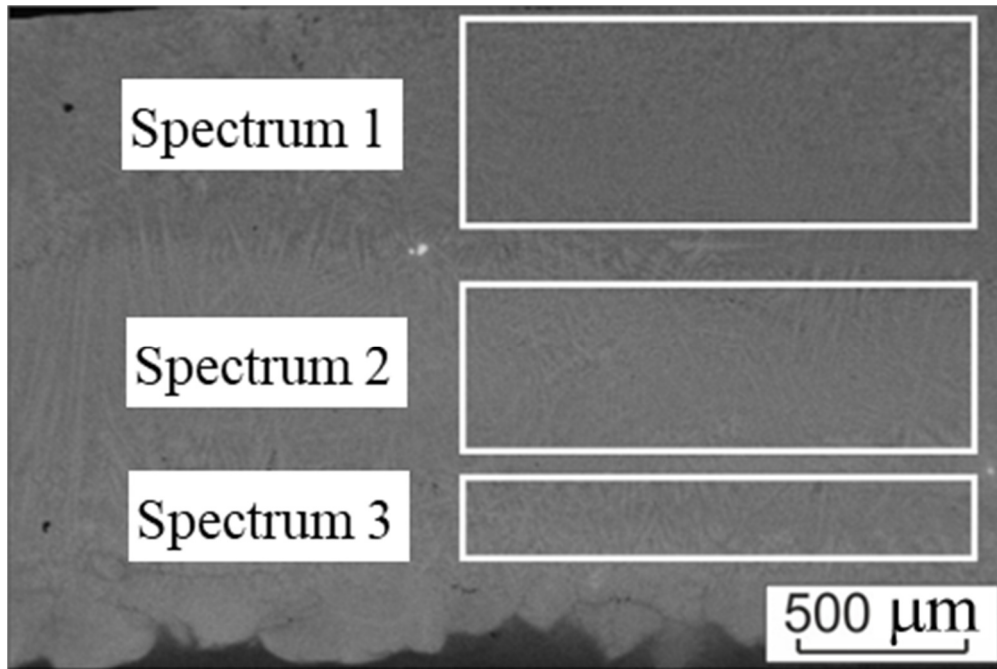


Fig.5. The average concentration of alloying elements in selected rectangular areas located at different depths of the deposited layer.

Previously, experiments were carried out on the formation of coatings by repeated surfacing of a mixture of Ta and Ti powders on a titanium base (unpublished results of Samoylenko V.V.). As a result of fourfold surfacing, a layer with a tantalum concentration of  $54\% \pm 3\%$  was obtained over the entire depth of the fourth layer. It follows from the X-ray diffraction pattern of this layer (Fig.7) that it mainly consists of the  $\beta$ -phase, but there is also a small amount of the  $\alpha'$ -phase. Since the cooling conditions of this sample were similar to the cooling conditions of the 48Ta-20Zr one, and a complete transition to the  $\beta$ -phase did not occur even at 54% Ta, we can conclude that the transition to the  $\beta$ -phase of the alloyed layer of the 48Ta-20Zr sample cannot be explained only by a high cooling rate. It remains to be assumed that Zr in the presence of a high concentration of Ta in the titanium matrix becomes an appreciable  $\beta$ -stabilizer in this ternary system. The observed single-phase structure is a factor that increases the corrosion resistance, which is confirmed by comparing the results of measuring the corrosion resistance of single and double surfacing layers presented below.

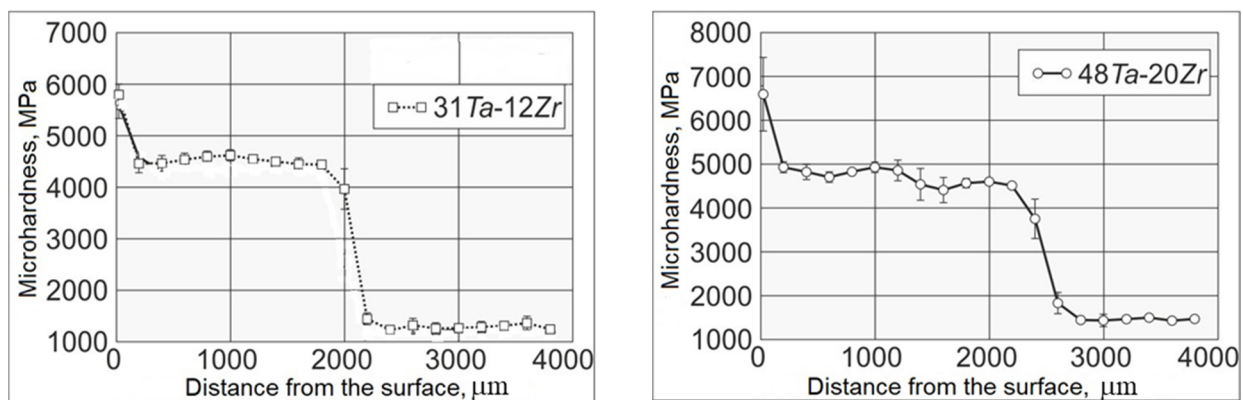


Fig.6. Distribution of microhardness over the cross section of single-layer and two-layer coatings.

The formed alloyed layers have increased hardness (Fig.6) compared to coatings of the

Ti-Ta-Nb system [1, 2, 7, 9]. Moreover, the hardness of a two-layer sample is slightly higher than the hardness of a single-layer one. The increased hardness can be explained by the large size of the zirconium atom compared to the atoms of Ti, Ta, Nb.

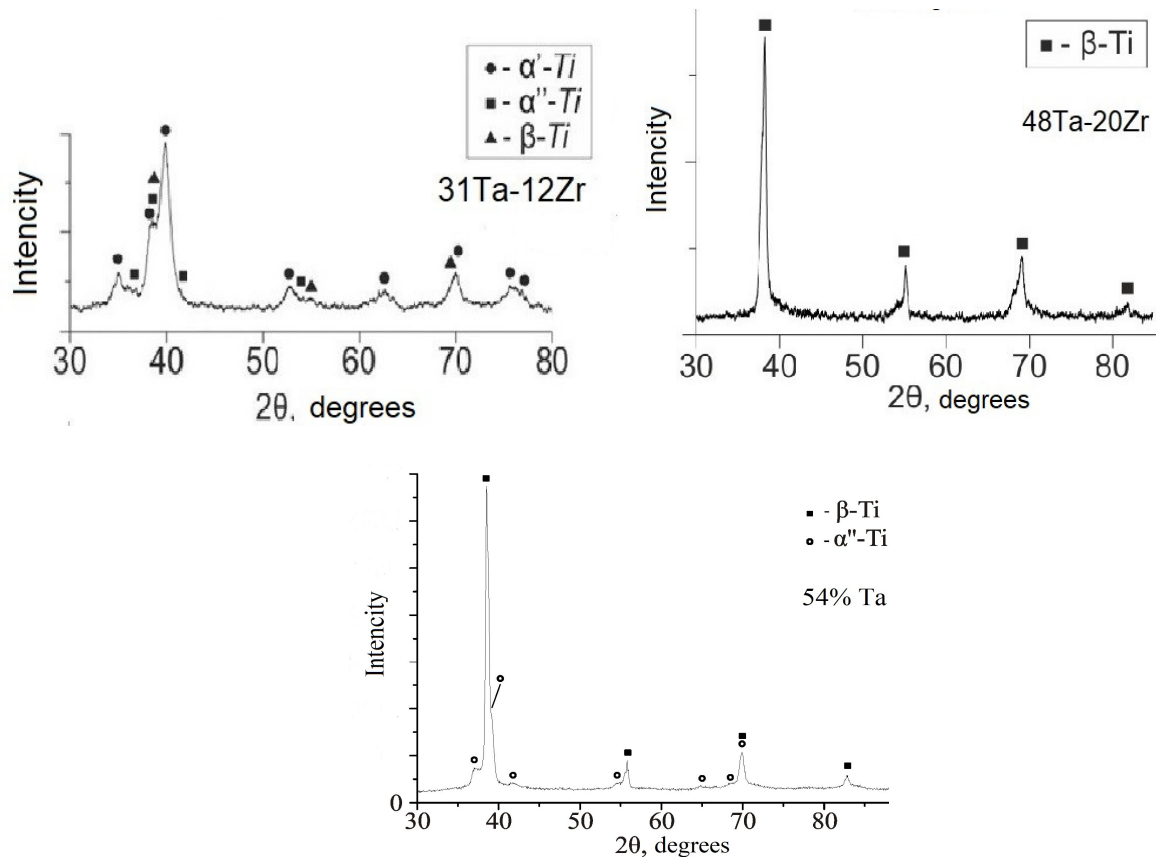


Fig.7. Results of X-ray phase analysis of corrosion-resistant layers.

#### 4. Corrosion resistance of fused layers

The test results in nitric and sulfuric acids are presented in Table 5, in hydrochloric acid – in Table 6. The duration of the tests in nitric acid was 120 hours. Due to the greater aggressiveness of sulfuric and hydrochloric acids, the time for testing the coatings under study in them was significantly reduced. The unstable VT1-0 titanium and the 31Ta-12Zr single-layer coating were tested for 50 min, the more resistant 48Ta-20Zr, zirconium, and tantalum were tested for 5 h. Weight loss during testing for all samples was approximately linear in time, i.e., no passivation effect of the surface layer was observed.

**Table 5.** Corrosion rate of surface alloyed layers and reference samples in boiling solutions of nitric and sulfuric acids of various concentrations, mm/year

| Material       | HNO <sub>3</sub> | H <sub>2</sub> SO <sub>4</sub> |        |        |        |        |
|----------------|------------------|--------------------------------|--------|--------|--------|--------|
|                | 65%              | 5%                             | 10%    | 20%    | 30%    | 40%    |
| Titanium VT1-0 | 0.191            | 41.5                           | 74.2   | 184.6  | 569.6  | 1980   |
| 31Ta-12Zr      | 0.143            | 0.8                            | 1.8    | 10.2   | 28.8   | 73.8   |
| 48Ta-20Zr      | 0.006            | 0.00*                          | 0.017* | 0.062* | 0.061* | 0.071* |
| Zirconium      | 0.001            | 0.00*                          | 0.00*  | 0.00*  | 0.00*  | 0.016* |
| Tantalum       | 0.000            | 0.00*                          | 0.00*  | 0.00*  | 0.00*  | 0.01*  |

\* test duration in H<sub>2</sub>SO<sub>4</sub> was 5 h

**Table 6.** Corrosion rate of surface alloyed layers and reference samples in boiling hydrochloric acid solutions of various concentrations, mm/year

| Material       | HCl   |       |       |       |
|----------------|-------|-------|-------|-------|
|                | 5%    | 10%   | 20%   | 30%   |
| Titanium BT1-0 | 13.8  | 35.1  | 242.6 | 389.2 |
| 31Ta-12Zr      | 0.1   | 1.9   | 57.6  | 239.4 |
| 48Ta-20Zr*     | 0.017 | 0.156 | 0.191 | 2.374 |
| Zirconium*     | 0.022 | 0.022 | 0.041 | 0.041 |
| Tantalum*      | 0.000 | 0.000 | 0.000 | 0.000 |

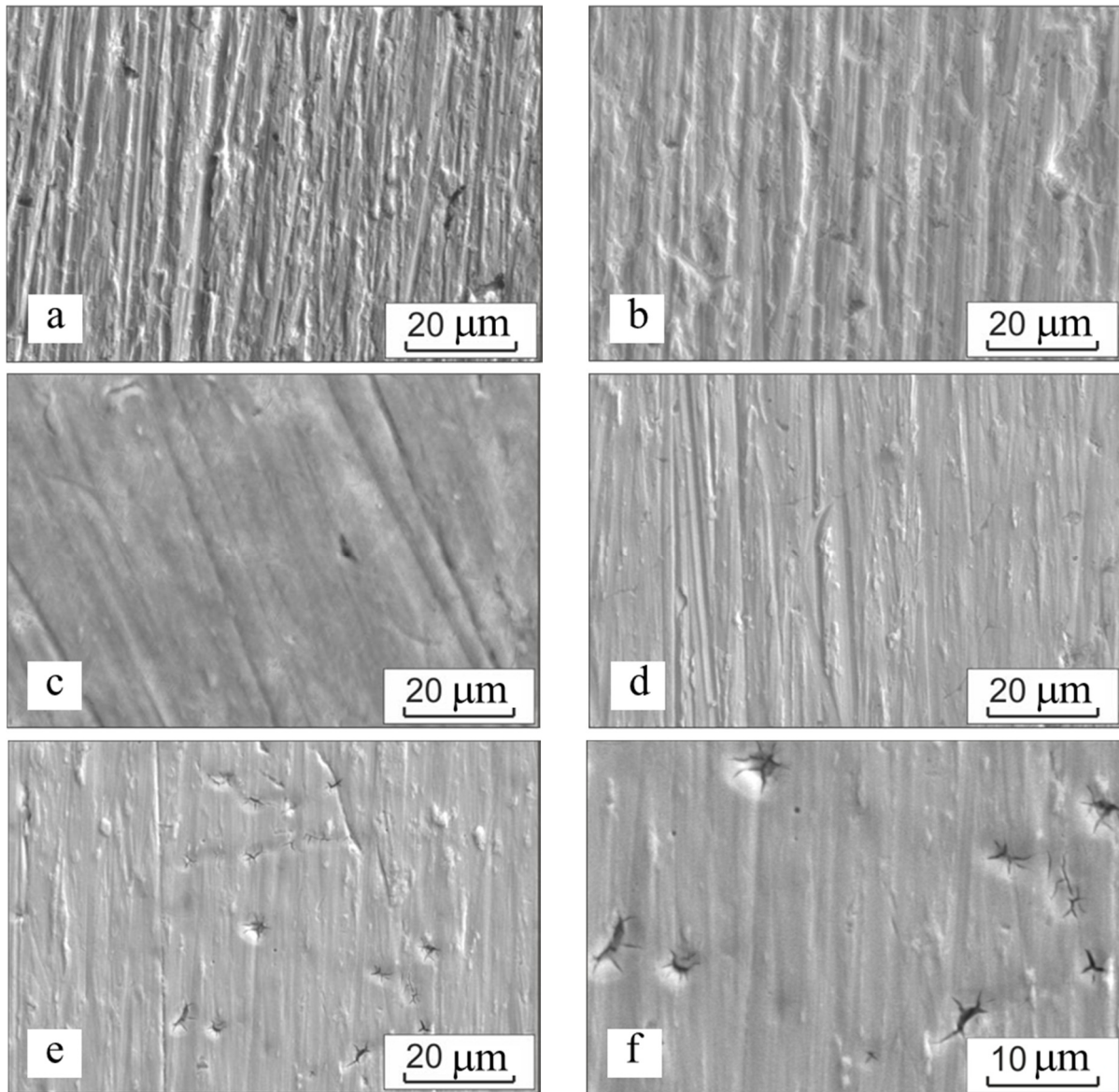
\* test duration in H<sub>2</sub>SO<sub>4</sub> was 5 h

Fig.8. Surfaces of alloyed layers and reference samples after testing for corrosion resistance in boiling hydrochloric acid solutions: a – tantalum in 5% HCl; b – tantalum in 20% HCl; c – 31Ta-12Zr and d – 48Ta-20Zr in 10% HCl.; e, f – 48Ta-20Zr in 20% HCl.

The resistance in nitric acid of the Ti-Ta-Zr system is generally lower than that of the Ti-Ta-Nb systems, however, the highly alloyed 48Ta-20Zr layer shows resistance in HNO<sub>3</sub> of 6 μm/year, which



corresponds to the category “very resistant” on a ten-point scale of corrosion resistance (Russian GOST 13819-68). In boiling sulfuric acid, only a double alloyed layer is operable up to a concentration of 40% (the “resistant” category). In boiling hydrochloric acid, a single-layer coating can only work up to a concentration of 5% (category “resistant”), and a two-layer one – according to Table 5 – up to a concentration of 20% (category “low resistant”).

On Fig.8 shows the corroded surfaces in hydrochloric acid, as the most aggressive. On Fig.8a, the tantalum surface is practically unaffected due to the low acid concentration of 5%. Unchanged risks from processing the sample with abrasive paper are visible. On Fig.8b, after the exposure of tantalum to 20% acid, some rounding of the relief is already noticeable. From a comparison of Fig.8c and 8d, it can be seen that under the same conditions in 10% acid, on a single-layer coating, the risks almost disappeared during the test of 50 minutes, while on a two-layer coating, during the test of 5 hours, the risks still remained. When immersed in 20% acid, the two-layer coating is already subject to noticeable corrosion (Fig.8e and 8f), as a result of which we conclude that its performance is limited to only 10% hydrochloric acid concentration.

## 5. Conclusions

With the use of a high-voltage electron beam extracted into the atmosphere, it is possible to form relatively thick highly alloyed layers of the Ti-Ta-Zr system on flat titanium substrates. The degree of alloying of the deposited layer increases significantly due to the double surfacing of the alloying powder composition. The double surfacing layer has a thickness of about 2 mm and consists only of the  $\beta$ -phase. The composite material obtained by double surfacing is resistant to corrosion in three boiling strong acids: nitric acid with a concentration of up to 65%, sulfuric with a concentration of up to 40%, and hydrochloric with a concentration of up to 10%. The estimated duration of its operation in these acids can presumably be: nitric – tens of years, sulfuric and hydrochloric – several years.

## Acknowledgement

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