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# **Development of a composite corrosion-resistant material** based on titanium for chemical industry vessels

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Abstract. This paper presents a brief review of research made by the authors to determine feasibility of using a titanium-based bilayer material in industrial applications. One layer, corrosion preventive, is formed by surface alloying with highly corrosion-resistant doping elements, in particular, Ta, Nb and Zr. These elements have significantly higher corrosion resistance than titanium. Applying them on the titanium substrate allows formation of a coating resistant, in particular, to boiling strong acids. Resistance of obtained coatings in said media is many times higher than that of titanium or stainless steel. The coatings are formed using a high-penetration electron beam ejected to the atmosphere. This article contains references to findings of previous works and offers some new data.

#### 1. Introduction

Titanium and its alloys are widely used due to combination of such properties as low density, corrosion resistance, strength and ductility [1]. High corrosion resistance makes titanium suitable for use in the chemical industry. Titanium however is not resistant to strong acids at boiling temperatures. Elements resistant to hot acids include Ta, Nb and Zr [2]. Doping titanium with these elements results in an alloy with a significantly higher resistance. An advantage offered by these elements is that they show high and, at temperatures higher than that of  $\alpha$ - $\beta$  transition for titanium, complete solubility in the titanium matrix [3]. Furthermore, alloys of titanium with Ta, Nb and Zr feature a high level of mechanical properties, in particular, strength and capability for hot plastic deformation. Considering the high cost of said doping elements, it would be expedient to use them for surface, rather than bulk, doping to the depth of 1-2 mm sufficient for most operation requirements. This depth can be achieved by surface alloying with powdered materials using a powerful high-penetration electron beam. The electron beam used by the authors is generated by industrial electron accelerators manufactured on a commercial scale by Budker Institute of Nuclear Physics of the Siberian Branch of Russian Academy of Science, Novosibirsk [4]. The beam is ejected to the atmosphere through a small diameter opening that allows avoidance of a common drawback of electron beam technologies, requirement for treatment in the vacuum chamber [5].

Technological constraints of the method allow only alloying on flat surfaces and in the form of bands of limited width and unlimited length. To apply coat to a sheet of industrial size, multipass surface alloying with consecutive lateral joining of bands is required. The purpose of this investigation is to show that the constraints of the above method of surface alloying do not preclude from using the

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obtained material for making various products of complex shape intended for industrial applications. This is sufficiently evidenced by the fact that the material can be used in such operations as listed below:

- Formation of coatings over large areas by lateral joining of surface bands without faults at the boundary between bands.
- Rolling and forming of the obtained sheet material.
- Weld joining of sheets obtained by surface alloying.

Besides the above requirements, corrosion resistant vessels may have to ensure high mechanical strength. As shown in [6-9], such corrosion resistant vessels can be made, if necessary, from a durable titanium alloy, not from commercially pure titanium (CP titanium) only.

Prospective areas of application for this material may include, for example, the nitric acid production industry or the spent nuclear fuel reprocessing (PUREX process) at its initial stage requiring dissolution of chopped fuel elements in hot nitric acid [10, 11].

## 2. Formation of bilayer material

Particulars of the effect made by the electron beam used in the research on the material are described in [12]. Beam power was 32–34 kW. The procedure of making specimens was similar to that described in [12-14]. Before alloying, a layer of powder mixture containing doping elements was applied to flat substrate plates of 10-12 mm depth. The length of plates for surface alloying does not have technological constraints. It was selected relative to the purpose of research. The alloying powder composition included also titanium powder and two fluxing fluoride components, CaF2 and LiF. Surface density (mass thickness) of the powder was 0.45 g/cm2. The substrate plates coated with a layer of powder were moved under scanning beam in a direction perpendicular to that of scanning with a velocity of 1 cm/s. The width of specimens used to study the quality of coating was 50 mm. The scanning range only slightly exceeded that value. In order to increase the concentration of doping elements, two or three layers of surface alloying can be made [15]. Before alloying each subsequent layer, it is required to remove slag crust from and clean the preceding layer.

## 3. Quality of coating

Surface alloying allows making of coatings that do not have pores, cracks or other faults such as inclusions of slag [12, 14, 16]. Occasionally, not completely dissolved particles of tantalum may occur. Though not detrimental to the performance properties of the coating, presence of such particles is not desirable considering tantalum reduction in the bulk of coating. Occurrence of undissolved particles is caused by insufficient beam power or excessively high concentration of tantalum in the original powder. Both disadvantages can be remedied by correct selection of settings. The formation of coatings is accompanied by dendritic segregation of doping elements that may reach several percent. Usually the most volume of the coating structure after alloying appears like plate-like martensitic  $\alpha'$  and  $\alpha''$ -phases of titanium [17]. Between the aforementioned martensitic plates, much thinner interlayers of the  $\beta$ -phase of titanium are located. Though most corrosion-resistant to boiling nitric acid, these coatings show resistance to diluted hydrochloric and sulfuric acids many times higher than that of titanium or stainless steel [16, 17].

## 4. Joining surfacing bands

To obtain specimens of a width exceeding the width of the band of surface alloying, joining of bands was made. Feasibility of joining bands without deterioration of the coating quality at the boundaries was studied for bands having a width of 55 mm and joining overlap of 5 mm. Figure 1 shows general cross-sectional view for a joint of surface bands at low magnification (a) and a section of that joint at higher magnification (b). Figure 1a also shows a line along which microhardness values were measured, the distribution of such values being shown in figure 2. Study of photographs made in different spots along the presumable line of band interface shows that everywhere continuity of material and mixing of melt at the boundary between bands is observed. The diffused boundary can be only determined approximately by variety of colour in the interface area. Uniformity of surfaced layer at the band interface is as well confirmed by microhardness distribution by the layer's depth.

Measurements were taken on 5 parallel tracks. Figure 2 shows average values and their standard deviations. It is obvious that hardness distribution by depth is quite uniform and hardness fluctuations are within the range of standard deviation.



**Figure 1**. Cross-section of interface between two bands of surface alloying at low (a) and medium (b) magnification. The vertical line in figure (a) shows the location of the microhardness measurement line.

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Figure 2. Microhardness distribution by depth of material in the area of band overlapping.

### **5.** Welding of two-layer sheets

Feasibility of electric arc welding in inert gases using a nonconsumable electrode was studied in [7]. The above conditions allow for butt and fillet welding with a filler rod. Both methods can be performed by double-sided and single-sided welding. Simpler in performance, double-sided welding can be applied when the welded volume is readily accessible from inside and outside. Otherwise, single-sided welding outside the corrosion-resistant vessel can be performed. In both cases, welding is made first on the corrosion-resistant coating and then on the titanium substrate. Considering that commonly the titanium substrate is significantly thicker than the coating, welding thereon necessarily requires beveling. Welding on the coating was made with filler rods of the same material as that of coating or tantalum wire was used as a filler. Rods of the material identical to coating were cut from the coating of specimens specially made for that purpose. Welding on the substrate was made with a filler in the form of standard welding wire for titanium alloys.

## 6. Sheet material rolling

Opportunities offered by hot rolling after surface alloying were studied in [9]. Specimens manufactured on both CP titanium and titanium alloy VT14 were subjected to multipass hot rolling on the laboratory rolling mill. The specimens had been preheated in the ambient atmosphere before rolling to a temperature of 850°C. Each pass resulted in reduction of the material thickness by 0.9 - 1.0 mm. The required number of passes under the rolls to achieve the preset value of thickness was 10. As a result of rolling, the thickness of material was reduced more than four times: from initial 10.5 mm (VT1-0) and 12.5 mm (VT14) to 2.5 and 3.0 MM, respectively.

Table 1 shows the chemical composition of the initial powders before surface alloying and the average content of doping elements in alloyed layers of the specimens after the rolling.

#### 7. Making and testing a corrosion-resistant reactor model

Feasibility of manufacture of workable reactors for chemical industry was tested on a small-size chemical reactor model specially built for that purpose. Substrates for surface alloying were made from a strong titanium alloy VT14 (88.78% Ti, 6.22% Al, 3.32% Mo, 1.24% V). Initial size of plates used to build the reactor was 150 x 300 x 12 mm. Content of the powder mixture used for surface alloying included tantalum, 30%, niobium, 7%, and titanium, 25%. Fluorides CaF2, 28.5% and LiF, 9.5% had been used as a flux. Cut along the edges to a size of 120 x 250 x 12 mm to optimize the reactor dimensions, the plates were then welded together. Side walls of the reactor were made of six plates arranged as a honeycomb. The bottom and top parts were welded to the side plates. Upon completion of welding, the part of the reactor adjacent to the top cover was cut off using the

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electrospark discharge machine to make it removable. Sections of tantalum pipes intended to serve as technological connecting branches of different purpose had been welded into one of the side plates and into the top cover. These branches were used to fill or drain acid, install an acid temperature meter and place water coolers to condense the vapours released by boiling acid and their return to the reactor in shape of acid drops. The walls for this model were made without rolling. Composition of the initial powder used for surface alloying and protective layer alloyed upon the surface was the same as that shown in table 1 for substrate VT14.

Table 1. Powder composition before alloying versus content of the alloyed layer of the
specimens subjected to rolling.

Initial composition of mixture of powders before surfacing	Substrate	Average concentration of alloying elements in the alloyed layer, weight %			
		Та	Nb	Al	
25 % Ta, 7 % Ni, 30 % Ti, 28.5 % CaF2, 9.5 % LiF	VT1-0	18.8±0.4	4.8±0.1	0.3±0.2	
30 % Ta, 7 % Ni, 25 % Ti, 28.5 % CaF2, 9.5 % LiF	VT14	23.8±0.5	5.1±0.5	3.1±0.3	

Figure 3 shows one of the reactor's sidewall plates with an opening for welding of a tantalum tube, figure 4 shows the outer appearance of the reactor model before the top part had been cut off.

The tested reactor was filled with acid about one quarter of its volume. To ensure better uniformity of temperature distribution, the reactor was heated placed an oil bath approximately to a quarter of its height. Corrosion resistance was determined by precision weighing of the reactor before and after the test. Four test cycles, five days of continuous boiling of acid in each had been carried out. It was the last test cycle only that resulted in development of a correct method of weighing the reactor that included, besides washing of the reactor, oven drying of the reactor for two hours at a temperature of 120°C. The reactor's loss of mass for 5 days was 0.50 g that corresponds, considering the reactor's total weight of 14.86 kg and walls area of 2508 cm<sup>2</sup>, to corrosion resistance of 26  $\mu$ m/year. It is obvious from comparison of the corrosion resistance value thereby obtained with that of layers having a similar composition alloyed on the substrate of CP titanium VT1-0 [13, 14, 15, 18] that the use of VT14 rather than VT1-0 as a substrate for surface alloying results in two or threefold reduction of corrosion resistance of the protective layer. Apparently, this is caused by presence of an unstable element, aluminium, in VT14. Nevertheless, corrosion resistance achieved is still high enough to ensure uninterruptable operation of the reactor for 30–40 years.



Figure 3. One of the reactor's sidewall plates with an opening for welding of a tantalum tube as seen from the side of the surface with alloyed coating.

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Figure 4. Outer appearance of the reactor model.

Considering the relatively low level of nitric acid in the reactor, it should be noted that most of the reactor walls' area including welding seams was exposed in the test to a vapor and condensate mixture of concentrated nitric acid at the boiling temperature. According to research [19], these conditions are considered most severe by the degree of aggressive action as compared to only fluid or vapor environment. Thus, the rating of corrosion resistance obtained from the test data can be considered as an upper-bound estimate.

#### 8. Conclusion

As shown by a number of research, there is an opportunity for manufacture of vessels made of titanium-based material with a corrosion-protective layer highly resistant to boiling strong acids. A protective layer of sufficiently high thickness of 2 mm is metallurgically bonded with the titanium substrate. Considering the use of boiling concentrated nitric acid as the operating medium, the period of continuous operation for chemical reactors made from the developed material is expected to be several decades.

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