Corrosion resistance of Ti-Ta-Nb and Ti-Ta-Zr coatings fabricated on VT14 Titanium alloy substrates using electron beam injected into the atmosphere

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In this study corrosion resistance of the coatings obtained on VT14 (4% Al, 3% Mo, Ti – the rest) titanium alloy substrates using focused electron beam with an energy of 1.4 MeV injected into the atmosphere was discussed. The two-layered material fabricated on the titanium substrate can be applied for corrosive-resistant reactors used in chemical industry. These reactors are exposed by nitric acid heated to approximately boiling temperatures. It was shown that in spite of penetration of alloying elements (Al and Mo) from the substrate to the coating, high anticorrosive properties of the coatings can be achieved. For this purpose, high alloying degree of the coatings with such corrosive resistant elements as Ta, Nb and Zr should be provided.

Устойчивост на корозия на покрития от Ti-Ta-Nb и Ti-Ta-Zr, нанесени на подложки от VT14 титанова сплав с помощта на електронен лъч инжектиран в атмосферата (В. Самойленко, И. Поляков, М. Голковски, Н. Куксанов, О. Ленивцева, И. Иванчик). *В това проучване се обсъжда корозионната устойчивост на покритията, получени върху подложки от титанова сплав VT14 (4% Al, 3% Mo, Ti - останалото), при използване на фокусиран електронен лъч с енергия от 1,4 MeV, инжектиран в атмосферата. Двуслоен материал, нанесен върху титанова подложка, може да се прилага за корозионно- устойчиви реактори, използвани в химическата промишленост. Тези реактори са изложени на азотна киселина, загрята приблизително до температурата на кипене. Показано е, че независимо от проникването на легиращи елементи (AL и Mo) от субстрата в покритието, могат да бъдат постигнати високи антикорозионни свойства на покритията. За тази цел, следва да се осъществи високо легиране на покритията с такива устойчиви корозивни елементи като Ta, Nb и Zr.*

Introduction

In a number of papers [1, 2] the properties of corrosive resistant coatings fabricated on the commercially pure (CP) titanium substrates (VT1-0 grade) were investigated. The coats were formed using the focused electron beam with electron energy of 1.4 MeV that was injected into the atmosphere. The double layered material fabricated by this method can be used for manufacturing the corrosive resistant reactors utilized in chemical industry under the influence of strong acids heated to the temperatures approximately equal to their boiling points. In this study, the rate of corrosion of the coatings fabricated on VT14 titanium alloy which served as a substitute of VT1-0 was investigated. This alloy possesses a significantly higher strength in comparison with CP-titanium. It was shown in this work that in spite of the penetration of alloying elements (Al and Mo) from a substrate to the coating the doped layers can demonstrate high corrosion resistance. It can be achieved by increase of alloying degree of the coatings. E.g. coatings with the highest alloying degree (22.3% Ta and 2.6% Nb) among the tested coatings demonstrated the lowest corrosion rate equaled to only 8.5 μm per year.

Materials and methods

Cladding was carried out on substrates made of titanium alloy (VT14 grade) with dimensions of 100 mm x 50 mm x 12 mm. Chemical composition of VT14 is shown in Table 1.

Table 1

Chemical composition of VT14 titanium alloy, wt. %

Ti	Al	Mo	V	W	Fe	Mg	Cr	Si	Ni	Zr	Mn	Impurities
the rest	6.22	3.32	1.24	0.162	0.096	0.057	0.042	0.038	0.021	0.07	0.06	0.35

Cladding was realized by the electron beam in the air atmosphere in the scanning regime. A width of the treated area was equal to a width of samples (50 mm). A powder mixture was homogeneously distributed on the surface of titanium workpiece before cladding. A surface density of the powder mixture was 0.45 g/cm^2. Formation of multilayered composites was realized by reduplication of the procedure. Table 2 shows the concentration of alloying elements in the blend and the sample labels.

Table 2

Compositions of the powder mixtures, wt. %

Sample label	Percentage of the components in the powder mixtures, wt. %					
	Ta	Nb	Zr	Ti	CaF_2	LiF
15Ta-4Nb	25	7	-	30	28.5	9.5
22Ta-8Nb Two layers						
3Ta-4Zr	8.2	-	8.2	40	32.7	10.9
9Ta-3Zr	17	-	8.5	35	29.63	9.88

An ELV-6 electron accelerator produced by the Budker Institute of Nuclear Physics SB RAS (Novosibirsk) was used for cladding. Beam current was 24 mA, rate of the sample movement under the electron beam was 10 mm/s; scanning amplitude was 25 mm; scanning frequency was 50 Hz.

Percentage of alloying elements in the cladded layer was determined by an INCA X-ACT (Oxford Instruments) energy dispersive X-ray (EDX) analyzer.

Corrosion resistance was tested in a nitric acid solution (65%) in water; estimation of the results was carried out by the gravimetric method. Samples for testing with dimensions of 1 x 15 x 20 mm were cut out of the cladded layers. Plates were hung up at the polytetrafluoroethylene (PTFE) threads and were immersed into the nitric acid solution. The acid temperature was 125 $^{\circ}$C. After particular periods of time samples were removed from the acid solution, washed and weighed. After that experiment was continued. The summarized duration of testing was 120 h. A reference sample (VT14) corrosion rate was also determined during testing. The surfaces of samples after corrosion tests were analyzed by a Carl Zeiss EVO 50 XVP scanning electron microscope (SEM).

Results and discussion

Table 3 shows a percentage of alloying elements in the cladded layers. It is clearly seen from this table that cladding of the second layer of Ta and Nb caused the increase of concentration of alloying components in the coating. Results of corrosion tests are presented in Fig. 1 and in Table 4.

Table 3

Percentage of alloying components in the coating determined by EDX analysis, wt. %

Sample label	Ta	Zr	Nb	Al	Mo
15Ta-4Nb	14.7	-	3.5	3.9	-
22Ta-8Nb	22.3	-	7.6	1.62	-
3Ta-4Zr	3.3	3.9		4.5	3.2
9Ta-3Zr	8.6	3.3		3.8	3.3

Table 4

Corrosion rate of substrate of VT14 titanium alloy and tested alloyed layers in the boiling concentrated solution of nitric acid in water.

Sample label	Corrosion rate, μm per year
VT14	476.8±15.8
15Ta-4Nb	39.3±14.7
22Ta-8Nb	8.5±4.2
3Ta-4Zr	392.0±35.7
9Ta-3Zr	296.0±7.9

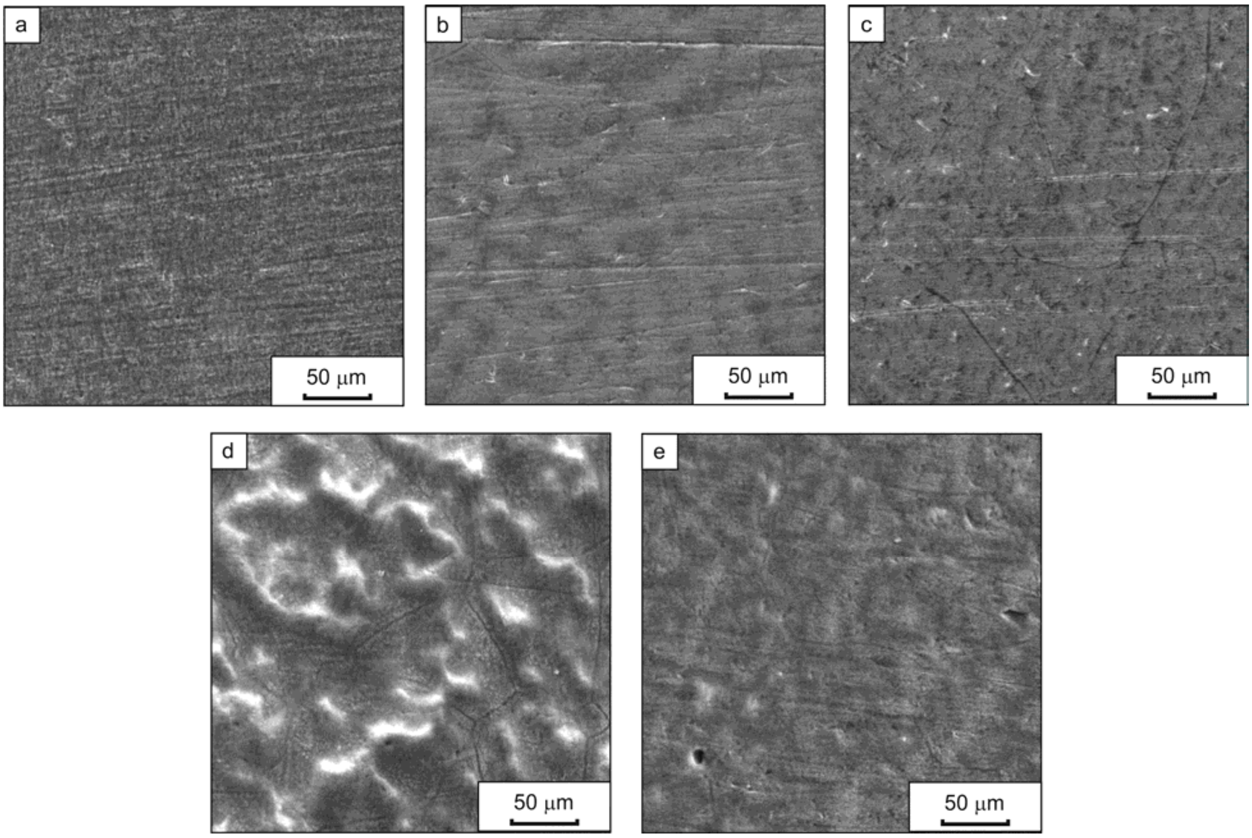

Fig. 2. Surfaces of the samples after corrosion tests in the boiling concentrated solution of nitric acid: a – VT14 titanium alloy; b - 15Ta-4Nb alloy; c –22Ta-8Nb alloy; d –3Ta-4Zr alloy; e –9Ta-3Zr alloy.

It was found that VT14 titanium alloy possessed the maximum dissolution rate in the boiling concentrated solution of nitric acid equaled to 477 μm per year. Dissolution rate of titanium alloy with 3% Ta and 4% Zr was 392 μm per year. Increase of the alloying degree with Ta up to 9% (9Ta-3Zr sample) led to 1.3-fold decrease of the corrosion rate comparing to VT14 alloy. Corrosion rate of this alloy was 296 μm per year.

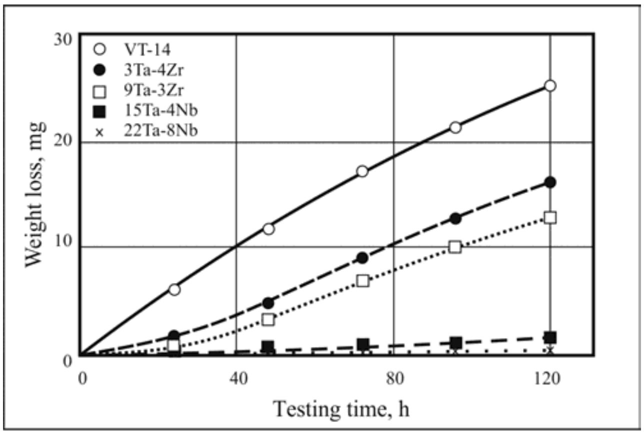

Fig. 1. Relation between mass loss of materials in the boiling solution of nitric acid and duration of testing.

The samples obtained by cladding of the Ti-Ta-Nb powder mixture possessed the maximum corrosion resistance. Dissolution rate of 15Ta-4Nb and 22Ta-8Nb alloys in the boiling acid solution was 39.3 μm per year and 8.5 μm per year respectively.

Surfaces of the samples after 120 h of testing in the boiling solution of concentrated nitric acid were analyzed by SEM. On the surfaces of samples traces of preliminary polishing were clearly seen (Fig. 2). Damage of the alloy with 3 % Ta and 4 % Zr caused by exposure of boiling nitric acid occurred predominantly in the areas corresponded to the inter-dendritic space (Fig. 2d). It was accompanied by formation of relief which was not revealed on the surfaces of other samples (Fig. 2).

Surface morphologies of alloys with enhanced percentage of alloying elements (9Ta-3Zr, 15Ta-4Nb and 22Ta-8Nb samples) were characterized by the similar structures after corrosive damage (Fig. 2, b, c, e). Different contrast can be observed between dendritic arms and inter-dendritic space. Increase of percentage of alloying elements in the coating led to decrease of etchability of inter-dendritic space by a corrosive solution.

Conclusions

Coatings obtained on the titanium substrates by non-vacuum electron beam cladding possessed high corrosion resistance in a boiling nitric acid solution. Alloying VT14 titanium with 22 % Ta and 8 % Nb led to 71-fold increase of its corrosion resistance.

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