Influence of chemical composition of initial powders on structure and properties of «Ti-Ta-Zr» coatings fabricated on cp-titanium substrates by electron beam cladding

V V Samoylenko[1], D V Lazurenko[1], O G Lenivtseva[1], I A Polyakov[1]

[1] Material Science in Mechanical Engineering Department, Novosibirsk State Technical University, 20 Prospekt K.Marksa, Novosibirsk, 630073, Russia

E-mail: samoylenko.vitaliy@mail.ru

Abstract. In this study «Ti-Ta-Zr» corrosion resistant coatings fabricated by electron beam treatment of Ti substrates were investigated. The series of experiments on varying Ta and Zr concentrations in initial powder mixtures aimed on identifying influence of the alloying components ratio on structure and properties of coatings were carried out. It was found that during the electron beam cladding the high-quality coatings with a dendritic structure exhibited uneven distribution of alloying components in a cross section were formed. Moreover scanning electron microscopy (SEM) revealed the formation of needlelike structure. However difference in Ta and Zr concentrations in initial powder mixtures did not cause significant structural transformations in the coatings. Meanwhile the direct dependence between microhardness of the surface layers and Zr content in it was revealed. The maximal microhardness level was detected in the coating containing 60 % Zr. The impact strength test indicated decrease of impact toughness of titanium samples after cladding by a factor of 1.5…2.

1. Introduction

Titanium alloys are considered to be the prospective structural materials which are widely-used in chemical and nuclear industries, aircraft and rocketry as well as in medicine due to their high specific strength in combination with corrosion resistance in the majority of corrosive media [1].

However titanium is exposed by intensive corrosion in boiling concentrated acids. In [2-4] it was shown that adding tantalum to titanium alloys allows increasing significantly their corrosion resistance which can reach in some cases the pure tantalum level. However applying Ti-Ta alloys is restricted by a high cost of Ta and complexity of capacity workpieces formation consisted in repetitive arc remelting. Herein highly doped Ti-Ta alloys are of a high density level, wherefore the weight of details and constructional element made of this alloys significantly increase. In order to save expensive tantalum and improve corrosion resistance of titanium it is reasonable to produce coatings containing tantalum on titanium workpieces.

The results of previous investigations showed that the most prospective technology of coatings formation is electron beam cladding which allows obtaining surface alloyed wear resistant [5-7] and corrosive resistant [8, 9] layers with a thickness of 2 mm on steel and titanium workpieces.

In this study «Ti-Ta-Zr» coatings fabricated on surfaces of cp-titanium substrates were investigated. The cladding process was realized in the Institute of Nuclear Physics SB RAS by the industrial accelerator ELV-6. Such accelerators are equipped with the system of differential pumping which allows injecting the electron beam in the air [10].

2. Materials and methods

Before the electron beam treatment a powder mixture consisted of Ta, Zr and a flux agent was poured on a working surface with dimensions of 100x50 mm. A thickness of titanium plates was 12 mm. The powder mixture weight was equal to 22.5 g. Adding Zr in an initial powder mixture allows replacing partially expensive tantalum. Moreover at the initial processing stage zirconium possessed a lower melting temperature comparing to tantalum acted as a wetting agent. The accelerator capacity reaches 33.5 kW. In order to increase efficiency the electromagnetical scanning coil was inserted at the outlet. Electromagnetical scanner was set up in such manner as to provide the peak-to-peak value equaled to 50 mm at the distance of 90 mm from the outlet.

During the experiment the series of samples was fabricated. With increase of tantalum in coatings zirconium amount decreased (table 1). A flux volume in a powder mixture in relation to a volume of alloying components was constant.

Table 1. Weight fraction of powders in initial mixture.

Sample №	Weight fraction of powders in initial mixture, wt. %.				Chemical composition of coating after cladding, wt. %.		
	Ta	Zr	CaF_2	LiF	Ta	Zr	Ti
1	0	60	30	10	0	52.87	47.13
2	10.5	52	28.13	9,37	5.25	27.63	67.12
3	21	44	26.25	8.75	10.76	22.89	66.35
4	31.5	36	24.38	8.12	18.30	21.93	59.77
5	42	28	22,5	7,5	22.43	15.49	62.08
6	52.5	20	20.63	6.87	27.43	10.99	61.58

Metallographic investigations were carried out using an optical microscope Carl Ziess Axio Observer A1m and a scanning electron Carl Zeiss EVO 50 XVP. Chemical composition was estimated by energy-dispersive X-ray spectroscopy (EDX) using an analyzer INCA X-ACT (Oxford Instruments). Microhardness of coatings was determined by a tester Wolpert Group 402MVD. The load on a diamond indenter was 0.98 N. The distance between impressions was 200 μm. Impact strength test was carried out by a vertical drop machine MetroCom. The samples dimensions were 50x10x10 mm. V-notch was cut perpendicular to a cladded layer. Fracture surfaces were analyzed by scanning electron microscope.

3. Results and discussion

Electron beam cladding of Ta and Zr powders in the air atmosphere led to the formation of a graded structure. In the cross section of samples three main zones were identified: a coating, a heat affected zone and a base material.

The coatings obtained by the electron beam cladding of powder mixtures of a different Ta-Zr ratio were structurally similar. During the crystallization of cladded layer a cast dendritic structure was formed. The direction of dendritic crystals growth is coincided with the grains orientation (Fig. 1, a, b). At a high magnification the alloy structure consists of fine needlelike crystals (Fig. 1, c, d). Formation of such a structure is typical for quenched titanium alloys. During the electron beam cladding a treated surface was heated up to the melting point while a lower part of a titanium plate was kept at the ambient temperature and as a result heat was abstracted from a workpiece surface into a depth of titanium substrate. This process led to suppression of equilibrium processes and realizing the diffusionless transformation.
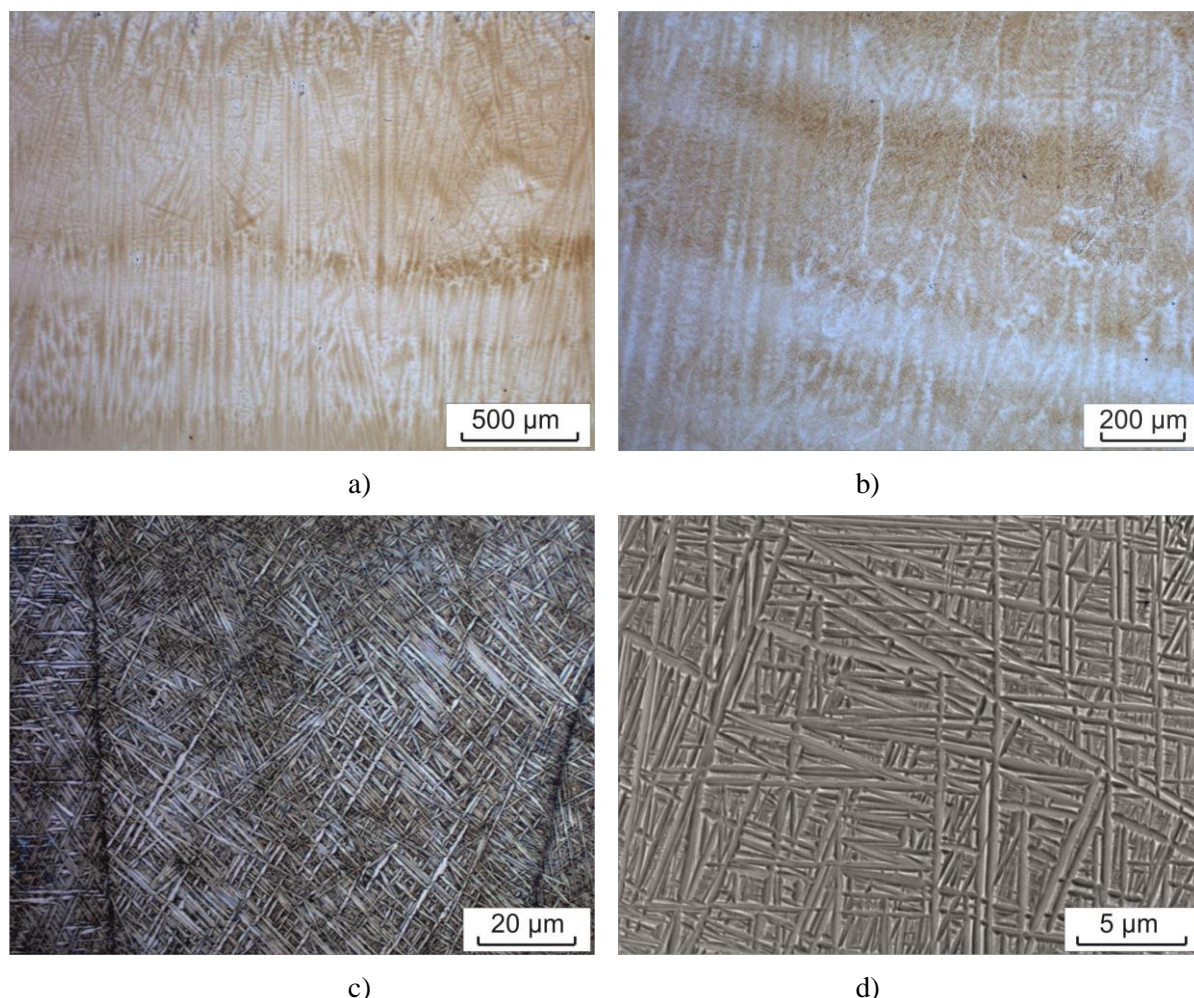
Figure 1. Typical microstructure of the coating after cladding: a, b – dendritic structure; c, d - needlelike structure.

EDX analysis results gave the evidence of increasing the tantalum volume fraction in coatings corresponding to its increasing in initial powder mixtures. The maximal tantalum concentration equaled to 27 wt. % was observed in the sample 6 (table 1). Herein the zirconium content in this sample was minimal and not exceeded 11 %. The maximal zirconium content (52.9 wt. %) was observed in the case of cladding the powder mixture containing only zirconium as an alloying component.

The presence of a contrast on SEM microphotographs made in the back scattered electrons regime indicated indirectly the difference in chemical composition between dendritic axes and interdendritic space. The elemental analysis of the sample containing 27 wt. % Ta and 11 % wt. Zr (Fig. 2) provided evidence of the enhanced tantalum content while in interdendritic space the increased content of zirconium was observed (Table 2).

Table 2. EDX-analysis of the coating

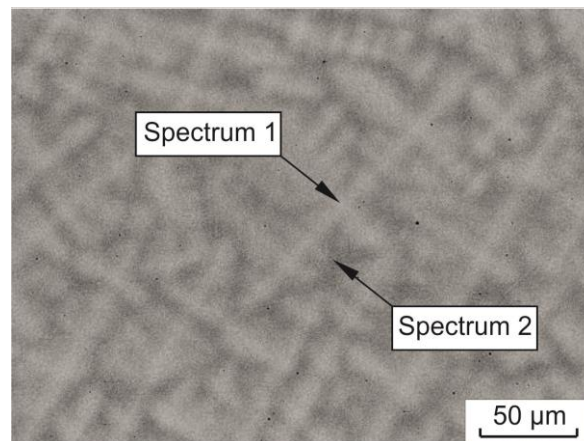| №	Contente, % (wt)		
	Ta	Zr	Ti
Spectrum 1	29.62	8.68	61.70
Spectrum 2	18.22	11.48	70.30

Figure 2. EDX-analysis of the coating

Microhardness of the cladded layers did not varied in the cross section. Microhardness level in the sample containing only zirconium as an alloying component was equal to 6000 MPa and decreased gradually corresponding to increasing tantalum in the initial powder mixtures (Fig. 3). At the distance of ~ 50 μm from a surface microhardness value of some coatings reached 6500 MPa. Hardness increase is explained by the aeration of subsurface layers. In going from coating to titanium substrate microhardness decreased to 1700 MPa.
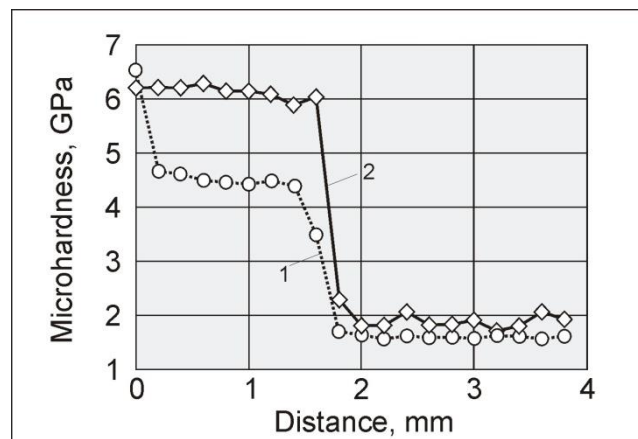

Figure 3. Microhardness distribution in the cross section of the sample containing: 1 – 22.43 wt. % Ta, 15.49 wt. % Zr; 2 – 52.87 wt. % Zr.

Impact toughness of bimetallic composites was approximately 1.5…2 – fold lower comparing to cp-titanium. The minimal fracture energy equaled to 81.2 J/cm^2 was obtained for the sample containing 5.25 wt. % Ta and 27.63 wt. % Zr. The sample containing 18.3 wt. % Ta and 21.93 wt. % Zr showed the highest impact toughness level (113.8 J/cm^2). The impact value of cp-titanium was equal to 160 J/cm^2. Decrease of the fracture energy is associated with the presence of a wide heat affected zone and a hard coating in samples. Fractographic analysis revealed the fracture of coatings according to the quasi-brittle mechanism. Elongated dimples were observed at the fracture surface (Fig. 4 a). Moreover the elements of intercrystalline fracture were revealed (Fig. 4 b). It should be noticed that there were no any cracks and fractures at the titanium-coating interface due to the good adhesion between the coating and the substrate (Fig. 4 c).
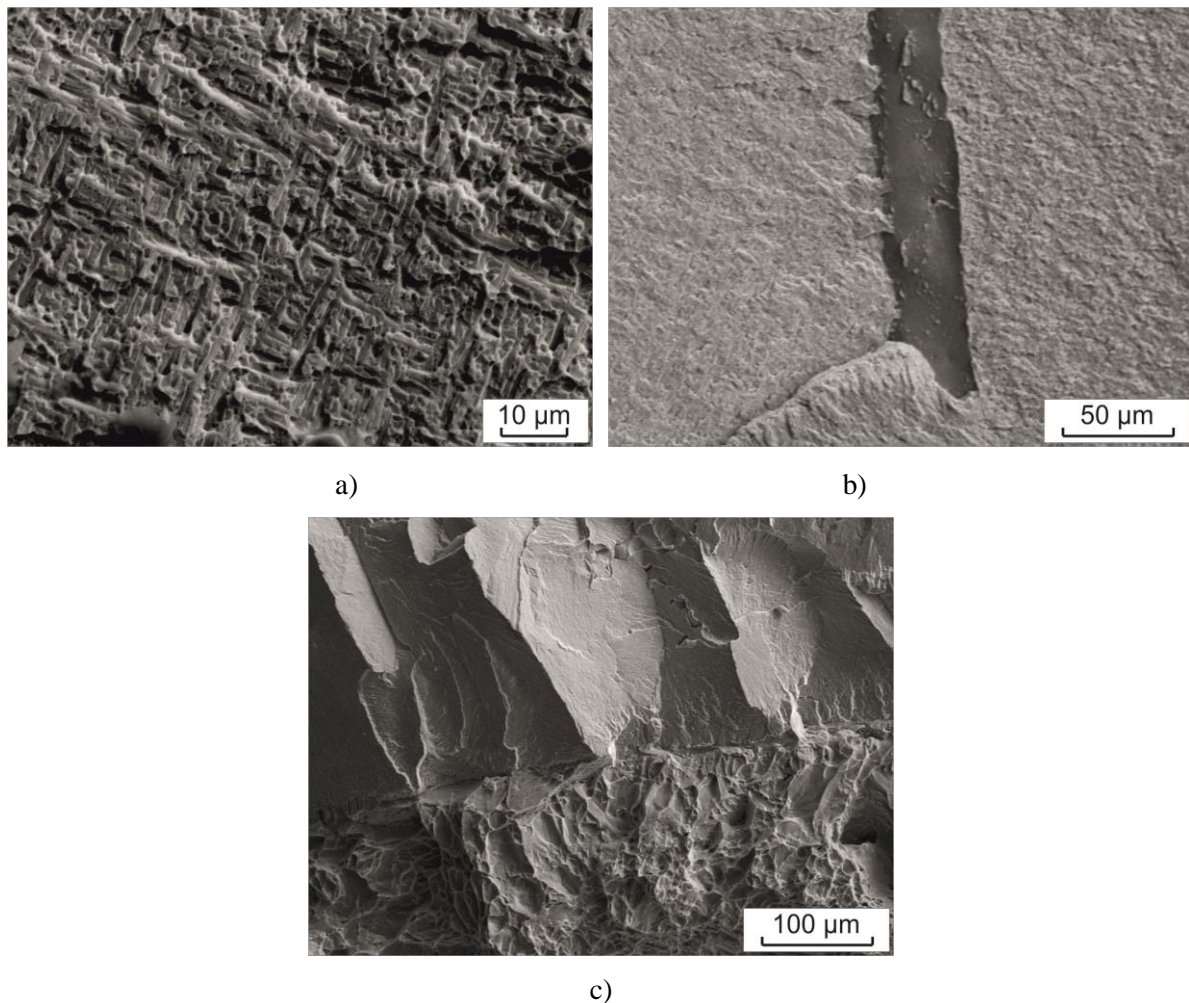
a)   b)

c)
Figure 4. Fracture surfaces of coatings (a, b); fusion zone (c).

4. Conclusions

The electron beam cladding of the powder mixtures containing Ta and Zr on Ti substrates allowed fabricating the high-quality defect-free coatings with high adhesion characteristics. Optical microscopy and SEM investigations revealed that the concentration of Ta and Zr in the initial powder mixtures had no significant influence on the coatings structure. All the coatings were characterized by the formation of dendritic structure and microsegregation. The fine structure of coating was represented by needlelike crystals. Microhardness measurements showed that the coating strength increased from 4500 MPa to 6000 MPa in accordance with increasing the zirconium content from 20 % to 60 % (in initial powder mixture). Meanwhile there was no revealed any dependence between impact toughness of samples and tantalum and zirconium content. Fracture energy of Ti after the electron beam treatment decreased by a factor of 1.5…2.

References
[1] Lütjering G and Williams J C 2007 *Titanium (Engineering Materials and Processes)* second ed Springer p 442
[2] De Souza K A and Robin A 2007 *Mater. Chem. Phys.* **103** pp 351–360
[3] Golkovski M G *et al* 2013 *Mater. Sci. Eng., A* **578** pp 310-317
[4] Ahn H *et al* 2008 *Surf. Coat. Technol.* **202** pp 5784-5789
[5] Lenivtseva O G *et al* 2013 *Obrabotka metallov* **61** pp 49-57

[6] Mul D O *et al* 2013 *Obrabotka metallov* **60** pp 115-120
[7] Bataev I A *et al* 2013 *Appl. Surf. Sci.* **284** pp 472-781
[8] Bataev I A *et al* 2012 *Obrabotka metallov* **54** pp 90-95
[9] Golkovski M G *et al* 2013 *Obrabotka metallov* **61** pp 43-48
[10] Fadeev S N *et al* 2004 *Probl. Atom. Sci. Technol. Ser. Nucl. Phys. Investigat.* **1** pp 178–180