

Element and Phase Composition, Mechanical Properties of Titanium Surface Layer Alloyed by Zr, Nb, Al Under the Action of Compression Plasma Flows

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Element, phase composition and mechanical properties of titanium surface layer alloyed by Zr, Nb, Al under the impact of compression plasma flows on “coating Nb-Ti-Zr-Al/Ti substrate” system were investigated in this work. An X-ray diffraction analysis, scanning electron microscopy, energy dispersion microanalysis, microhardness measurements and tribological tests were used as investigation techniques. The findings showed that plasma impact resulted in dissolution of coating and formation of Ti surface layer with the thickness of ~ 10 μm alloyed by Zr, Nb and Al atoms. Increase of the energy absorbed by the surface layer resulted in alloyed elements concentration diminishing. Solid solution on the basis of α Ti and martensite α Ti phase were observed in the alloyed layer. Surface titanium nitride was formed after plasma impact due to the usage of nitrogen as a plasma generating gas. Alloying by plasma impact led to microhardness increase and friction coefficient decrease.

Keywords: surface alloying; phase composition; microhardness; friction coefficient; compression plasma flows; titanium.

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Introduction

The surface alloys producing by action of high-energy charged particles beams or plasma flows on the substrates with preliminary deposited metal coatings are actively synthesized and investigated nowadays (Pogrebnjak et.al., 1998; Struts et.al., 2002; Mueller et.al., 2005; Yan et.al., 2007; Batrakov et.al., 2008; Makhlay et.al., 2009; Cherenda et.al., 2022). The mentioned type of materials treatment forms the surface layer containing both coating and substrate elements together due to intensive mass transfer. However, such experiments are limited to alloying with one element while the materials for industry applications contain three and more components to reach high level of the physical properties. For instance, the high-entropy alloys with five and more components at the approximately equal concentrations (5-35 at. % for each component) are of interest to investigation. The high-entropy alloys possess higher mechanical strength in comparable to steels and other alloys (Miracle et.al., 2014; Kumar et.al., 2016; Pickering et.al., 2016; Ye et.al., 2016; Li et.al., 2017; Miracle et.al., 2017). Besides, there is no cold-brittleness threshold of temperature for the high-entropy alloys that allow their application at negative temperatures.

The purpose of the present work is to synthesize the multicomponent surface layers in titanium by means of Nb-Ti-Zr-Al coating deposition on the surface followed by compression plasma flows treatment. The previous study showed the titanium surface layers alloyed with Zr and Al atoms by this approach had improved mechanical properties (Astashynski et.al., 2016).

Experimental

The multicomponent coating was grown on the surface of CP titanium by means of plasma-assisted cathode arc deposition in the QUINTA equipment (Prokopenko et.al., 2021). The separated Zr and Nb cathodes as well as composite cathode of 50% Ti – 50% Al were used simultaneously. The surface of the titanium samples was previously cleaned with PINK-P gas-plasma generator. Two types of coatings with different ratios of the elements (Table) were formed. The elemental composition of the coatings was investigated by means of energy-disperse X-ray microanalysis on the surface.

Table. Elemental composition of the multicomponent coatings

	Concentration, at.%			
	Al	Nb	Zr	Ti
Composition 1	27.3	26.4	26.8	19.5
Composition 2	9.9	47.9	28.4	13.8

The obtained samples of titanium with the multicomponent coatings were subjected to compression plasma flows (CPF) impact in a magnetoplasma compressor of compact geometry in the residual nitrogen atmosphere (the pressure in the chamber was 400 Pa). The samples were treated by three pulses with a duration of every pulse of 100 μ s. The absorbed energy density (Q) was varied in the range of 30-43 J/cm² (per pulse) due to change of the distance between the samples and the electrode from 8 to 12 cm.

The cross-section morphology of the treated samples was studied by scanning electron microscopy (SEM) with the LEO1455VP microscope. The elemental composition in the surface layers of the samples was investigated by means of energy-disperse X-ray microanalysis with the Oxford Instruments detector working together with the scanning electron microscope. Structure and phase composition of the alloyed surface layers were determined by means of X-ray diffraction with the Rigaku Ultima IV diffractometer in Cu K α radiation in the parallel beams geometry. The microhardness of the samples was measured by the Vickers method using the 402MVD Instron Wolpert Wilson Instruments equipment. The load of 100 g and the holding time of 10 s were chosen. To investigate the wear resistance of the modified surfaces the friction coefficient was measured using the TAU-1M tribometer with the load of 50 g on the WC-8Co indenter. The relief of the surface was analyzed on the basis of waviness measured by the MarSurf SD 26 profilometer.

Results and Discussion

The study of cross-section morphology of the multicomponent coatings before the plasma impact showed the elements distribution not to be uniform along the depth (Fig. 1a). The coating consists of several layers with different contrast obtained in the backscattered electrons detection mode during the SEM analysis that indicates the different element composition inside the layers. The multilayered systems are obtained due to rotation of the samples during the deposition process. However, it was impossible to find the difference in the elements distribution on the

cross-section because of low resolution of the X-ray microanalysis method (about 1 μm). The Fig. 1b demonstrates that concentration of elements at the coating surface is in the range of 20-25 at. % that corresponds to the data received from the surface (Table). It should be noted that the niobium concentration falls to 14 at. % while the aluminum and zirconium concentrations increase to 28-30 at. % with increase in coating depth.

The CPF impact on the multicomponent coatings results in surface layer microstructure change and redistribution of niobium, aluminum, zirconium atoms (Fig. 1c, d). After melting of the surface layer containing both the multicomponent coating and the titanium substrate surface layer during plasma impact, the liquid components are mixed with each other under the hydrodynamic convective motion (Astashynski et.al., 2016; Leyvi et.al., 2017). After crystallization of the melted part, the surface layer with a thickness of 10 μm containing all elements from the coating forms. The boundary between the coating and the substrate is not so clear viewed on the SEM-image that it was in the initial state.

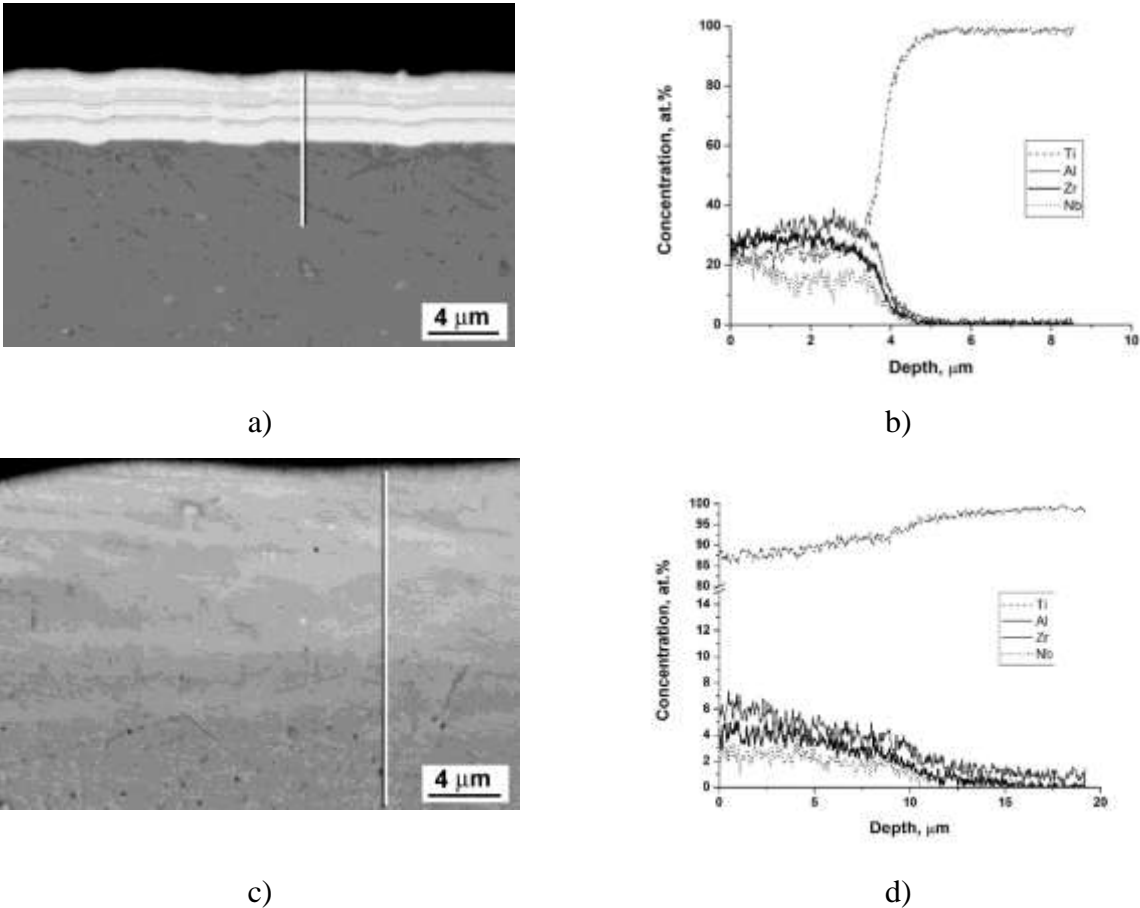


Figure 1. Cross-section morphology (a,c) and distribution of elements along the depth (b,d) in coated sample (composition 1) before (a,b) and after CPF treatment at $Q=37 \text{ J/cm}^2$ (c,d).

The concentration of the alloying elements on the surface decreases with the absorbed energy density rising (Fig. 2). For the samples with coating of composition 1 the content of the elements in the modified layer is varied in the following ranges: 1 – 4 at. % (for Nb), 3 – 8 at. % (for Zr) and 2 – 8 at. % (for Al). The titanium concentration belongs to the range 80 – 94 at. %. So high titanium concentration is explained by the presence of the titanium from substrate as the main element in the formed alloy. The smaller Nb concentration in the surface layer after the CPF treatment in contrast to other alloying elements is due to its lower content in the coating after the deposition (Fig. 1b). The obtained results show that the concentration of the alloying elements in the modified layer to be determined by both the composition of the coating and the parameters of the CPF impact.

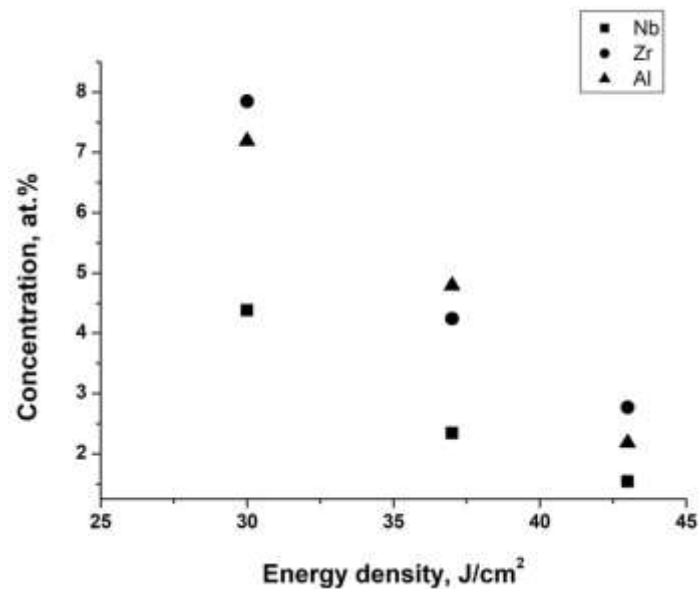


Figure 2. Concentration of alloying elements at the surface of the samples with coating (composition 1) treated by CPF at different energy absorbed by the surface.

As described in (Cherenda et.al., 2015; Leyvi et.al., 2017; Cherenda et.al., 2019), the main reasons of the elements concentrations decrease in the surface layer after the CPF impact with high absorbed energy density are following. The first reason is the increase in the melted depth and redistribution of all elements over the whole melted layer. Second one is the erosion of the surface. The existence of the surface erosion is confirmed by the measured mass loss of the samples after the CPF treatment (Fig. 3). The results demonstrate the growth of the mass loss from 10 to 65 $\mu\text{g}/\text{mm}^2$ after the CPF treatment of the coating with the composition 1 and from 3 to 52 $\mu\text{g}/\text{mm}^2$ after the CPF treatment of the coating with the composition 2 (with higher

concentration of Nb). It is evidently the higher erosion resistance of the coating with composition 2. The hydrodynamic motion of the surface melt is the main reason of the erosion (Tereshin et.al., 2003; Cherenda et.al., 2015; Martynenko, 2015; Leyvi et.al., 2017). The plasma stream interacts with the target and spreads over the surface in radial directions that provides the melt ejection out of the sample. This mechanism of the surface erosion prevails if the lateral size of the sample is less than the plasma stream diameter in the interaction area. The coating enrichment with niobium results in rising of melting point and decreasing in the viscosity of the liquid state. It reduces the lifetime of the melted state on the surface and, in turn, the amount of the deleted mass is reduced too.

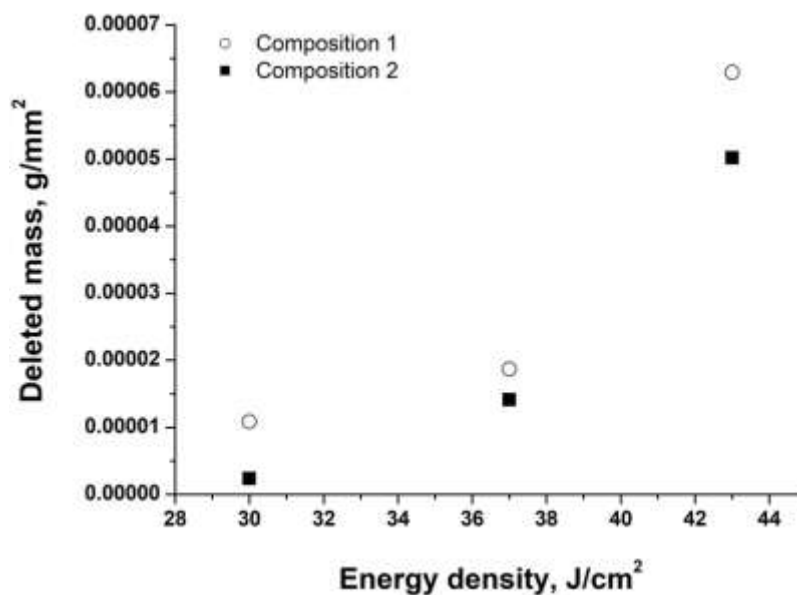


Figure 3. Dependence of the mass removed from surface unit area of samples with coating on the energy density absorbed by the surface after CPF treatment.

The results of phase composition of samples with coatings before and after the CPF treatment are presented in Fig. 4 and 5. There are three wide diffraction peaks in the range of diffraction angles 35 – 40 degree, 65-70 degree and 75 – 80 degree on the XRD patterns of the multicomponent coatings before the treatment. These peaks correspond to the (Nb,Zr,Ti,Al) solid solution with bcc lattice. The lattice parameters of the solid solution are 0.3436 nm (for the coating with composition 1) and 0.3406 nm (for the coating with composition 2). The solid solution (Nb,Zr,Ti,Al) formed in the coating with the composition 2 possesses the lattice parameter close to that of pure niobium (0.3307 nm). The niobium content in the coating with the composition 2 is approximately 48 at.% (Table), so the solid solution is based on niobium containing zirconium, titanium and aluminum. The solid solution in the coating with the

composition 1 has the lattice parameter higher than that of pure niobium. Indeed, according to the elemental composition analysis the coating 1 contains equal ratios of elements that produce solid solution with deformed crystal lattice. The big values of the full widths of the diffraction peaks on a half maximum confirm disperse structure of the coating and variable composition in the solution. The latter one was revealed by SEM (Fig. 1a). Apart from the observed diffraction peaks of the (Nb,Zr,Ti,Al) solid solution, additional diffraction reflexes were found in the close angle range. The additional peaks can be associated with phases based on zirconium or aluminum presenting in the coatings. The narrow diffraction peaks with low intensity in initial samples with coating belong to the titanium substrate.

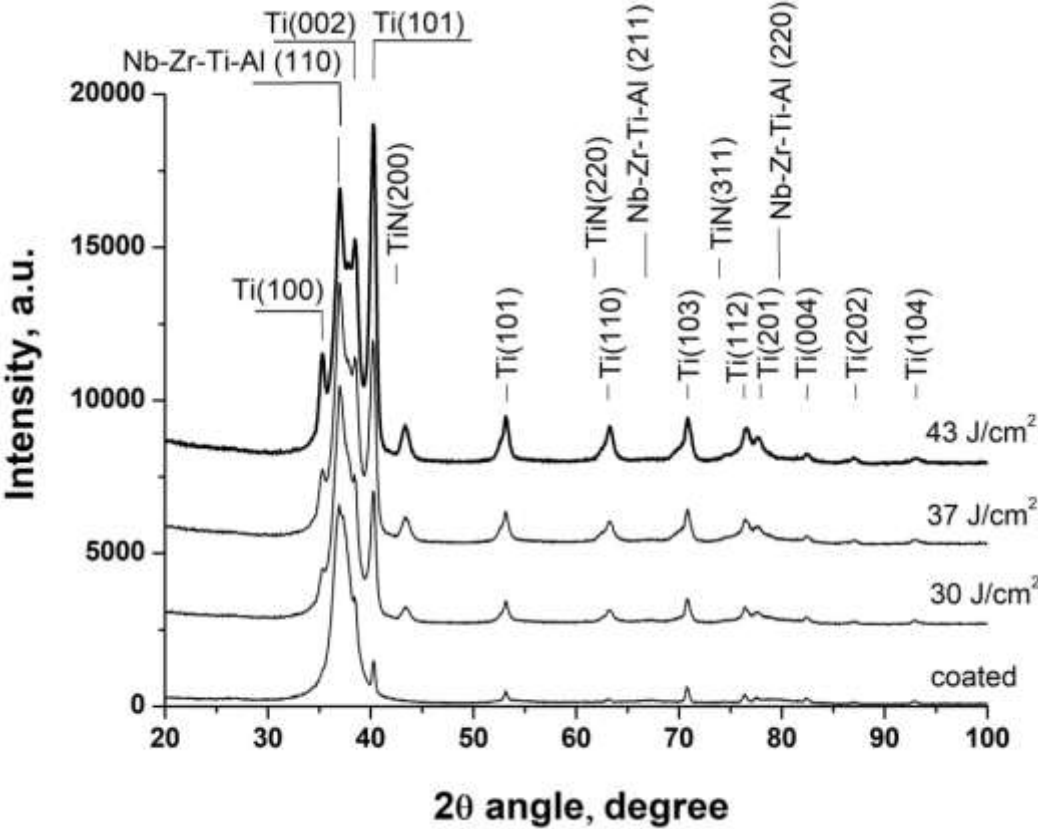


Fig. 4. Diffraction patterns of alloy samples with coating (composition 1) before and after compression plasma flows treatment with different energy absorbed by the surface.

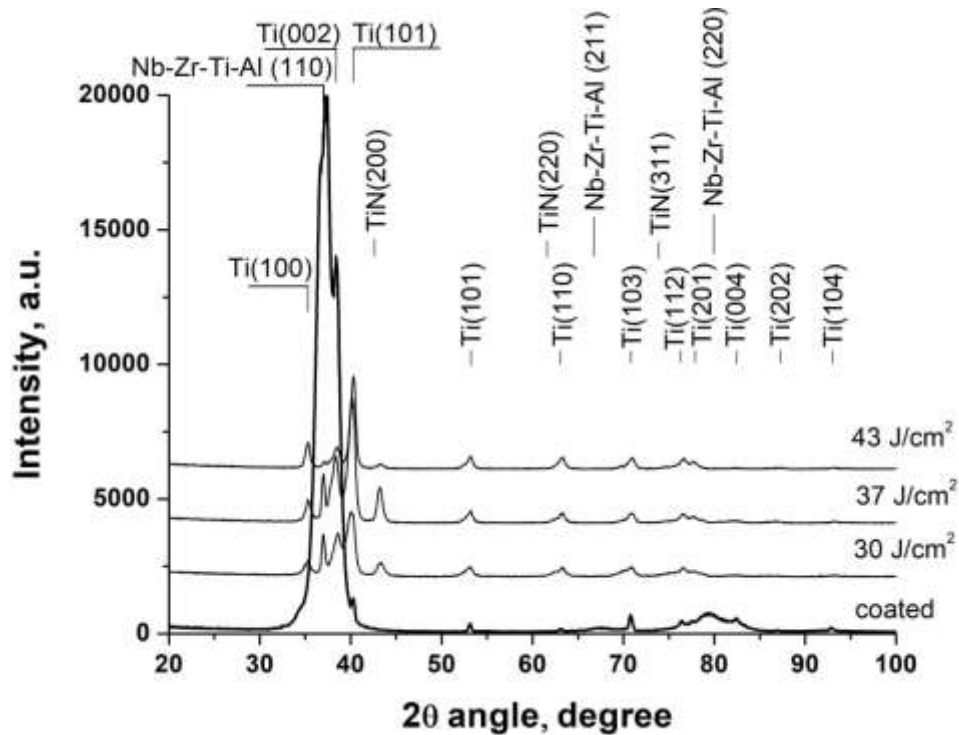


Fig. 5. Diffraction patterns of alloy samples with coating (composition 2) before and after compression plasma flows treatment with different energy absorbed by the surface.

The plasma impact results in melting of the coating and a surface layer of the titanium substrate, consequent mixing in the liquid state and the crystallization of the melted state in the condition of high cooling rate providing the change in the phase composition of the samples surface layer (Fig. 4 and 5). First of all, the intensity of the diffraction peaks of titanium increases that is a result of the titanium volume fraction growth due to melting of the titanium substrate. In contrast, the intensity of the diffraction peaks of the (Nb,Zr,Ti,Al) solid solution falls. The (Nb,Zr,Ti,Al) solid solution was found in the sample with the coating of composition 1 after the CPF treatment with the highest absorbed energy density ($Q=43 \text{ J/cm}^2$). It means the coating material was not totally dissolved in surface titanium layer. The XRD data correlate with the results of elemental composition changes in the surface layer (Fig. 2).

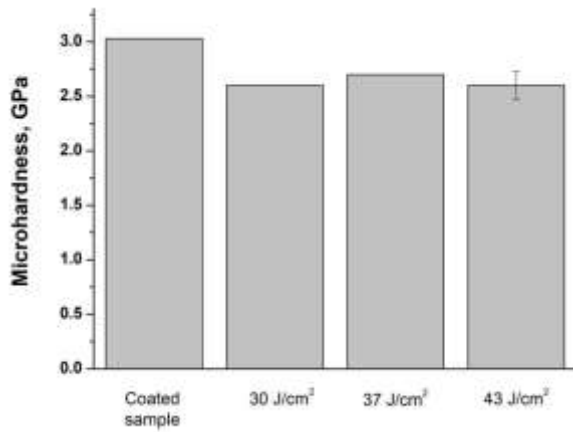
The diffraction peaks of α -Ti shifted towards the higher diffraction angles on the XRD patterns from the samples treated with CPF (Fig. 4, 5). The change in the diffraction peaks positions is caused by decreasing the lattice parameters of hcp structure of α -Ti. When rising the absorbed energy density from 30 to 43 J/cm^2 , the c parameter of the hexagonal unit cell of α -Ti falls from 0.4677 to 0.4668 nm. The formation of solid solution based on the low-temperature α -Ti phase with the elements of less atomic radius than that of titanium reduces the lattice

parameters. Moreover, the internal stress arising from excess vacancy concentration can also provide decreasing in the lattice parameters.

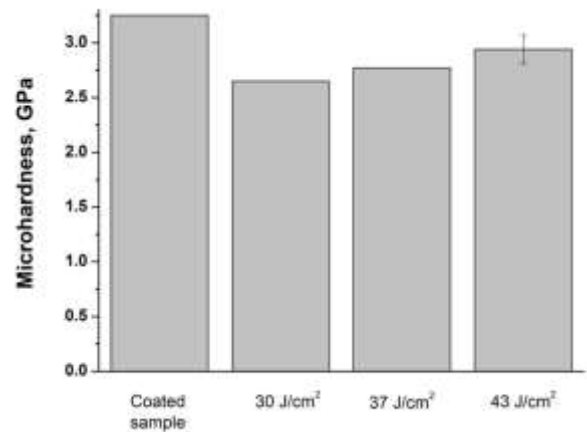
The detailed study of the XRD patterns allowed to find the “shoulders” near each diffraction peak of α -Ti. The appearance of the “shoulders” indicates the formation of hexagonal crystalline structure with the lattice parameters some higher than those in hcp titanium lattice. This structure is the titanium-based martensite phase forming after high cooling rate solidification with dissolved atoms of the alloying elements.

The plasma forming gas, nitrogen, interacts with the surface of the metal target during the CPF impact. According to the previous results (Cherenda et.al., 2012), the nitrogen atoms penetrate to the surface layer due to diffusion in the solid state after crystallization. As titanium is the main element presenting in the modified layer, the titanium nitride phase forms predominantly. The diffraction peaks corresponding to the titanium nitride are also observed in the XRD patterns (Fig. 4, 5). The angular positions of the diffraction peaks are close to the position of those for cubic titanium nitride TiN with fcc crystal lattice. However, the lattice constant of the observed titanium nitride is some less than that for ideal TiN lattice. It seems that titanium nitride phase forms with a lack of nitrogen or like substitutional solid solution Ti(Nb,Zr,Al)N. Intensity of nitride diffraction peaks increases with the growth of energy density for the samples with coating of composition 1 while for the samples with coating of composition 2 this dependence is not monotonic and has a maximum at $Q=37 \text{ J/cm}^2$.

The initial plate of titanium had the microhardness of 1.7 GPa. The multicomponent coatings deposited on the titanium surface have some higher microhardness which is varied in the range 3.0 – 3.3 GPa (Fig. 6). After the CPF impact the microhardness of the surface layer decreases down to 2.6 – 2.9 GPa and does not depend on the parameters of the plasma treatment. At the same the mean value of the alloyed layer microhardness is higher than that of the initial titanium plate. The main factors influencing on the microhardness of the surface layer after the CPF treatment are solid solution hardening, and martensite and nitride phases formation. The disperse structure formed because of high cooling rate during solidification can also lead to the microhardness growth (Astashynski et.al., 2016).



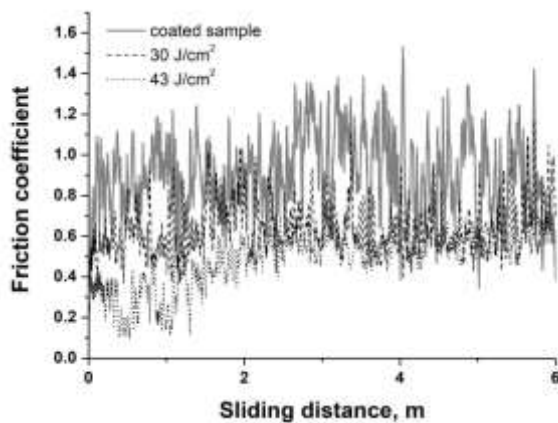
a)



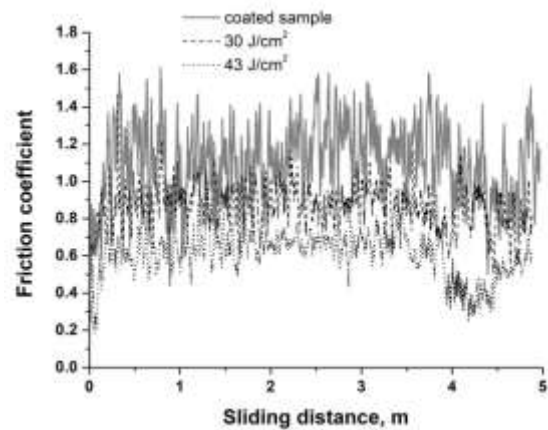
b)

Fig. 6. Microhardness of samples with coating before and after compression plasma flows treatment with different energy absorbed by the surface: a - composition 1, b - composition 2.

The tribological tests of the multicomponent coatings showed that the friction coefficient of the surface leaves on the same level as that in the initial titanium plate. But the friction coefficient of the surface after the CPF impact tends to decrease (Fig. 7).



a)



b)

Fig. 7. Dependence of friction coefficient on sliding distance for samples with coating before and after compression plasma flows treatment with different energy absorbed by the surface: a - composition 1, b - composition 2.

Change of microhardness and surface relief are the main factor affecting the friction coefficient after plasma impact. In these experiments the microhardness weakly depends on the absorbed energy density. At the same time the waviness of the surface (W_a) increases from

0.120 – 0.475 μm (in the multicomponent coating of both compositions) to 3.336 – 6.047 μm (after the CPF treatment at the highest absorbed energy density of 43 J/cm^2). It should be noted that the waviness grows with the absorbed energy density increase. This result correlates to the friction coefficient changes. Waviness increase leads to diminishing of the contact area in friction pair thus leading to friction coefficient decrease. So, the surface relief can be considered as one of the main factors affecting the tribological behavior of the plasma treated surfaces.

Conclusions

The impact of the compression plasma flows on the “Nb-Ti-Zr-Al coating / Ti substrate” system results in formation of the 10 μm titanium surface layer containing niobium, zirconium and aluminum atoms. The concentration of the alloying elements in the titanium surface layer is determined by their content in the coating and the absorbed energy density during plasma treatment. The alloying elements (Nb, Zr, Al) concentration falls in the surface layer with the absorbed energy density increasing. The surface erosion is one of the factors leading to alloying elements concentration decrease. Increase of niobium concentration in the deposited coating improves the surface erosion resistance under the plasma impact.

The multicomponent Nb-Ti-Zr-Al coatings deposited on the titanium surface consist of series of solid solutions with variable composition and based on the bcc crystal lattice. The plasma impact melts the coating and a part of titanium substrate resulting in formation of solid solution on the basis of α -Ti and martensite α -Ti phases after the crystallization. The surface layer also contains the titanium nitride TiN grown due to interaction between the heated surface and plasma forming gas.

The multicomponent coatings have the microhardness 3.0 – 3.3 GPa which slightly decreases to 2.6 – 2.9 GPa after the compression plasma flows impact. The plasma treatment decreases the friction coefficient of the surface due to the waviness rising mainly.

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