Modification of chromium/titanium system phase composition and mechanical properties by compression plasma flows

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Phase composition and mechanical properties changes of the titanium surface layer nitrided and alloyed by chromium under the action of compression plasma flows have been investigated. The findings showed the formation of an alloyed layer with the thickness of up to 27 μm containing α-Ti, α′-Ti and β-Ti(Cr) phases. The volume fraction of these phases was dependent on treatment regimes. The titanium nitride formation in the surface layer was observed. Treatment by compression plasma flows allowed to increase 2.5 times the surface layer microhardness and to diminish 4.2 times the friction coefficient.

1. Introduction

Titanium and its alloys have been widely used in industry due to their low specific gravity, stiffness, good corrosion resistance and biocompatibility. However, well-known shortcomings such as unsatisfactory corrosion resistance in acid environment, poor wear resistance, a high coefficient of friction and serious oxidation at high temperature limit titanium alloys applications. Different types of surface modification techniques are used to overcome these shortcomings. Alloying by different metals using high-intensity plasma beams [1] and double plasma surface alloying technique [2, 3] can improve both corrosion resistance [1] and mechanical properties [1-3] of the titanium surface layer. Different types of nitriding techniques: laser [4, 5], gas [6,7], plasma [8, 9] and ion-beam nitriding [10, 11], etc. are widely used for the enhancement of surface layer tribological properties.

Compression plasma flows (CPF) generated by quasi-stationary plasma accelerators can be applied to combine processes of titanium surface layer alloying and nitriding. The modified layer formation can be described in the following way [12]. At the first stage a coating consisting of one or a few elements to be alloyed is deposited on the surface of a material. At the second stage CPF treatment of the formed system is carried out. CPF impact with the surface is accompanied by melting of the coating and some part of the substrate material. Convection whirls which appear in the liquid phase due to high concentration and temperature gradients lead to mixing of the coating and substrate elements in the melt. Subsequent crystallization of the melted layer at a high cooling rate ($\sim 10^7$ K/s) results in the formation of the mixed layer with the same thickness containing elements of the coating and the substrate. Besides diffusion of nitrogen atoms from residual atmosphere (if nitrogen is used as a plasma forming gas) can take place in a thin surface layer (~ 1 μm) thus leading to nitride formation [12, 13].

Chromium was chosen as an alloying element in this work. It is known that chromium is a β- eutectoid forming element and is used in many titanium alloys [14]. Chromium additions can also increase burn resistance [3], tensile properties and creep resistance [15] of titanium alloys. Titanium surface layer alloying by chromium combined with nitriding by means of "chromium-titanium" system treatment with compression plasma flows generated in nitrogen atmosphere was the main aim of this work.

2. Experimental

The samples used (10x10x2 mm) were made of technically pure titanium (0.18% Fe, 0.12% O, 0.07% C, 0.04% N, 0.01% H, in wt.%). The chromium coating was formed using cathodic arc vapour deposition with the following process parameters: the arc current of 100 A, the bias voltage of -120 V, the deposition time of 10 min (the corresponding coating thickness ~ 1 μm).

CPF were obtained using a gas-discharge magneto-plasma compressor of compact geometry described in detail earlier [13]. The pressure of the plasma forming gas

was 400 Pa during the discharge. The discharge duration in the MPC is around 100 μs. Treatment of the formed chromium-titanium system samples was carried out by three pulses of compression plasma flows to provide homogeneity of the mixed layer. The time interval between pulses was 20 s. The energy density absorbed by the surface layer changed in the range of 13-35 J/cm^2 per pulse.

The concentration profile of nitrogen was measured by Auger electron spectroscopy (AES) using PHI-660 (Perkin Elmer). LMM Ti and KLL N transitions overlapped at the AES spectrum. That is why the nitrogen concentration was evaluated by subtracting LMV Ti line intensity from the sum of LMM Ti and KLL N lines intensity (multiplied by the corresponding sensitivity factors). The phase composition of the samples was investigated by the X-ray diffraction analysis (XRD) in Bragg- Brentano geometry and Cu Kα radiation using a DRON 4-13 diffractometer. Cross-section morphology as well as samples element composition was analyzed by means of scanning electron microscopy using a LEO1455VP device equipped with an energy-dispersive X-ray Röntec detector. Before investigations the samples cross-sections were etched in 0.5 ml HF + 2.5 ml HNO_3 + 1.5 ml HCl + 2.5 ml H_2O solution. The microhardness of the samples was tested by means of a PMT-3 microhardmeter with a Vickers indenter under the load ranging from 0.5 to 2.0 N. The tribological test was of 'pin-on-plane' type, dry sliding dynamic friction. The linear velocity was 0.4 cm/s. The pin was made of a hard alloy (92 wt.% WC, 8 wt.% Co). The load on the pin was 0.5 N.

3. Results and discussion

The data of the energy-dispersive X-ray microanalysis showed that the increase of the energy absorbed by the surface layer during treatment resulted in the chromium concentration decrease in the surface layer with the thickness of ~ 1 μm. The corresponding concentration for the energy density of 13, 19, 23 and 35 J/cm^2 amounted to 6.8±1.3 at. %, 3.7±0.6 at. %, 1.3±0.6 at. % and 0.2 ± 0.1 at. %, respectively. The increase of the melted layer thickness with the growth of the energy absorbed was the main reason for this effect. Convection in a thicker melted layer led to a deeper penetration of the alloying element and hence to the decrease of the average alloying element concentration in it. This effect is illustrated by Fig. 1 showing chromium distribution along the cross-sections of the samples after CPF treatment. One can see that the thickness of the alloyed layer increased from 11 μm (at 13 J/cm^2) to 27 μm (at 23 J/cm^2). The chromium concentration after CPF treatment at 35 J/cm^2 was too small (at the background level) to receive its characteristic line distribution along the cross-section.
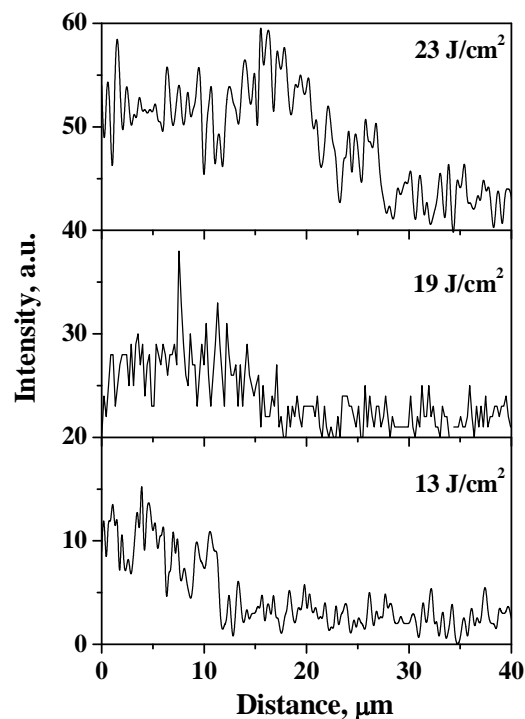

Fig. 1. Distribution of characteristic X-ray radiation of Cr Kα along the cross-section of Ti samples with the Cr coating treated by CPF at different energy absorbed by the surface layer.

The growth of the energy absorbed also led to the decrease of the nitrogen concentration in the surface layer (Fig. 2). The reason for such nitrogen behaviour is under investigation now. One can see that the nitrogen profile can be represented as a sum of two diffusion profiles. Similar nitrogen distribution was received after laser nitriding of iron [16]. The profile constituent which was closer to the surface was attributed to the iron nitride fall-out while the other constituent – to inward diffusion of nitrogen dissolved in liquid iron [16]. Thus the formation of titanium nitride in our case can be assumed.
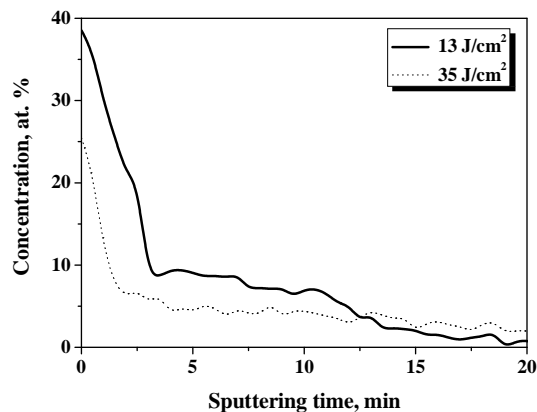

Fig. 2. AES nitrogen depth profiles in Ti samples with the Cr coating treated by CPF at different energy absorbed by the surface layer.

The change of the alloying element concentration in the mixed layer influenced its phase composition (Fig. 3). XRD analysis showed β-Ti(Cr) solid solution formation in the range of absorbed energy density 13-19 J/cm^2. This range correlates with the chromium concentration (6.8-3.9 at.%) which is comparable with the critical concentration (8.4% [17]) necessary to stabilize β-Ti phase in equilibrium conditions at room temperature. Though the experimentally determined chromium concentration was less than the critical one, the presence of β-Ti can be explained either by local heterogeneities in chromium distribution or by the influence of a high cooling rate on the value of the critical concentration [18]. The decrease of the chromium concentration in the alloyed layer resulted in the growth of the β-Ti(Cr) lattice parameter (Fig. 3). The diffraction line at 2θ=40.2° was formed by the superposition of (101) α-Ti and α´-Ti diffraction lines. The growth of the energy absorbed led to the decrease of α´-Ti volume fraction, which can be associated with the decrease of the impurities concentration in hcp titanium lattice and is consistent with the data of the element composition analysis. The diffraction line at 2θ=37.8° can be attributed to (002) α´-Ti or (200) ε-Ti$_2$N with a distorted lattice. The diffraction lines at 37.1° and 43.2° can belong either to ε-Ti$_2$N either to δ-TiN$_x$ (δ-(Ti,Cr)N$_x$). Nitrogen distribution in titanium after CPF treatment allows to suppose the formation of both ε-Ti$_2$N and δ-TiN$_x$ type of nitrides (Fig. 2). No diffraction lines of nitrides were observed after CPF treatment at 35 J/cm^2 (Fig. 3) though ε-Ti$_2$N formation at least could be expected at the nitrogen concentration of 20-25 at.% (Fig. 2).
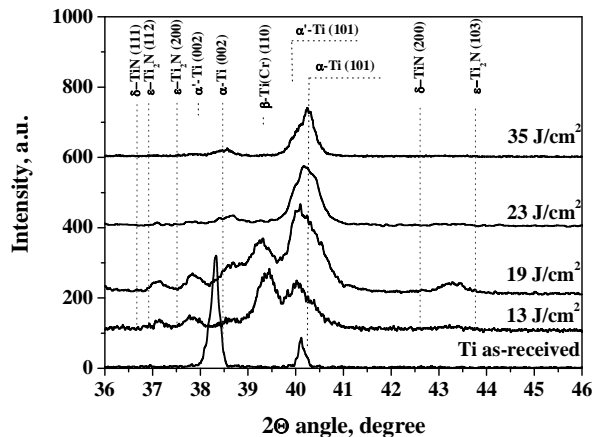

Fig. 3. The XRD patterns of the Ti sample as-received and Ti samples with the Cr coating treated by CPF at different energy absorbed by the surface layer.

A typical microstructure of the modified layer is presented in Fig. 4 (a). Three sublayers can be found in the surface layer. The first sublayer with the thickness of ~ 1 µm for this treatment regime can contain titanium nitride according to the element composition analysis (Fig. 2). The second sublayer has an acicular structure which is characteristic of α´-Ti [4]. Its thickness (10-12 µm at 19 J/cm^2) corresponds to the thickness of the alloyed layer.

Thus the second sublayer should contain β-Ti(Cr) phase for the corresponding treatment regimes. The third sublayer is a heat affected zone with the thickness of up to 30 µm containing α-Ti grains of a changed shape.

One can see that the first sublayer contains dendrites growing into the bulk (Fig. 4b). A similar dendritic structure was obtained by laser nitriding of titanium in [5]. The growth of dendrites into the bulk was associated with the formation of δ-TiN$_x$ having a high melting temperature (3220 K at x=1 [5]) and the beginning of solidification from the bulk. Thus one can suppose δ-TiN$_x$ or δ-(Ti,Cr)N$_x$ formation for all CPF treatment regimes (though δ-TiN$_x$ was not detected by XRD analysis at 35 J/cm^2) because the dendrites growth into the bulk from the surface was found for all treated samples. In case of treatment at 35 J/cm^2 δ-TiN$_x$ can create only crystallization centers at the surface (thus forming a thin nitride layer which cannot be detected by the XRD apparatus used) while the following crystallization process in conditions favourable for the dendrites growth (a high overcooling rate) can take place on the basis of hcp α-Ti or α´-Ti lattice. ε-Ti$_2$N formation can also be supposed at the interface between δ-TiN$_x$ and α-Ti.
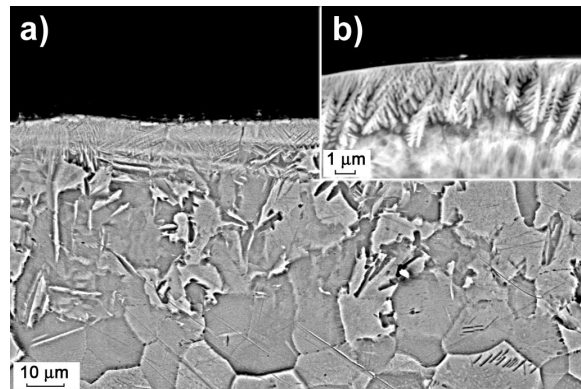

Fig. 4. Cross-section morphology of the Ti sample with the Cr coating treated by CPF at 19 J/cm^2 (a) and 35 J/cm^2 (b).

The change of the phase composition results in the modification of microhardness (Fig. 5) and the friction coefficient (Fig. 6). The microhardness increase up to 6.4 GPa was found after CPF treatment at 13 J/cm^2, which can be connected with the surface nitride formation and the maximum content of α´-Ti and β-Ti(Cr) phases. A further increase of the energy absorbed led to the microhardness decrease up to 3.8 GPa in the surface layer with the thickness of 2 µm (at 35 J/cm^2). For this treatment regime the microhardness increase in the layer with the thickness of 4 µm in comparison with that of the initial sample of titanium can be connected with α´-Ti(N) phase because the chromium concentration is small (~0.2 at. %). The influence of the modified grain structure and size as well as that of the defect structure in the melted layer on the microhardness value is also possible.

Tribological tests showed that the minimal friction coefficient (0.1-0.2) was observed after treatment in the

range of 13-19 J/cm^2 (Fig. 6), which can be attributed mainly to the influence of β-Ti(Cr) and titanium nitride according to the data of XRD analysis (Fig. 3). The friction coefficient became greater for the treatment regimes of 23-35 J/cm^2 when no β-Ti(Cr) phase was found (Fig. 3) and only a thin nitride layer was supposed to be present at the surface.
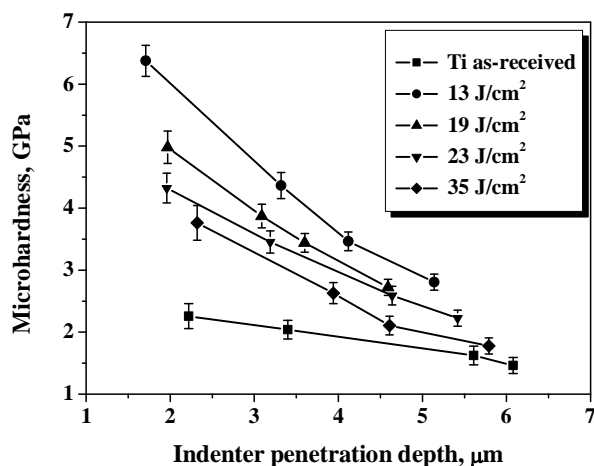

Fig. 5. The microhardness dependence on the indenter penetration depth of the Ti sample as-received and Ti samples with the Cr coating treated by CPF at different energy absorbed by the surface layer.
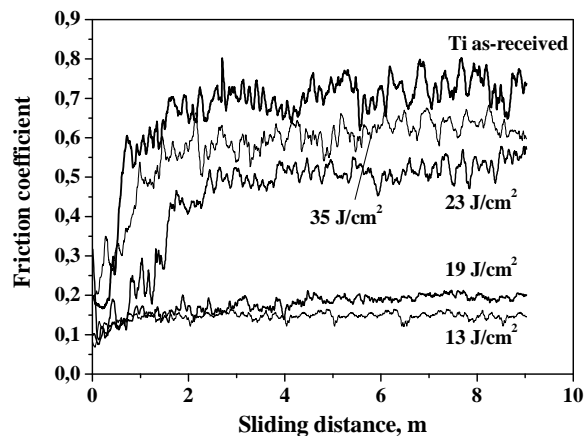

Fig. 6. The friction coefficient dependence on the indenter sliding distance of the Ti sample as-received and Ti samples with the Cr coating treated by CPF at different energy absorbed by the surface layer.

4. Conclusions

The findings showed that treatment of the "chromium-titanium" system by compression plasma flows generated in nitrogen atmosphere allowed to alloy the surface layer of titanium by chromium atoms and to nitride it concurrently. The structure of the modified surface layer can be described as follows. δ-TiN$_x$ or δ-(Ti,Cr)N$_x$ nitride is formed at the surface. The alloyed layer with the thickness of 11-25 μm (depending on treatment regimes) contains β-Ti(Cr), α´-Ti and α-Ti phases. The underlying heat affected zone with the thickness of up to 30 μm includes α-Ti grains of a changed shape. The increase of the energy absorbed by the surface layer results in growing the alloyed layer thickness and reducing the nitrogen and chromium concentration, thus leading to the decrease of the nitride, β-Ti(Cr) and α´-Ti content.

Alloying by chromium and nitriding by compression plasma flows provide the titanium microhardness increase up to 6.4 GPa and the friction coefficient decrease up to 0.1.

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