

# Surface Alloying of Ti–6Al–4V with Zirconium by Pulsed Electron-beam Melting of Zr/Ti Multilayers<sup>1</sup>

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**Abstract – Surface alloying of Ti–6Al–4V with Zr aiming at depletion of Al and V was realized by liquid-phase intermixing of multi-layer film [Zr(20 nm)/Ti(20 nm)]<sub>12</sub> of total thickness of 480 nm with substrate (Ti–6Al–4V) using a low-energy (~20 keV), high-current electron beam (2.5 μs, 3.5 J/cm<sup>2</sup>). Scanning electron microscopy and energy dispersive X-ray spectroscopy, Auger electron spectroscopy, X-ray diffraction, and atomic force microscopy were used to study the surface morphology, microstructure, elemental and phase compositions of the alloyed layer. It was found that a homogeneous intermixing of all Zr/Ti nanolayers and diffusion of Zr into the substrate up to a depth of ≈1 μm take place after a single-shot pulsed melting. The surface layer of depth of ≈0.5 μm is free of Al and V and contain ≈30 at % Zr. The near-surface layer, due to quenching from the melt, has a submicrocrystalline grain structure with an average grain size of 112 nm. The post-irradiation vacuum annealing (500 °C, 2 h) leads to enrichment of alloyed layer with O and C impurities, and decrease of grain size up to 90 nm. As a result, the nanohardness of the alloyed layer was increased in comparison with the substrate.**

## 1. Introduction

Titanium alloy Ti–6Al–4V has been widely used for surgical implants, like artificial joints and other due to high specific strength, corrosion resistance, bio- and mechanical compatibility [1]. However, its wear resistance is relatively low. During cyclic loading of implant a fretting-induced damage of thin passive TiO<sub>2</sub> film and the release of metal ions into the adjacent tissues are occurred. The most potential harmful effects are caused with V and Al [2].

In [3–6] it has been shown, that the surface alloying of metallic materials by pulsed melting of film-substrate systems with a low-energy (~20 keV), high-current electron beam (LEHCEB) of microsecond duration is a promising method of the surface modification without impairing mechanical bulk properties.

In present work, the pulsed electron-beam alloying of Ti–6Al–4V with zirconium in order to reduce the V and Al content in the surface layers has been realized. Zirconium was chosen because it is biocompatible metal [2], and its addition increases the corrosion resistance and strength of Ti. Moreover, Zr is fully dissolved in the both α- and β-Ti [7] that simplifies a formation of surface Ti–Zr alloys by pulsed melting.

## 2. Experiment

The multi-layer film [Zr(20 nm)/Ti(20 nm)]<sub>12</sub>/substrate (Ti–6Al–4V) system was used for experiments. The total thickness of Zr/Ti film was 480 nm. Ti and Zr layers were alternately deposited onto 18 mm diameter and 3 mm thick Ti–6Al–4V substrates using magnetron sputtering of pure Ti (99.9%) and Zr (99.9%) targets. Prior to deposition, the substrates were mechanically polished using diamond paste and then irradiated with a LEHCEB with pulse duration 2.5 μs at energy density 2.5±3 J/cm<sup>2</sup> and pulse number 40. The purpose of pre-treatment is efficient purification and homogeneity of the surface layer in order to decrease significantly the probability of the local delamination of the thin film at pulsed melting because of surface cratering [4].

[Zr/Ti]<sub>12</sub>/Ti–6Al–4V system was subjected to one-pulse melting with LEHCEB (2.5 μs, 3.5 J/cm<sup>2</sup>). Selected surface-alloyed samples were annealed (550 °C, 2 h) in the oil-free vacuum (10<sup>-4</sup> Pa) in order to decrease the residual stresses induced by pulsed heating.

The topography and point chemical composition of the surface regions of samples, before and after surface alloying, were investigated by scanning electron microscope (SEM), with energy-dispersive X-ray (EDX) analysis (Philips-SEM 515 EDAX). The surface topography also was studied with atomic force microscope (AFM). The depth profiles of elements were determined by Auger electron spectroscopy (AES) using a system Microlab310F. The phase composition of the surface layers was examined by grazing incident X-ray diffraction (GIXRD) analysis at an incident angle ω = 1÷4° with a diffractometer D5000 using CuK<sub>α</sub> radiation. The thickness of an analyzed

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layer for Ti target was  $0.1 \div 0.8 \mu\text{m}$ . The mechanical properties of surface-alloyed layers were studied by nanoindentation using a nanoindenter NanoTest 600.

### 3. Results and discussion

According to the calculations, the irradiation of film/substrate system leads to melting of all Zr/Ti nanolayers with Ti-6Al-4V substrate. The total thickness of the melted layer is  $\sim 1 \mu\text{m}$  and the lifetime of the melt is  $\sim 3 \mu\text{s}$ . The surface evaporation at the pointed above e-beam parameters is negligible.

As it follows from AES, the as-deposited system contains, except Ti and Zr, also C and O impurities. Carbon is located mainly in the surface layer of  $\sim 10 \text{ nm}$  thickness, while oxygen is observed at the surface and the film/substrate interface as well.

Figure 1, *a* shows the AES depth profiles of elements in the surface-alloyed layers formed by pulsed melting of the studied system. It can be seen that the uniform intermixing of all Ti/Zr nanolayers as well as diffusion of Zr into substrate in  $\approx 0.5 \mu\text{m}$  depth was occurred.

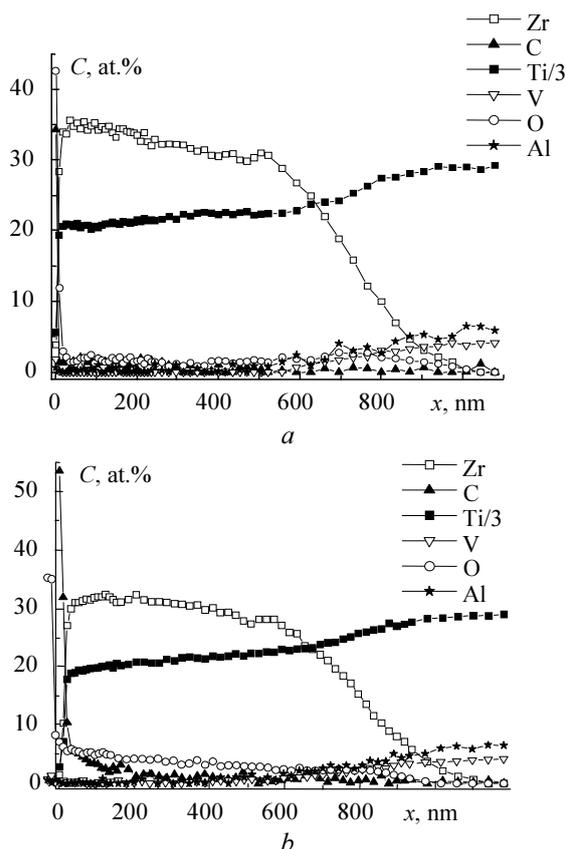


Fig. 1. AES depth profiles of elements of  $[\text{Zr/Ti}]_{12}/\text{Ti-6Al-4V}$  system subjected to pulsed melting (*a*) and post-irradiation vacuum annealing (*b*)

Thus, the total thickness of Zr-alloyed layer is  $\approx 1 \mu\text{m}$ , which is in agreement with calculated melt depth. Herewith, the surface alloy Ti - (30-35 at.% Zr) of thickness  $\approx 0.5 \mu\text{m}$  free of Al and V was formed.

The uniform intermixing of Zr/Ti nanolayers and formation of the diffusion layer at the film/substrate interface is in agreement with an estimation of the diffusion length of these metals in the melt. Taking into account that the calculated lifetime of the melt  $t_m \sim 10^{-6} \text{ s}$ , and putting the liquid-phase diffusivity  $D = 5 \cdot 10^{-5} \text{ cm}^2/\text{s}$ , we obtain the diffusion length  $l \sim (2Dt_m)^{0.5} \approx 100 \text{ nm}$ , which is  $\sim 5$  times more than a thickness of separate Ti and Zr layers.

Post-irradiation vacuum annealing (see Fig. 1, *b*) leads to the enrichment of surface layers with O and C impurities from the vacuum chamber. It is accompanied with a small decrease of the Zr and Ti content in the surface layers. Herewith, as before, Zr-alloyed layer of thickness of  $\approx 0.5 \mu\text{m}$  is free of Al and V.

Figure 2 shows the GIXRD patterns of film/substrate system as-deposited, after pulsed melting, and post-irradiation vacuum annealing.

The GIXRD pattern of as-deposited system (2) contains the  $\alpha$ -Ti and  $\alpha$ -Zr diffraction peaks. Pulsed melting leads to a loss of both  $\alpha$ -Ti and  $\alpha$ -Zr single phases and an appearance of new broader peaks, which have  $2\theta$  position in the immediate vicinity of the  $\alpha$ -Ti and  $\beta$ -Ti reference peaks. A comparison of XRD and AES data (see Fig. 1, *a*) leads to the conclusion that the dissolution and intermixing of Ti/Zr layers and subsequent high-rate resolidification of the melt result in the formation of the two-phase structure which consist of  $\alpha(\text{Ti, Zr})$  and  $\beta(\text{Ti, Zr})$ -solid solutions and contain at the average 30-35 at.% Zr. The broadening of the new reflections is associated with the formation of microstresses at pulsed melting [3, 5]. Post-irradiation annealing (4) leads to arising of the additional unidentified reflections at angles  $2\theta \sim 37$  and  $\sim 52^\circ$ .

Figure 3 presents AFM surface topography images of the studied Zr-alloyed samples before and after vacuum annealing.

As it follows from Fig. 3, *a*, the near-surface layer has submicrograin structure with average grain size  $(112 \pm 31) \text{ nm}$ . The formation of the similar submicrograin and nanosized structures are observed under electron-beam melting of the carbon and alloyed steels containing the carbide particles, as well as the multi-layer film/substrate  $[\text{Al/Si}]_3/\text{Al}$  and  $[\text{Al/C}]_2/\text{Al}$  systems [3, 5].

The post-irradiation annealing results in decrease of the average grain size up to  $(90 \pm 27) \text{ nm}$  (Fig. 3, *b*). This can be related to processes of the pre-recrystallization polygonization [8]. Really, after resolidification is complete, the surface layers will subject to thermoelastic quasi-static compressive stresses at the surface plane, induced by high temperature gradients during a cooling. As a result, the plane stress-strain state with increased dislocation density and residual tensile stresses is formed [3, 5].

For titanium alloys the recrystallization temperature is in the range of  $575 \div 700^\circ\text{C}$ . Herewith, the O

and C impurities observed in the near-surface layer (see Fig. 1, *b*) increase the recrystallization temperature [7]. In view of those circumstances, it is possible to suggest, that decrease of grain size in the surface alloy  $\alpha$ -Ti<sub>70</sub>Zr<sub>30</sub> under annealing at 550°C (Fig. 2, *b*) occurs because of initial stage of recrystallization, so-called pre-recrystallization polygonization.

During this stage, the redistribution of the dislocations, the formation of cell walls, and transformation

of the cells to randomly oriented subgrains take place [8]. Herewith, the subgrain growth can slow down due to the precipitations of the (Ti, Zr) oxides and carbides.

The surface roughness of film/substrate samples as-deposited, after pulsed melting, including post-irradiation annealing is about 30÷40 nm (for square of 15 × 15 μm), which corresponds to that of pre-irradiated Ti-6Al-4V substrate.

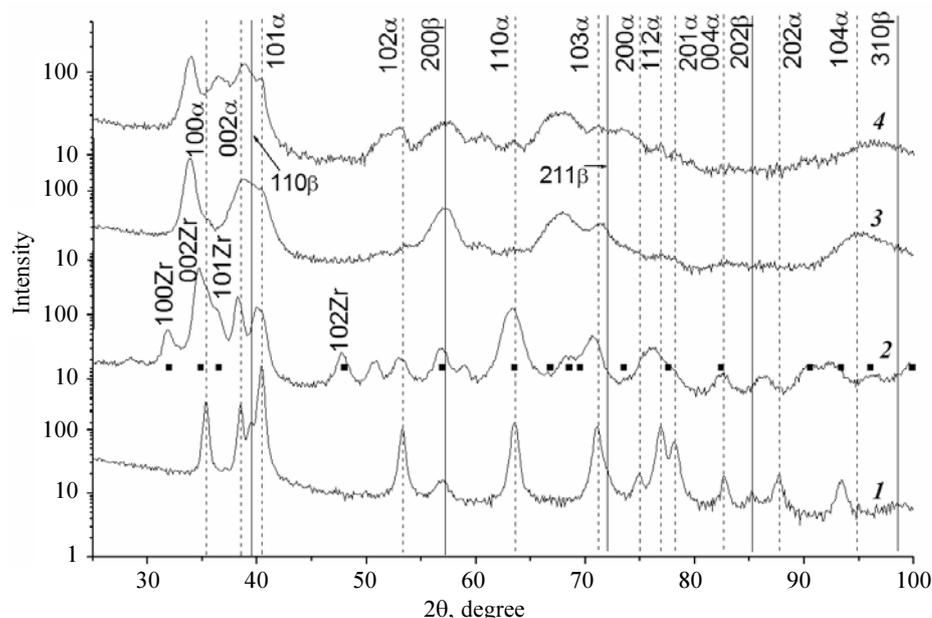


Fig. 2. GIXRD patterns of the near-surface layers of the Ti-6Al-4V substrate (1), [Zr/Ti]<sub>12</sub>/Ti-6Al-4V system as-deposited (2), after pulsed melting (3), and post-irradiation vacuum annealing (4). The Ti reflections are given at the top; Zr reflections are marked as (•). The thickness of analyzed layer is 0.2÷0.3 μm ( $\omega = 2^\circ$ )

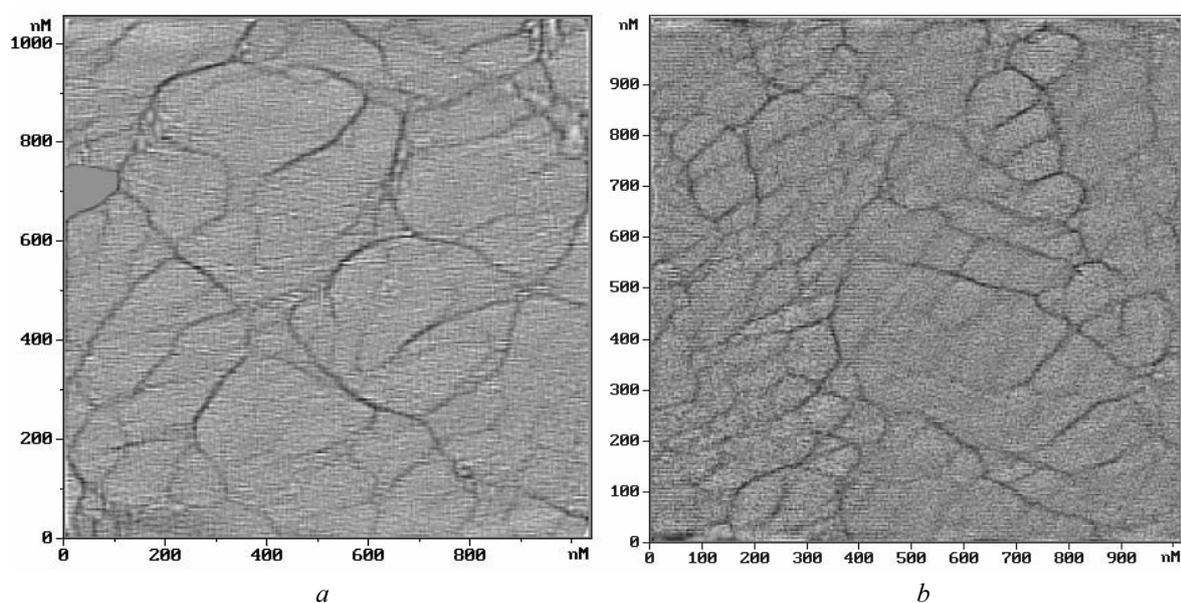


Fig. 3. AFM surface topography images of [Zr/Ti]<sub>12</sub>/Ti-6Al-4V system after pulsed melting (*a*) and post-irradiation vacuum annealing (*b*)

Figure 4 shows the nanohardness depth profiles of the substrate and film/substrate system in the various states. As it can be seen from curves 1 and 2, the pre-deposition multiple pulsed melting of Ti-6Al-4V substrate does not result in its surface hardening.

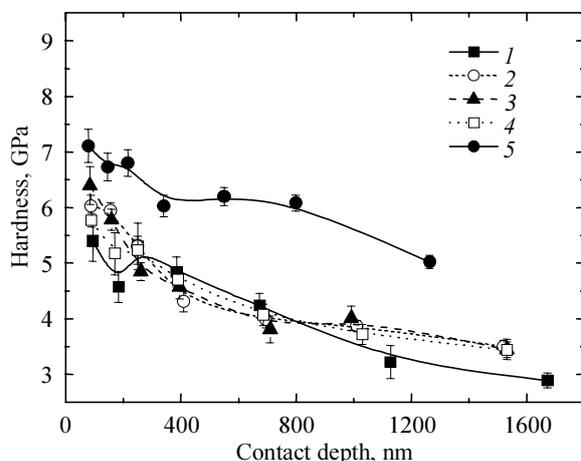


Fig. 4. Nanohardness depth profiles for Ti-6Al-4V substrate before (1) and after multiple pulsed melting (2), [Zr/Ti]<sub>12</sub>/Ti-6Al-4V system as-deposited (3), after pulsed melting (4), and pulsed melting followed by vacuum annealing (5)

The deposition of multilayer Zr/Ti as well as its pulsed melting resulting in the formation of the Ti-Zr surface alloy also does not effect on nanohardness depth profiles (see curves 3 and 4). In contrast, the post-irradiation annealing of Zr-alloyed surface layers result in the noticeable surface hardening (see curve 5).

The lack of hardening of either substrate or Zr-alloyed surface layers can be associated with residual tensile stresses, formed under pulsed e-beam irradiation [9]. In turn, the increase in hardness after annealing can be associated with decrease in residual stresses as well precipitation hardening due to formation of (T, Zr) oxides and carbides.

In conclusion, the pulsed melting of the multilayer [Zr/Ti]<sub>12</sub>/Ti-6Al-4V system with LEHCEB of microsecond duration allows forming Zr-alloyed surface layer of thickness of  $\approx 0.5 \mu\text{m}$  free of Al and V. This layer after post-irradiation vacuum has nanocrystalline structure with increased hardness. Such structure should possess the increased corrosion resistance due to its homogeneity and more uniform distribution of impurities along the grain boundaries. The deve-

loped method has the great potential for biomedical applications. It can be used for surface finish of surgical implants made of Ti-6Al-4V to enhance their corrosion behavior and biocompatibility. The increase in the thickness of Zr-alloyed layer up to  $5\div 10 \mu\text{m}$ , which is acceptable for many implants, can be achieved by multiple alternating deposition of the Zr/Ti nanolayers and its pulsed melting. This approach can consider as alternative to new bulk surgical  $\beta$ -Ti alloys (Ti-13Nb-13Zr, Ti-15Zr-4Nb-4Ta, etc.), where Al and V are substituted by non-toxic alloying metals (Zr, Nb, Ta, etc.).

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