

STRUCTURE of Ti-Ta ALLOYS FABRICATED BY  
ELECTRON-BEAM SURFACE ALLOYING

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Received on April 28, 2022

Presented by P. Atanassov, Member of BAS, on June 21, 2022

Abstract

In the present study, Ta coatings with a thickness of 1.7 and 4.2  $\mu\text{m}$  were deposited on Ti samples through reactive magnetron sputtering. The coatings are furthermore treated by a scanning electron beam in order to form the Ti-Ta surface alloy. A change in the phase composition of the Ti-Ta alloy was observed through X-ray diffraction (XRD). The microstructure and the chemical composition of the samples were studied via scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The results indicate that in both cases the thickness of the alloyed zone remains the same at about 50  $\mu\text{m}$ . The concentration of Ta in the alloyed zone increases with the increase in thickness of the pre-applied coating. The sample with the 1.7  $\mu\text{m}$  Ta coating has a single-phase hexagonal closed packed structure, corresponding to the  $\alpha$  phase, whilst the sample with the 4.2  $\mu\text{m}$  coating exhibits a biphasic hexagonal closed-packed structure and a body-centred cubic structure, corresponding to  $\alpha'$  martensitic and  $\beta$  phases.

**Key words:** Ti-Ta alloys, electron-beam surface alloying, phase composition, microstructure

**Introduction.** In recent years the increasing number of bone fractures and bone diseases has led to the increasing application of bio-engineered implants. In

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This research was funded by the Bulgarian National Science Fund; Grant Number KP-06-M37/5.

DOI:10.7546/CRABS.2022.09.04

order to increase the spectrum of application a vast amount of materials have been and are still continuously studied. The biomaterials used for the design and manufacturing of medical implants have to possess certain properties such as a low Young's modulus, similar to that of human bones, high friction resistance, low cytotoxicity, and high bio-integration, high corrosion resistance, and high tensile strength [1]. It has been found that Ti has excellent biocompatibility due to its low cytotoxicity and excellent bone integration [2–4]. It is one of the most commonly used materials in bio-medicine.

Nevertheless certain obstructions in the application of Ti have been observed such as poor shear strength and poor friction resistance. In addition, despite the low Young's modulus of Ti (about 100 GPa), its value is still significantly higher than that of human bones (9–28 GPa [5]). This could lead to the rejection of the implant. Many different methods for overcoming those issues have been proposed. Such a method is the introduction of Ti alloys [6,7]. The fabrication of Ti-Ta surface alloys is highly applicable since they possess lower Young's modulus than pure Ti, closer to that of human bone, have high wear resistance, great tensile strength, and are completely non-toxic [8]. The effect of different contents of Ta in the Ti-Ta alloys has been widely studied [9–12].

The techniques based on the treatment and alloying by electron beam gain popularity due to the short process time, the possibility of precise process control, etc. [13]. The authors of [14] studied the possibilities of formation of Ti-Ta coatings on NiTi substrates by electron-beam cladding at atmospheric pressure. They found that the tensile strength and resistance to corrosion strongly depend on the amount of the Ta element. Similarly, the improvement of the mechanical behaviour of NiTi substrates via the fabrication of Ti-Ta coatings has been reported by MEISNER et al. [15]. Our previous study [16] was based on investigations of the possibility of the formation of Ti-Ta alloys via an electron-beam method in a high vacuum environment, and the corresponding influence of the technological conditions on the structure and properties of the alloyed zone. However, the effect of the Ta coating's thickness has yet to be evaluated.

The purpose of this research is the fabrication of Ti-Ta surface alloys via a scanning electron beam and to study the effect of different Ta concentrations on the structure of the alloyed zone. The usability in the field of bio-engineering of the formed intermetallic compound is debated and conclusions are made accordingly.

**Experimental part.** In order to obtain the Ti-Ta alloy a two-step experimental process is employed. Ta thin layers have been applied on  $\alpha$ -Ti substrates via magnetron sputtering in a high vacuum environment. The working pressure was set to  $8 \times 10^{-2}$  Pa, the discharge current was 1 A, and the discharge voltage was 480 V. The time of the Ta film's deposition was 30 min and 90 min, corresponding to a layer thickness of 1.7  $\mu\text{m}$  (sample 1) and 4.2  $\mu\text{m}$  (sample 2), respectively. The surface alloying is conducted via a scanning electron beam system. The electron beam's power was set to 1500 W with a scanning frequency of

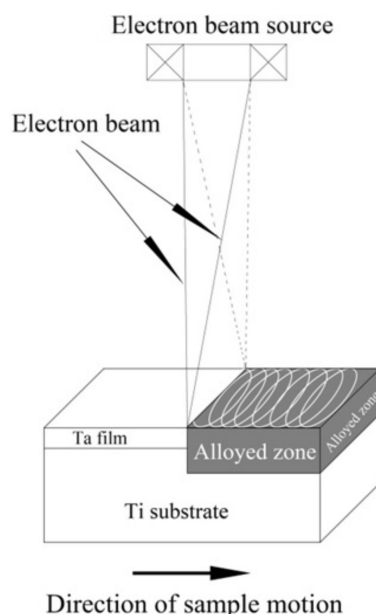


Fig. 1. A scheme of the electron-beam alloying process of titanium substrate with tantalum film

200 Hz. The velocity of the samples during the alloying was 5 mm/s. A graphical representation of the Ti-Ta alloying process is depicted in Fig. 1.

Information regarding the investigated samples' phase structure was obtained by X-ray diffraction (XRD) using Cu  $K\alpha$  characteristic radiation (1.54 Å). The diffraction peaks were investigated from 20 to 80°, with a step of 0.1°. The counting time of each step was 10 s.

Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were used in order to examine the microstructure and chemical composition of the samples. During the SEM investigations, back-scattered electrons were used. The accuracy of the EDX measurements is ensured by the P/B ZAF correction factor, the X-ray adsorption correction factor, and the fluorescence correction factor integrated.

**Results and discussion.** Cross-sectional micrographs of samples 1 and 2 (Ti substrate alloyed with a 1.7  $\mu\text{m}$  and 4.2  $\mu\text{m}$  Ta films, respectively) are shown in Fig. 2 (a) and (c). The alloyed zone and the Ti substrate are depicted as A and B, correspondingly. The SEM micrograph of sample 1 indicated that the alloyed zone's thickness is about 50  $\mu\text{m}$  in both cases, indicating no significant difference between the thicknesses of the alloyed zones in both samples. The thickness of the pre-applied Ta coating does not affect the depth of the alloyed zone. Energy-dispersive X-ray spectroscopy method was used to evaluate the

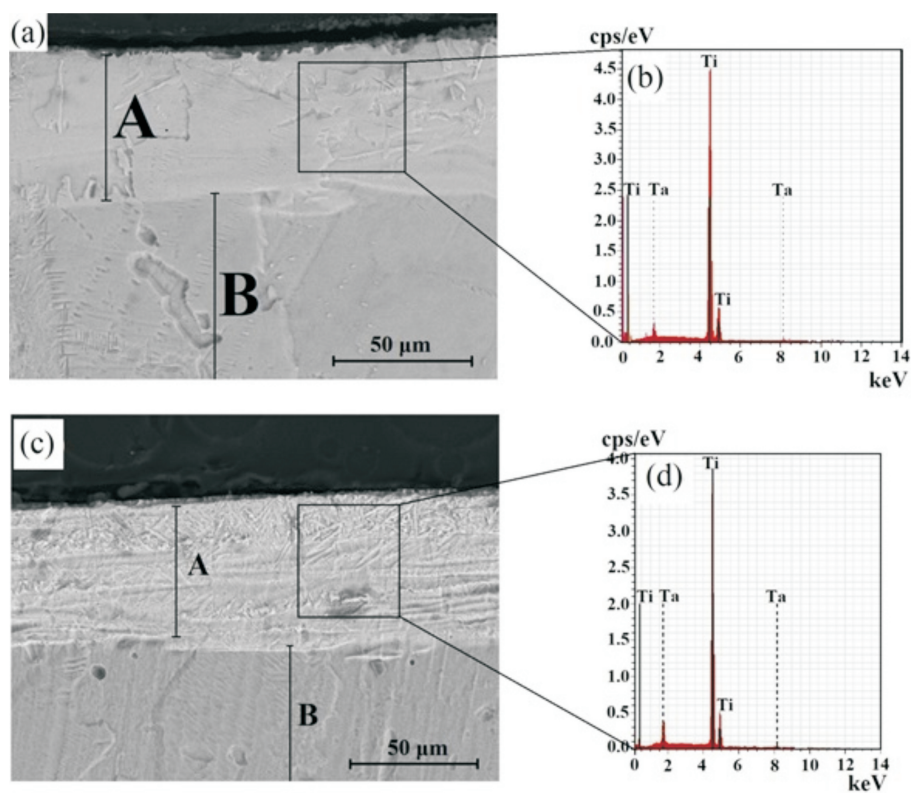


Fig. 2. A cross-sectional SEM micrograph of the (a) sample 1, (b) EDX results of the fabricated surface alloy at sample 1, (c) sample 2, (d) corresponding EDX spectrum taken from the alloyed zone at sample 2

elemental distribution within the alloyed zones of both samples, and the results are depicted in Fig. 2 (b) and (d). The formed chemical compositions are highly uniform in both cases, without the presence of undissolved particles of Ta or any other types of irregularities. Due to the deposition of a thicker Ta layer on sample 2 a higher concentration (15 %wt) of Ta in the alloyed zone is detected in comparison with sample 1, where the concentration of Ta is found to be 3.5 %wt.

The XRD patterns are registered in a symmetrical Bragg–Brentano (B-B) mode and are shown in Fig. 3 (a) and (b). Sample 1 has a single-phase hexagonal closed-packed structure, corresponding to the structure of the bulk substrate material (i.e.  $\alpha$ -Ti). This indicates that the alloying procedure with a 1.7 μm Ta layer does not lead to a transformation in the phase structure of the titanium substrate. Double phase hexagonal closed-packed (hcp) –  $\alpha'$ martensitic and body-centred cubic (bcc) –  $\beta$  structures have been detected at sample 2. The formation of non-equilibrium phases, such as  $\alpha'$ martensite is due to the large thermal cycling gradient during the fabricating procedure. Usually, such martensitic structures exist in  $\alpha + \beta$  type of alloys. It is known that at the electron-beam surface alloying

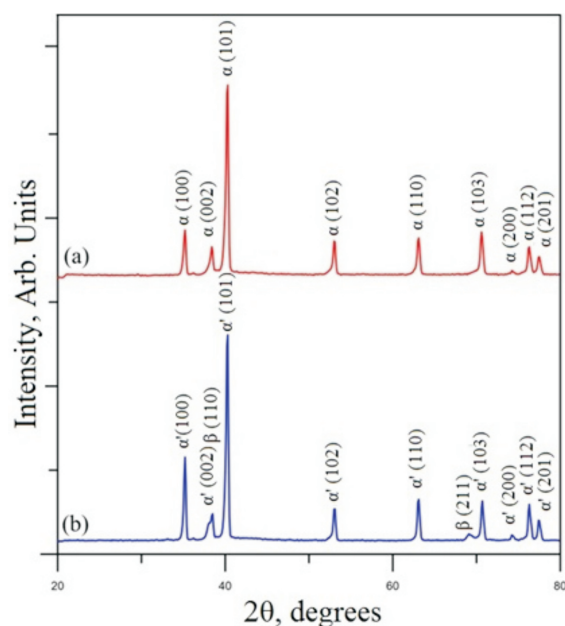


Fig. 3. XRD patterns of the Ti-Ta surface alloys:  
(a) sample 1; (b) sample 2

procedure, the cooling rate is quite high (about  $10^5$  K/s), leading to martensitic transformation [17]. The  $\beta$ -phase is a well-known structure from the Ti-based alloys and is a high-temperature modification of the titanium (known as  $\beta$ -Ti and is stable above  $882.5^\circ\text{C}$  [17]) and is metastable at room temperature. At high temperature its chemical composition could be of pure Ti. However, its existence could not always be related to the high temperature reasons; it could appear at room temperature when some amount of beta-stabilizing elements, such as V, Nb, Ta, etc., is incorporated into the Ti matrix. Also, the formation of such phases again could be attributed to the very high cooling rate of the electron-beam alloying procedure and non-equilibrium nature of this process. In this case, it is in the form of a solid solution between titanium and the  $\beta$ -stabilizing elements (Ta in the present particular case), where the registered concentration of Ta is 15 wt. %. ZHAO et al. [18] have found that no changes in the phase composition of Ti in the Ti-Ta intermetallic compound can be observed when the Ta concentration in the alloyed zone is up to 6 %wt. With the increase of the Ta concentration from 12 to 25 % wt. the amount of the  $\beta$  phase increases, and this is consistent with our results. No peaks corresponding to pure tantalum can be observed, meaning that the deposited Ta films were completely dissolved within the Ti matrix, and form Ti-Ta alloys. All registered diffraction maxima correspond to the formed Ti-Ta surface alloy.

As mentioned previously, Young's modulus of the implant material should be low and comparable with the values of the discussed mechanical characteristic of the human bones. The authors of [19] demonstrated that the  $\beta$ -Ti phase has the lowest Young's modulus amongst the Ti-based phases. This makes the  $\beta$ -Ti highly bio-compatible and an excellent choice for the manufacturing of bio-implants. However, Young's modulus can be influenced not only by the phase composition of the material but also by the bonding forces, which can be affected by the distances between the atoms within the crystal lattice. Here, the atomic distance was assessed by the evaluation of the unit-cell volume of the main phase (i.e. the hcp phase), where the calculated value for the sample 1 is  $0.1057 \text{ nm}^3$ , while the unit-cell volume of sample 2 is  $0.1063 \text{ nm}^3$ . The unit-cell volume of sample 2 is higher than that of sample 1. This means that the bonding forces between the atoms are weaker in the case of alloying of Ti with the thicker  $4.2 \text{ }\mu\text{m}$  Ta film. This, together with the presence of the  $\beta$  phase is very important for this material to be introduced for implants manufacturing. According to the authors of [10], the lowest Young's modulus was obtained when the phase composition of the fabricated Ti-Ta alloy was in the form of a single phase structure of  $\beta$ , where the measured value was 67 GPa. Also, the results of the same authors [10] showed that the discussed mechanical characteristic is in the range of 100 GPa to 80 GPa when the phase composition is in the form of single  $\alpha'$  martensite, where the lowest value was measured in the case of the largest unit-cell volume. Similarly, the authors of [16] demonstrated the possibility of fabrication of Ti-Ta surface alloys by electron-beam surface alloying technology using different power of the electron beam. Their results showed that the highest tantalum concentration within the alloy leads to the largest amount of the  $\beta$ -phase and Young's modulus is about 60 GPa. The increase in the beam power led to thicker alloyed zone and lower concentration of Ta, corresponding to lower amount of  $\beta$ -phase. However, the measured Young's modulus was about 60 GPa due to the larger unit-cell volume of the main phase, corresponding to weaker bonding forces between the atoms [16]. This means that the existence of the  $\beta$  phases and weaker atomic bonds correspond to lower Young's modulus of sample 2 than sample 1. The promising implant materials should possess low Young's modulus, which is much closer to that of the human bones. These findings could have significant importance for implant materials manufacturing, as well as their implementation in modern biomedicine.

**Conclusion.** The results presented in this study confirm the potential of the electron beam surface alloying method concerning the formation of Ti-Ta surface alloys. With the increase of the pre-applied Ta coating's thickness the concentration of Ta in the alloyed zone increases, while the treated zone has a constant thickness of about  $50 \text{ }\mu\text{m}$  in all cases. The structure of the sample alloyed with a  $1.7 \text{ }\mu\text{m}$  Ta layer is a single-phase structure of hexagonal closed-packed, corresponding to  $\alpha$  phase. The sample alloyed with a  $4.2 \text{ }\mu\text{m}$  Ta layer exhibits a biphasic structure hexagonal closed-packed and body-centred cubic,

corresponding to  $\alpha'$  martensitic and  $\beta$  phases. Also, the bonding forces between the atoms are weaker in the case of alloying of Ti with the thicker 4.2  $\mu\text{m}$  Ta film. The existence of the  $\beta$  phase and weaker atomic bonds correspond to lower Young's modulus, much closer to that of the human bones, which could open novel applications of these materials.

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