Electron-beam surface alloying of Ti substrates with Ta films

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Abstract. We report electron-beam surface alloying of Ti substrates with Ta. The Ti substrates were covered by a Ta coating with a thickness of 2 μm. The samples were alloyed by a scanning electron beam, with the beam deflection geometry in the shape of the infinity symbol (\(\infty\)). Two experiments were implemented, where the width of the infinity symbol was kept constant at 8 mm, while the height was 8 mm for the first experiment and 4 mm for the second one. The phase composition of the specimens produced was studied by X-ray diffraction (XRD). The microstructure and chemical composition were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively. The results showed that the phase composition consisted of a double phase structure of \(\alpha'\) martensitic and of beta phases. Some amount of pure Ta remained in the alloyed layer produced by the first experiment. Also, the distribution of the alloying element into the substrate was significantly more homogeneous in the case of the second one.

1. Introduction

Nowadays, titanium and its alloys are widely used for the manufacturing of implants, artificial joints and in other branches of modern medicine due to titanium’s biocompatibility, excellent corrosion resistance, and static and fatigue strength [1-3]. However, some limitations due to the poor wear resistance should be mentioned. Since the surface of the discussed materials is exposed during the implants use, the discussed limitations can be overcome by an appropriate surface-treatment technology.

A number of methods for surface modification exist, such as thin-film deposition [4], surface treatment and alloying by high-energy fluxes (i.e. electron [5, 6] and laser [7] beams), etc. Presently, alloying by a flux of accelerated electrons is widely studied due to the shorter process time and the possibility of controlling precisely the technological conditions. In this technology, the electrons interact with the surface of the alloyed material where the technological conditions are so optimized as to reach its melting temperature and form a melt pool. The alloying elements are introduced into the molten material; after its solidification, a surface alloy is formed with significantly improved functional properties in comparison with the initial material [8].

Currently, the formation of surface alloys and coatings of the Ti-Ta system is considered as very promising for various biomedical applications due to the improved corrosion resistance and biocompatibility [9, 10]. The Ti-Ta materials are known as a non-toxic beta alloy, which exhibits high specific strengths, toughness, and fracture resistance. Furthermore, this material exhibits a high-temperature shape memory effect, while its hardness and Young’s modulus are much closer to that of
human bones. The authors of [11] have demonstrated the formation of Ti-Ta coatings on TiNi substrates by pulsed electron-beam melting of the film/substrate system. The results showed that the coatings exhibited better elastoplastic properties in comparison with the substrate. It was found that in the depth the hardness and depth recovery ratio decrease, while the plasticity increases. Golkovski et al. [12] have studied the possibilities of the formation of Ti-Ta coatings on VT1 titanium substrates by atmospheric electron-beam surface alloying. The results showed the formation of surface layers with thicknesses of about 2 – 2.5 μm and an α(α’) + β structure. An increase in the Ta content led to a significant increase in the tensile strength and the corrosion resistance. However, the capabilities of the electron-beam surface alloying of pure Ti substrates with Ta films, as well as the influence of the process conditions on the structure of the Ti-Ta coatings, are currently less well investigated. Therefore, this study aims to investigate the possibilities of forming Ti-Ta coatings by alloying pure titanium substrates with a Ta film via electron-beam surface alloying with a continuously scanned electron beam. Further, the influence is also discussed of the alloying process conditions defined by the geometry of the electron-beam deflection on the structure of the produced layer.

2. Experimental part
In our study, Ti-Ta surface alloys were produced on commercially pure Ti substrates by using DC magnetron sputtering to deposit Ta films with a thickness of about 2 μm. The deposition process took place in Ar atmosphere with a working pressure of 8×10⁻² Pa. The discharge voltage was 440 V, the discharge current was 1 A, and the deposition time was 1 hour. The samples were then electron-beam surface alloyed in an Evobeam Cube electron-beam unit. A scheme of the electron beam alloying is presented in fig. 1 (a). During the alloying process, the accelerating voltage was 60 kV, the electron beam current was 25 mA, the speed of the specimen motion was 5 mm/s, and the electron-beam scanning frequency was 1 kHz. It should be noted that the electron-beam equipment used for the experiments allows one to implement a number of beam deflection geometries, such as line, circle, ellipse, parable, infinity, etc. For the needs of these experiments, a continuously scanned electron beam was used, where the scanning figure had the form of the infinity symbol (fig. 1 b). In this case, a significant overlap of the beam trajectory takes place, leading to an increase in the melt pool lifetime. The dimension of the scanning figure was varied to realize two experiments, namely, the width of the infinity symbol was kept constant at 8 mm, while the height was chosen to be 8 mm for the first experiment and 4 mm for the second one (Figure 2).

![Figure 1](image_url)  
*Figure 1.* Electron-beam surface alloying of a Ti substrate with a Ta film a) a scheme of the process; b) electron-beam scanning figure.
Figure 2. Dimensions of the electron-beam scanning figure a) for the first experiment; b) for the second experiment.

The phase composition of the samples was characterized by X-ray diffraction (XRD) with CuKα (1.54 Å) radiation. The experiments were carried out in a symmetrical Bragg-Brentano (B-B) mode at a 2θ scale within the range from 30° to 75°, a step of 0.1° and a counting time of 10 sec per step.

The layers produced were studied by means of a scanning electron microscope (SEM) equipped with an EDX detector, which integrates a true standardless analysis with P/B ZAF corrections (Z being the atomic number correction factor; A, the X-ray absorption correction factor; F, the fluorescence correction factor). During the experiments, back-scattered electrons were used.

3. Results and discussion

Fig. 3 presents the experimentally obtained XRD results. The phase composition of the obtained surface alloys consists of a double phase structure of hexagonal close-packed (hcp) α’ martensitic and of body-centered cubic (bcc) beta phases. Additionally, the diffraction pattern for the first experiment exhibits peaks of pure Ta, meaning that some amount of the tantalum film has not been dissolved into the Ti matrix. The diffraction peaks of the beta phase and Ta are almost overlapped because both compounds have the same crystal structure (body-centered cubic bcc) and very similar lattice parameters [13]. The identification of the discussed phase was done according to ICDD (International Center for Diffraction Data) database, for hcp α’ (ICDD PDF # 44–1294); for bcc β (ICDD PDF # 44–1288); for Ta (ICDD PDF # 04–0788). The formation of non-equilibrium phases such as the metastable martensitic phase in the system of Ti-Ta is due to the very high cooling rate during electron-beam surface alloying [14]. During the alloying process, the temperature reaches the values of the transformation from α to β. The subsequent transformation from beta to alpha is difficult due to the very high cooling rate [15]. At the same time, the Ti-Ta materials can be retained in a metastable state at room temperature due to the beta stabilizing effect of the tantalum. The authors of [16] have studied the structure and properties of Ti-Ta alloys formed by selective laser melting, and their results showed that the phase composition of Ti-Ta consists of a double-phase structure of α’ martensitic and beta phases. Also, the same authors [16] showed that the amount of β phase rises with an increase in the Ta content. These statements are in agreement with our results obtained by XRD pointing to the formation of the double-phase structure of hcp α’ martensitic and bcc beta phases.
Figure 3. X-ray diffraction pattern of Ti-Ta surface alloys a) first experiment; b) second experiment

Figure 4 a) and b) presents a cross-sectional SEM image of the Ti-Ta surface alloy formed by the first and second experiment, respectively. The chemical composition of the specimen was studied by EDX at several points (for the surface alloy obtained in the first experiment), and areas (for the surface alloy obtained in the second experiment), which are marked in figure 4; the results are summarized in Table 1. Figure 4 (a) demonstrates that the structure of the surface alloy produced in the first experiment is strongly inhomogeneous, with the thickness varying from about 8 μm to 15 μm. The results show that a significant amount of undissolved Ta is present on the top of the formed layer. However, in the deeper parts, the structure contains Ti-Ta. The results obtained by SEM/EDX are in agreement with those from the XRD investigations pointing to the formation of a Ti-Ta surface alloy with a significant amount of undissolved Ta. The structure of the specimen obtained via the second experiment is shown in figure 4 b). The alloyed zone is marked as zone A, while the substrate is indicated as B. It is obvious that the formed layer is much more uniform in comparison with that of the first experiment. The alloying element is distributed significantly more homogeneously into the Ti matrix, and no, or a very small amount of, undissolved Ta fraction is visible. The results for the chemical composition, which are summarized in Table 1, show that a surface alloy in the system of Ti-Ta was successfully formed. It is found that the alloyed layer consists of Ti–18 wt% Ta. Such Ti-Ta alloys are considered promising materials for modern biomedicine [16].

Figure 4. Cross-sectional SEM image of the Ti-Ta surface alloy formed in the a) first experiment and b) second experiment
Table 1. Chemical composition of Ti-Ta surface alloy formed in the first and second experiment

|          | Ti, wt%  | Ta, wt%  |
|----------|----------|----------|
| Point 1  | 9.7±0.4  | 90.3±3.0 |
| Point 2  | 70.5±1.9 | 29.5±1.0 |
| Point 3  | 100.0±2.6| 0        |
| Alloyed zone (A) | 81.5±2.3 | 18.5±0.8 |
| Substrate (B)   | 100±3.5  | 0        |

The results obtained in this study show the possibility of forming Ti-Ta-based surface alloys by means of electron-beam surface alloying of a Ti substrate with a Ta film. The influence was studied of the dimensions of the electron-beam scanning figure (defined by the trajectory of the electron-beam scanning) on the structure of the alloyed layers. During the experiments, the scanning figure was in the form of the infinity symbol (fig.1 b), where a significant overlap of the beam trajectory exists leading to an increase in the lifetime of the melt pool. The dimension of the scanning figure was varied, with the width of the infinity symbol kept constant at 8 mm, while the length was chosen to be 8 mm for the first experiment and 4 mm for the second one (figure 2). It was found that in the second experiment the alloying element is homogeneously distributed within the Ti matrix, without undissolved Ta fractions, in contrast with the results obtained in the first experiment. In the case of a larger scanning figure (first experiment), the heat input is significantly lower in comparison with the other one. This leads to a lower melt pool temperature, and thus, a low miscibility between the alloying element and the substrate [17]. Moreover, the use of a smaller electron-beam scanning figure (second experiment) leads to a much higher heat input and sufficient mass transport for melt homogenization. These statements are completely in agreement with the results of the present study where the smaller electron-beam scanning figure during the alloying process leads to the formation of a much more homogeneous structure of the surface alloy.

4. Conclusions

The results obtained in this study show the possibility of producing Ti-Ta based surface alloys by means of electron-beam surface alloying of a Ti substrate with a Ta film. The influence was studied of the dimensions of electron-beam scanning figure (defined by the trajectory of the electron beam) on the structure of the alloyed layers. During the experiments, the scanning figure was an infinity symbol. The dimension of the scanning figure was varied – the width of the symbol was kept constant at 8 mm, while the length was chosen to be 8 mm for the first experiment and 4 mm for the second one. It was found that the phase composition of the surface alloys produced consists of a double phase structure of α’ martensitic and beta phases, while some amount of pure Ta exists in the alloyed layer obtained in the first experiment. The distribution of the alloying element into the substrate was significantly more homogeneous in the case of the second experiment. The conclusion is drawn that the heat input is of major importance for melt homogenization of the surface alloys formed by selective electron-beam alloying, which can be controlled by the dimension of the electron-beam scanning figure.

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