Phase formation tuning of oxygen-implanted layer on Ti6Al4V and Ti by annealing

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A B S T R A C T

Ti6Al4V and Ti were implanted by oxygen plasma based ion implantation at the pulsed negative voltages of 30 and 50 kV with a constant fluency of 4×10^{17} O/cm². In order to tune phase formation in the oxygen-implanted layer, the implanted samples were treated by subsequent annealing in atmosphere or vacuum for 1 h at the temperatures from 500 to 700 °C, respectively. The annealing mediums such as vacuum or atmosphere have a strong influence on the structure in the implanted layer. The annealing in atmosphere could promote phase formation and transformation. The higher voltage (50 kV) implantation forms directly nanosize rutile in the implanted layer. And the subsequent annealing induces the growth of rutile, but does not lead to anatase phase with increasing temperature. The lower voltage (30 kV) implantation does not lead to rutile, but the annealing can precipitate mixture phases of anatase and rutile in the oxygen-implanted layer at 650 and 550 °C for Ti6Al4V and Ti, respectively. Post implantation annealing contributes a larger increase in surface roughness with increasing temperature.

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1. Introduction

Titanium and titanium alloy are widely used in aerospace and medicine due to its good combination of mechanical, chemical, physical and biocompatibility, with the last one arising from the presence of a thin native oxide layer at the surface [1–3]. However, this material exhibits poor tribological performance. In addition, cell toxicity of aluminum and vanadium may become troublesome in the case of disruption of the thin protective surface oxide layer [4,5]. Therefore, appropriate surface treatments are necessary to improve the alloy’s wear resistance and biocompatibility. Although coatings can improve wear resistance performance and biocompatibility, the bonding strength between coating and titanium substrate needs to improve [6].

Plasma based ion implantation (PBII) is a promising surface modification technique, which has the advantages of non-line-of-sight and batch treatment. It is thus capable of processing large and complex-shaped components [7–10]. Especially, the technique can form the modified layer with excellent adherence to substrate due to there is not sharp interface between the implanted layer and substrate [11]. Some reports have demonstrated the modified layer by oxygen plasma based ion implantation (O₂-PBII) has good resistance wear and biocompatibility [3,6,11–14].

As titanium oxide, rutile has higher hardness and the most stable thermodynamically [15]. Anatase has a good catalytic activity and bioactivity due to more open structure [16]. The implantation is a non-equilibration process, and the phase formation and transformation are different from that of conventional equilibration situation. Therefore, it is worth to reveal phase formation by implantation and following annealing for different applications. Thought some reports have studied the phase formation of oxygen-implanted layer [17–20], there is lack of work on the phase tuning by annealing. In this paper, the effect of annealing conditions on the phase formation was investigated systematically to reveal the phase evolution in the oxygen-implanted layer on Ti and Ti6Al4V.

2. Experimental details

As the substrate materials, industrial pure Ti and Ti6Al4V were used. Prior to implantation, the samples were mechanically grounded and polished to a mirror-finish, and cleaned with ultrasonic bath in acetone medium. The PBII treatment was carried out in a homemade DLHZ-01 installation of Harbin Institute of Technology at a base pressure of 5×10^{-3} Pa and a working pressure of 0.1 Pa with oxygen gas of 99.999% in purity. The oxygen plasma was generated by radio frequency at 400 W. In order to keep a low temperature, the working table was cooled by an oil-cooling system and the implanted temperature was below 180 °C. In the experiment, the pulsed voltages of −30 and −50 kV were applied with a length of 30 μs, frequency of 100 Hz, and the dose was 4×10^{17}O/cm². After oxygen implantation, the subsequent annealing was employed. The selected annealing temperatures are from 500 to 700 °C in vacuum or atmosphere for 1 h.

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Glancing angle XRD was carried out on a Philips X’-Pert with a CuKα-line (λ = 0.154 nm), a fixed incident angle θ = 1°, and stepsize 0.05°. The microstructure was observed by a JEM-2010 high resolution transmission electron microscopy (HRTEM). TEM specimens were prepared through grinding the unimplanted side to less than 50 μm with emery paper, and thinning by chemical polishing on the single side (the implanted side was protected). The surface topography was observed by a DIMENSION 3100 atomic force microscope (AFM), operated in contact mode.

3. Results and discussion

Ion implantation is a non-equilibration process; thus, the phase formation and transformation of the oxygen-implanted layer should be different from the oxide layer on titanium substrate by conventional treatment such as thermal oxidation. Post implantation annealing in vacuum or atmosphere may be having a remarkable influence on phase formation in the oxygen-implanted layer. Fig. 1 shows XRD spectra from the implanted samples after and before annealing in vacuum or atmosphere at 650 °C. The diffraction peaks from anatase and rutile appear for both annealed samples, but the peaks of annealed sample in atmosphere are far stronger than that of annealed sample in vacuum. The results imply that the annealing in atmosphere is easier to promote phase formation. Thus the annealing in atmosphere is a preference to tune phase formation in the present work considering the phase precipitation effect and cost.

Figs. 2 and 3 show XRD spectra from the implanted Ti6Al4V annealed in atmosphere. Oxygen implantation with a higher voltage (50 kV) directly forms rutile in the implanted layer, but lower voltage implantation does not lead to titanium oxide. Subsequent annealing has a diverse influence on phase formation in the oxygen-implanted layer. For the higher voltage implanted sample, rutile peaks become strong and no other oxide phases appear with increasing annealing temperature. However, for the lower voltage implanted sample, the mixture of anatase with rutile forms in the implanted layer after annealing at 650 °C. While the annealing temperature is rising to 700 °C, only rutile exists in the implanted layer. As a reference, the corresponding XRD spectrum (Fig. 3b) shows weak rutile and anatase peaks appear and this related with the formed thin oxide layer. Furthermore, the sample local surfaces have an oxide skin to peel off for the unimplanted sample at 650 °C in atmosphere.

As a higher temperature phase, rutile mostly was transformed from the lower temperature phase of anatase. However, the present work revealed the implantation with a higher voltage (50 kV) directly forms rutile in the implanted layer at a lower implanting temperature. The reasons can be explained as follows. The higher voltage implantation leads to a larger heat peak in the local region of the implanted layer. And the heat peaks make temperature increase in the local region and promote the rutile nuclei and make it grow. The lower voltage implantation does not form rutile in the implanted layer due to lower local temperature, but produces many defects. The defects contribute to the formation of crystal nuclei; thus, the subsequent annealing leads to mixture of anatase and rutile in the implanted layer. With increasing temperature, anatase will transform into rutile; thus only rutile exists in the oxygen-implanted layer after annealing at 700 °C. Higher voltage implantation does not form anatase with increasing temperature. The reason is that higher voltage implantation directly forms rutile in the implanted layer; thus the subsequent annealing make previous rutile grow rather than anatase nuclei form. Additionally, a little TiO and Ti2O3 exist in the implanted layer, and they will transit to TiO2 and contribute to formation of rutile and anatase with the increase of temperature.

Fig. 4 shows TEM micrographs of sample implanted at −30 kV and annealed in atmosphere at 650 °C. After the annealing at 650 °C, many precipitate particles (black particles) appear in the implanted...
Fig. 4. TEM micrograph of Ti6Al4V implanted at −30 kV and annealed in atmosphere at 650 °C. (a) Microstructure of oxygen-implanted layer. (b) Diffraction pattern. (c) Rutile HRTEM image of black particle located in (a). (d) Anatase HRTEM image of black particle located in (a).

Fig. 5. AFM surface morphologies of polished Ti6Al4V substrate (a), Ti6Al4V implanted with −50 kV before (b) and after annealing in atmosphere at 650 °C (c) and 700 °C (d).
layer. In Fig. 4b, there are two kinds of diffraction patterns from rutile and anatase. The above results are in good agreement with that from GXRD spectra. In order to identify the precipitate size, HRTEM was used to observe phase images and they are shown in Fig. 4c and d. From HRTEM image of precipitate particles, the lattice image is observed, and its size is about 30 nm. The interplanar distances of 0.327 and 0.324 nm are consistent with that of rutile (110) and anatase (101), respectively.

AFM surface morphologies were shown in Fig. 5. Polished Ti6Al4V surface has a typical feature with many acute peaks from the polish process. After implantation, sample surface become smooth and roughness Ra decreases from 3.9 nm to 3.6 nm due to the leveling effect of sputtering and re-deposition. By annealing, titanium oxides were formed and grown; thus many salience appears and become high on sample surface with increasing temperature. And detectable sample roughness Ra increases from 3.6 to 14.2 nm for the implanted sample before and after annealing in atmosphere at 700 °C.

Compared to Ti6Al4V, the phase evolution in the oxygen-implanted layer on Ti has a similar trend during annealing from the corresponding GXRD spectra in Figs. 6 and 7. With increasing temperature, rutile diffraction peaks become strong for the higher voltage implanted sample, and the mixture of rutile and anatase could be formed in the oxygen-implanted layer of the lower voltage implanted sample. The diverse is a lower temperature to form titanium oxide for Ti compared with Ti6Al4V. For the lower voltage implanted sample, the mixture of anatase with rutile forms in the implanted layer after annealing at 550 °C. While the annealing temperature is rising to 600 °C, only rutile exists in the implanted layer. Above results show the phase formation and transformation temperature of the oxygen-implanted layer on Ti is far lower than that of Ti6Al4V. The reason is related that the alloy elements of Al and V restrain phase formation and transformation.

4. Conclusions

Annealing was used to tune the phase formation in the oxygen-implanted layer on Ti6Al4V and Ti. The annealing medium such as atmosphere and vacuum has a remarkable influence on the structure in the implanted layer. The annealing in atmosphere could promote phase formation and transformation. The higher voltage (50 kV) implantation forms directly nano-size rutile in the implanted layer. And the subsequent annealing induces the growth of rutile, but does not obtain anatase phase with increasing temperature. The lower voltage (30 kV) implantation does not lead to rutile, but the annealing can precipitate mixture phases of anatase and rutile in the implanted layer at 650 and 550 °C for Ti6Al4V and Ti substrate, respectively. Post implantation annealing contributes a larger increase in surface roughness with increasing temperature.

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