

Effects of applied voltage on the phase constitution and corrosion behaviors of micro-arc Ti6Al4V coating

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Abstract. The in-situ ceramics coating were fabricated by the micro-arc oxidation technology in order to improve the corrosion resistance of Ti6Al4V alloy. The silicate electrolyte system was introduced to reduce the applied voltage of the MAO coating. The influence of applied voltage on phase composition, surface morphology and dynamic polarization behavior was investigated. The addition of applied voltage make the MAO pore bigger and quantity of MAO pore reduced. The introduce of MAO coating on the surface of Ti6Al4V alloy improved corrosion resistant performance.

Introduction

Titanium alloys were very attractive materials for a number of engineering applications due to their low density and high static and dynamic strengths as well as good corrosion resistance. Ti6Al4V alloy, which was mostly used in the aerospace, marine and biomedical industries. Ti6Al4V began to lose its popularity after recognition of toxicity arising from in-vivo release of vanadium present in the composition. Titanium based implants exhibited different trends to some degree when their surface topography and composition were changed by appropriate surface modification techniques^[1-3]. The MAO technology was widely used in aviation and marine industries due to its special technological features and had become an important method to improve the corrosion and wear resistance of light alloys such as Al and Mg, et al. Compared with coating made by traditional anodic oxide methods, the film by MAO was much thicker and harder and attaches to the substrate more firmly. Furthermore, most of the existing literature focused on the structure and composition of ceramic coating^[4,5]. However research on some special electrolytic system were relatively rare. Based on above consideration, we investigated the effect of the applied potential on the phase composition and surface morphologies of the Ti6Al4V MAO coating. The other objective of the present study was to characterize the corrosion behavior of the Ti6Al4V MAO coating in the NaCl solution.

Materials and method

The commercial Ti6Al4V plate was cut into the 10 mm×10 mm×2mm as substrate. The TC4 alloy specimen and the wall of the stainless steel container were used as the anode and cathode, respectively. A solution including Na₂SiO₃, NaOH, KF and EDTA-2Na was applied as basic electrolyte solution with pH value of 11~12. The micro arc oxidation coating deposition process was kept in 10min. The electrolyte temperature was controlled within 25°C~30°C. The additives composed of Na₂SiO₃(25g/L), NaOH(12g/L), KF(4g/L) and EDTA-2Na (4g/L) were mixed into basic electrolyte solution. The above solution were configured to evaluate their effects on the

MAO coating. The voltage was varied from 240V to 360V with the interval of 30V and the specimen was designed as S240, S270, S300, S330 and S360, respectively. The frequency and duty of the DC field were 500 Hz and 10%. Each sample was oxidized for 10 min and then cleaned ultrasonically in acetone and de-ionized water before further analysis. The phases of five group specimens were evaluated by X-ray diffraction using Cu_k radiation, between 15° and 85° with increments of 0.02° . Microstructure of the specimens was observed by a scanning electron microscope (S-4700, Hitachi). The chemical composition of the layer was analyzed with an energy dispersion spectroscope at an acceleration voltage of 300 kV. Surface roughness was measured by a self focusing laser microscope. The corrosion resistances of various specimens were investigated by a potential dynamic polarization technique on an electrochemical workstation. The tests were performed in a NaCl solution at 37°C in a cell with three electrodes, a platinum plate as the counter electrode and a saturated calomel electrode as the reference electrode. The treated Ti6Al4V alloy specimens were used as working electrodes, the sample area exposed being 1cm^2 . Tests were performed at a scanning rate of 0.5mV/s and starting from 100mV below open circuit potential and were stopped when a potential of 1500mV was reached.

Results and discussion

Phase composition of the MAO coating

The phase composition of MAO coating was determined by XRD pattern and the results were depicted in Fig.1. As shown in Fig.1, the TiO_2 MAO coating was composed of rutile and anatase phases. With the increase of the applied voltage, some Ti and diffraction peaks of anatase type TiO_2 disappeared and more diffraction peaks of rutile- TiO_2 emerged. As the applied voltage increased, the intensity of the diffraction peaks of rutile type TiO_2 became stronger and the intensity of the diffraction peaks of anatase type TiO_2 and Ti turned weaker gradually. The diffraction peaks at 36.94° , 53.89° and 55.06° was corresponding respectively to the (103), (105), and (211) planes of anatase type TiO_2 phase.

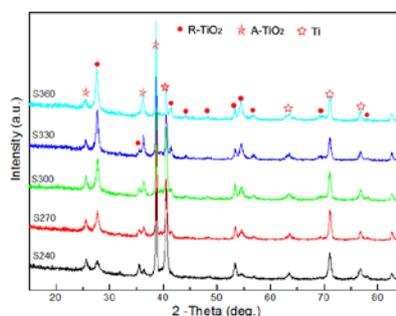


Fig.1 XRD spectra of MAO films of the Ti6Al4V in different applied voltage.

A new diffraction peak of rutile TiO_2 phase was detected when the diffraction peaks was 54.32° , 39.19° and 56.64° was found as rutile TiO_2 phase, which was corresponding to the (211), (200) and (220) plane. The above results indicated that the increase of the applied voltage would lead to crystallization of the MAO TiO_2 coating and the anatase phase of TiO_2 phase was converted into the rutile type TiO_2 phase in the MAO ceramics coatings.

Surface Morphology of oxide MAO coating

The surface morphology of TC4 MAO coating with different applied voltage were listed in Fig.2. The pore dimensions increased and the quantity reduced as applied voltage increased. When applied voltage was less than 270V, the average diameter of the MAO pore was less than $0.4\ \mu\text{m}$. Meanwhile, the pore size was uniform and coating surface was smoother. When applied voltage was beyond 270V, coating surface became coarse. So the smooth degree of micro arc oxidation coating can be controlled by the introduce of appropriate applied voltage. As indicated by the EDX spectra shown in Fig.2f), compared with Ti6Al4V substrate, some additional elements (such as O, Si, Al, Ti and K) were detected in the Ti6Al4V MAO ceramics coating, in which Si and K elements came from the electrolyte and O probably presented in TiO_2 which was formed in the process of micro-arc oxidation. The addition of the KF was responsible for the decline of applied voltage

during the MAO process.

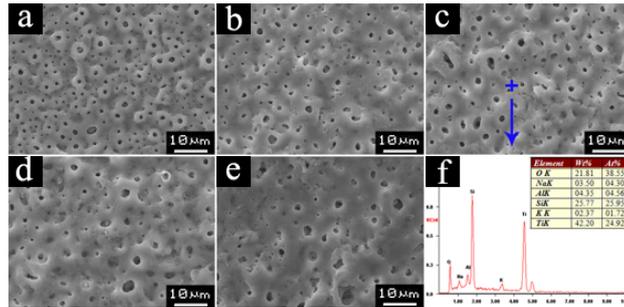


Fig.2 Surface morphologies of Ti6Al4V MAO coating prepared in different applied voltage. a)~e) represented applied voltage 240V, 270V, 300V, 330V and 360V.

The three-dimensional shape of the Ti6Al4V MAO ceramics coating was recited in Fig.3. a), b) and c) represented applied voltage 240V, 300V and 360V. As showed in Fig.3, there was no obvious difference for the depth of MAO pore of Ti6Al4V alloy even if applied voltage was different.

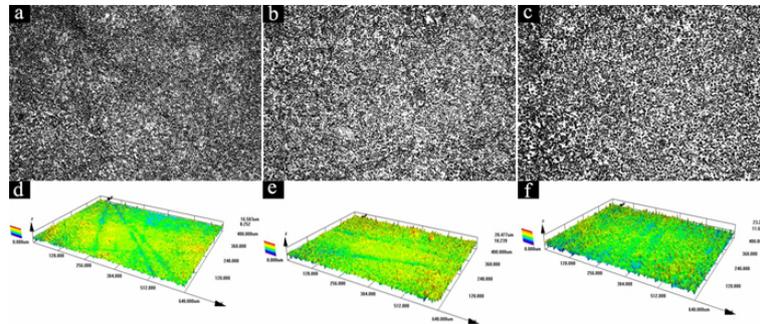


Fig.3 morphologies of Ti6Al4V MAO coating prepared in different applied voltage.

Corrosion resistance of oxide coating

The anodic potentiodynamic polarisation curves of different specimens under different prepared potential was showed in Fig.6. The corrosion potential of all the MAO treated specimens was higher than that of the substrates and corrosion potential of S240, S270, S300, S32 and S360 was about -0.376V, -0.399V, -0.409V, -0.441V and -0.475V. At the same time, the their corrosion current densities were lower than the matrix materials, which of S240, S270, S300, S32 and S360 was closed to 2.7×10^{-5} A, 3.89×10^{-5} A, 4.38×10^{-5} A, 7.06×10^{-5} A and 1.03×10^{-4} A. So it can be said that the corrosion resistance of Ti6Al4V in the NaCl solution had clearly improved after the MAO treatment. The oxide film increased the chemical stability of the specimen and it made corrosion potential shift positively. Therefore, applied voltage was very important for fabricating MAO coating with good corrosion resistance.

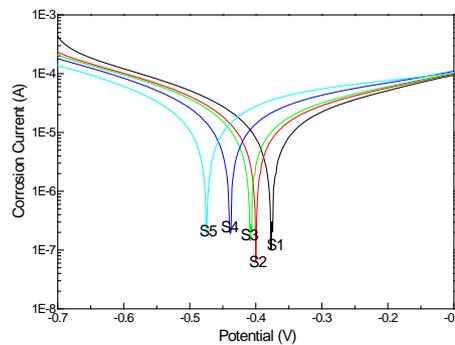


Fig.4 The anodic potentiodynamic polarisation curves of different applied voltage.

Conclusion

In this paper, TiO₂ MAO coating with rough surface were fabricated successfully by micro arc oxidation technology. The effect of the applied voltage on the phase composition, surface

morphology and dynamic polarization behavior of the TiO₂ MAO coating was investigated. The increase of applied voltage led to crystallization of TiO₂ coating and anatase type TiO₂ phase was converted into rutile type TiO₂ phase. The addition of the KF was responsible for the decline of applied voltage during the MAO process. The ceramics coating was mainly consisted of rutile-TiO₂ and anatase-TiO₂ phase.

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