

Electrochemical behavior of Calcium Titanate Coated Ti-6Al-4V Substrate in Artificial Saliva

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Abstract In this study, calcium titanate (CaTiO_3) gel was prepared by mixing calcium nitrate and titanium isopropoxide in 2-methoxy-ethanol. CaTiO_3 gel was single-layer coated on Ti-6Al-4V using a sol-gel dip-coating technique. The coating was calcined at 750°C in air by utilizing a very slow heating rate of $2^\circ\text{C}/\text{min}$. The crystalline phases of the coating were characterized by x-ray diffraction using a slow scan rate of $1^\circ/\text{min}$. The morphology of the coating was analyzed by scanning electron microscopy. The corrosion behavior of Ti-6Al-4V samples coated with CaTiO_3 films were tested in an artificial saliva solution by potentiodynamic polarization and were quantified by the Tafel extrapolation method. The electrochemical parameters showed a considerable increase in the corrosion resistance for the CaTiO_3 -coated Ti-6Al-4V samples compared to bare substrates.

Key words CaTiO_3 , Ti-6Al-4V, artificial saliva, corrosion resistance.

1. Introduction

Bone injuries and failures often require the inception of implant biomaterials. Research in this area is receiving increasing attention worldwide. A wide variety of artificial bone materials, such as metals, polymeric materials, composites and ceramics, are being explored to replace diseased bones^{1,2,3}. In particular, metallic implant materials, e.g. titanium (Ti) and Ti alloys (e.g. Ti-6Al-4V) are widely used as orthopaedic and dental implant materials. Ti-6Al-4V (TAV) is preferred load-bearing implant material due to their relatively low modulus, excellent strength-to-weight ratio, good fracture toughness, and superior biocompatibility and corrosion resistance.⁴ It has been demonstrated that TAV are well accepted by human tissue compared to other metal materials.⁵ However toxic release of ions like Al and V into body fluids over the period of time has caused serious concerns.⁶ It is quite well known that by employing biocompatible coatings to the implants, it is possible to exploit wide range mechanical and biological properties and thereby enhance implant's interaction with the surrounding tissues. Recently calcium titanate (CaTiO_3) thin films on metallic implants have received great attention in the biomedical field because of their excellent osteoconductive properties. In vitro studies have shown that

CaTiO_3 (CTO) significantly improves the osteoblast adhesion and proliferation.⁷ Soaking of CTO coated substrates in simulated body fluid (SBF) has also shown increase in rate of formation of HA on the substrate.⁸ However there is not much reported study on the corrosion behavior of CTO coatings on the metal substrate, which is a key to any implant fabrication. The present work focuses on the corrosion characteristics of the CTO coatings deposited on TAV surfaces by sol-gel route. Potentiodynamic polarization method was used to compare the corrosion behavior of both CTO coated and bare samples in artificial saliva solution at 37°C . The coated samples showed significant improvement in the corrosion resistance compared to its bare counterparts.

2. Experimental Procedure

The CTO sol was synthesized by mixing $\text{Ca}(\text{NO}_3)_2$ (98%, Oriental Chemicals, Korea) and Ti-isopropoxide (Oriental Chemicals, Korea) in 2-methoxyethanol, where $\text{Ca}/\text{Ti} = 1 : 1$ ratio and stirred at room temperature.⁹ TAV alloy (Hyundai Titanium, Korea) was cut into thin discs (20 mm diameter and 2 mm thickness) and discs were micropolished (using $1\ \mu\text{m}$ alundum powder). Two sets of samples were prepared: a) Bare (micro-polished) disc and b) coated (CTO). The single dip-coating (withdrawal rate of $2\ \text{mm}/\text{min}$) of CTO was applied on to bare samples

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and calcined at 750°C in air for 30 min, employing a slow heating and cooling rate of 2°C/min. These samples were designated as CTO-coated samples. The electrolyte used for the study was artificial saliva having a composition mentioned elsewhere in literature.¹⁰⁾ Freshly prepared solution was used for each test. A three-electrode set-up¹¹⁾ with working electrode, a saturated standard calomel reference electrode (SCE) and platinum counter electrode connected to a potentiostat (Wenking model LB 81) interface to a computer. As working electrode a teflon standard case was used to hold the specimens which had an open polished area of 196 mm² exposed to the solution. The potentiostatic technique¹²⁾ was used for gaining the current density versus potential plots. A constant open circuit potential was maintained between the sample and the reference electrode for 30 min. The polarization tests were repeated thrice for each specimen (micropolished before each test). The corrosion rate was estimated with the following equation as mentioned in literature elsewhere¹¹⁾

$$\text{Corrosion rate (mpy)} = 0.13 \times i_{\text{corr}} \times \text{EW}/d \quad (1)$$

where mpy is mils per year, EW is an equivalent weight i.e. 11.975 g, d is the density i.e. 4.51 (g/cm³) of titanium metal, and i_{corr} is a corrosion current density ($\mu\text{A}/\text{cm}^2$), obtained graphically by intersecting point of the cathodic Tafel and the anodic Tafel slope. X-ray diffractometry (XRD) (under slow scan rate of 1°/min) and scanning electron microscopy (SEM) were used to analyze the microstructure and phases present.

3. Results and Discussion

Fig 1a. shows the SEM image of the CTO coated sample. The CTO coating showed dense uniform layer on the substrate with no cracks. Slow heating and cooling rate ensured that no thermal stresses were induced in the

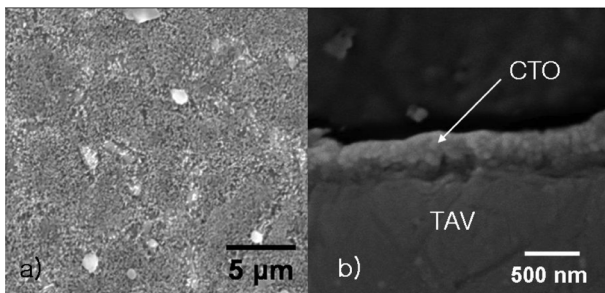


Fig. 1. SEM image of CTO coating processed at 750°C on TAV substrate.

sample which prevented the formation of cracks. Fig 1b. shows the cross-sectional image of the CTO coated TAV. The coating thickness was found to be ~500 nm. The X-ray diffraction patterns of the bare and CTO coated samples are shown in Fig. 2. The XRD examination of the structure showed that the CTO coating exhibiting crystalline structure at 750°C.

Fig. 3 indicates the OCP–time curves. The OCP of the bare sample exhibited negative values and reached a potential of 124 mV after 20 min compare to coated samples which showed more noble OCP of +252 mV. In general, the samples showing more positive corrosion potential tend to be noble compare to negative value ones. The tendency of the bare sample to move towards the negative values could be due to the dissolution of weak TiO₂ layer that occur at the metal surface. The OCP for the coated sample indicating relatively higher values in positive direction shows the protective nature of the coatings on TAV specimens.

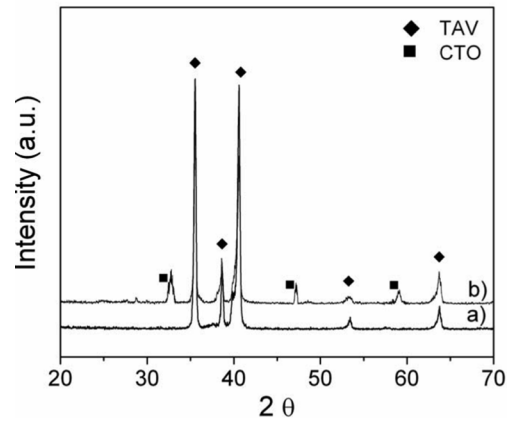


Fig. 2. XRD analysis of a) bare TAV substrate b) CTO coating layer on TAV processed at 750°C.

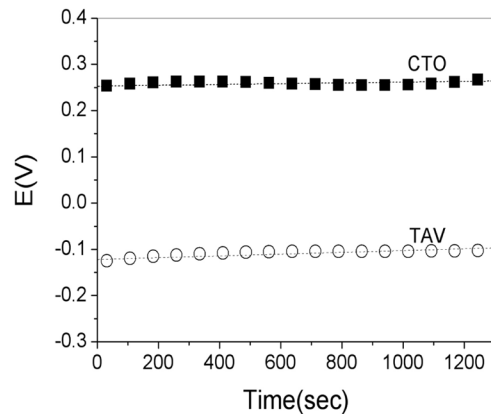


Fig. 3. Profile showing OCP Vs Time for bare TAV and CTO coated TAV.

Fig. 4 presents the Tafel plot for coated and bare samples in artificial saliva at 37°C. Both specimens showed an active to passive transition behavior. These curves showed qualitatively similar behavior but with different values of their electrochemical data (Table 2).

It was also observed that the corrosion rate (in terms of i_{corr} and mpy) of coated sample was much lower than that of bare ones. The higher values of i_{corr} in TAV samples indicate the susceptibility of the bare alloy towards corrosion on immersion in artificial saliva. The increased susceptibility towards corrosion attack of the bare surface could be due to the thinning of the passive film and from intergranular galvanic corrosion arising between grain boundaries of dissimilar metals in the alloy matrix. Where as the coated samples indicate that the coatings prevent the surface from attack of anions with no major dissolution of the coating. This means that the CTO coating impedes the ingress of anions like Cl^- in the electrolyte from attacking the metal-CTO interface. The dissolution of the passive film is controlled by migration of charged species, such as metal cations (outward) and/or oxygen anions (inward) or, more likely, their vacancies. In this case, the electrical resistance of the CTO film may be regarded as a direct measure of the corrosion resistance, and the current density is an important parameter for evaluating the rate of titanium release when there is no significant chemical dissolution of the film. Previously it was revealed that a natural passive film on titanium formed in the phosphate buffered saline (PBS) solution exhibits a

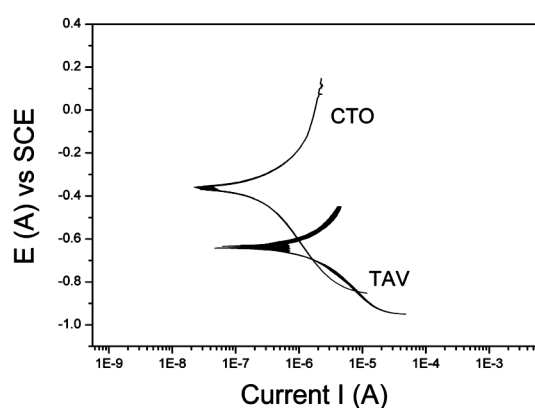


Fig. 4. Tafel plot for bare TAV and CTO coated TAV.

Table 2. Corrosion Properties of bare TAV and CTO coated TAV.

Sample	E(mV)	E_{corr} (mV)	I_{corr} (mA)	Corrosion rate (mpy)
TAV	-124	-638	30.2	10.42
CTO-TAV	252	-366	0.13	0.04

two-layer feature, with an inner layer resistance of about $5 \text{ M}\Omega\text{cm}^2$ and a negligible outer layer resistance because of the electrolyte filled-in open pores.¹²⁾ From the present electrochemical results it seems that for CTO/TAV, the resistance of the inner layer is higher. The higher resistances of the CTO film imply a higher corrosion resistance compared to that provided by a passive film of TiO_2 on TAV. Natural passive films formed on titanium in different synthetic physiological solutions are only a few (~2-6) nm thick.^{13,14)} For CTO/TAV in the present study, the i_{corr} is very low. This low value indicates that the CTO film on titanium implants may actually prevent titanium release into the biological environments. The charged CTO layer⁷⁾ may exhibit n-type semiconductor behavior. It is known that the donor sites in passive and anodic films are dominated by oxygen vacancies and that the kinetics of titanium corrosion in neutral solutions are controlled by migration of oxygen vacancies across the oxide film. The natural passive oxide film which is only a few nm thick contains a relatively high level of oxygen vacancies. Consequently, corrosion of titanium may occur in aggressive biological environments in the form of either oxide growth, if the oxide is insoluble, or titanium release, if the oxide is partially soluble, as evidenced by several in vivo observations.^{15,16)} On the other hand, the CTO coating applied here is about 500 nm (Fig. 1b) thick and contains a low level of oxygen vacancies. Hence the film is less defective and a very slow mass transport process across the film can be expected. This explains the observed high resistance and low passive current density and predicts a low rate of titanium release and a long-term stability for this material in biological environments.

After corrosion tests, no flaking off of the coatings was seen. These trends for the coated samples indicate that the coatings are stable in immersion. Thus, the results of the above studies indicate that CTO coatings could be a viable alternative for improving the corrosion resistance of TAV as well as the biocompatibility^{7,8)} of implant devices. However future XPS and Raman-spectroscopy will be required to understand exact nature of corrosion that is occurring near the CTO-TAV interface.

4. Conclusion

Thin surface films of calcium have been deposited onto the TAV substrates for biomedical applications. CTO coatings can have a beneficial and desired effect on corrosion behavior of TAV and decrease the corrosion rate significantly. The above results indicate that CTO coatings can be deployed as a viable alternative for improving corrosion resistance of TAV for enhancing the biocompatibility of the implant devices.

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