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ORIGINAL PAPER

Corrosion behavior of TiN and TiN/Ti composite films on Ti6Al4V alloy in Hank's solution

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Abstract Surface films of TiN and TiN/Ti were deposited on Ti6Al4V alloy by arc ion plating (AIP). Open-circuit potential, potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) were employed to investigate the corrosion performance of TiN and TiN/Ti films in Hank's simulated body fluid at 37 °C and pH 7.4. Scanning electron microscopy (SEM) was used to study the surface morphology of the corroded samples after the potentiodynamic polarization tests. The results show that the TiN and the TiN/Ti films can provide effective protection for the Ti6Al4V substrate in Hank's fluid, and the TiN/Ti composite film showed a corrosion resistance superior to that of the TiN film. The outer TiN layer of the composite film mainly acted as an efficient barrier to corrosion during short-term experiments. In contrast to the bare Ti6Al4V, no pitting was observed on the surface of the TiN and TiN/Ti films deposited on the bare alloy after potentiodynamic polarization.

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1 Introduction

Ti6A14V alloy has been widely used as a biomaterial for orthopaedics. For applications in implants, the alloy may encounter problems related to corrosion in body fluid and cells, in which some metallic ions (aluminium and vanadium), may be released into tissue and, even in only small amounts, lead to adverse biological reactions and even to mechanical failure of the implanted device [1, 2]. To solve such problems, deposition of hard and wear-resistant coatings with the desired corrosion resistance and biocompatibility is essential [3–5].

With high hardness and good corrosion resistance, titanium nitride (TiN) thin films and composite TiN/Ti films show great potential as protective coatings for biomedical devices. Several techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD), ion implantation, plasma nitriding etc. have been developed for deposition of TiN films on various metallic and nonmetallic materials. The mechanical performance and the corrosion resistance of TiN films has been studied [6–8], but more research needs to be carried out on the corrosion behavior of arc ion plated (AIP) TiN films on Ti6Al4V alloy. Also, a complete characterization of the corrosion resistance of TiN/Ti composite film on Ti6Al4V alloy in physiological environments has not been reported in the literature. The purpose of this work is to study the corrosion behavior in body fluids of TiN and TiN/Ti composite films deposited by AIP on Ti6Al4V alloy.

2 Experimental details

2.1 Preparation of the specimens

Specimens of 20 mm × 10 mm × 2 mm were machined from Ti6Al4V alloy plate, the chemical composition of which is shown in Table 1. Specimens were polished with SiC paper down to 600 grit, peened with glass balls, then ultrasonically cleaned in alcohol and acetone, successively. Titanium nitride (TiN) films were deposited on Ti6Al4V alloy substrate. In some cases a film of Ti approximately 8 μm in thickness was first deposited on the substrate by AIP, followed by the TiN film, in other cases the TiN film was deposited directly on the substrate. In both cases, before the TiN film was deposited, the surfaces were sputter-cleaned using Ar ion under −400 V bias voltage for 2 min to remove any residual oxide or contaminants on the surfaces, to ensure good adhesion of the deposited films.

The Ti depositing parameters were: argon pressure Par = 0.2 Pa, bias voltage −20 V, substrate temperature $T = 100$ °C. The parameters of the TiN deposition process are summarized in Table 2. Both the deposited TiN film and the TiN/Ti composite film were about 10 μm in thickness.

2.2 Electrochemical examination

The electrochemical measurements were carried out in a three-electrode glass cell containing 230 ml of Hank's balanced salt solution (HBSS) at 37 °C. The chemical composition of Hank's solution is given in Table 3.

The solution was buffered with Trishydroxymetyl aminometane (Trizma) and 0.1 mol L^{-1} hydrochloric acid (HCl) at a physiological pH of 7.4.

The Ti6Al4V alloy specimens without and with deposited films, a large area of Pt screen and a saturated calomel electrode (SCE) were adopted as working electrodes, counter-electrode and reference electrode, respectively.

Both the open circuit potentials (OCP) and the potentiodynamic polarization curves were measured with an EG&G PARC potentiostat (Model 273). The variation of OCP with time was recorded for approximately 2 h at 10 s intervals. The OCP was determined when a test electrode reached steady state after immersion in the electrolyte, which implied the formation of a stable surface oxide scale. The potentiodynamic polarization experiments were carried out after the OCP measurements, at a scan rate of 1 mV s^{-1} from a potential of −250 mV with respect to its free corrosion potential (Ecorr), up to a potential of 3,000 mV. The results were analyzed using Cview2 software.

Table 1 Composition of Ti6Al4V alloy/wt.%

Al	V	Fe	C	N	O	H	Ti
6.2	4.1	0.04	0.01	0.014	0.11	0.001	Rest

The electrochemical impedance spectroscopy measurements were made using a PARC potentiostat (Model 273) connected with a PARC 5210 lock-in amplifier. The range of scan frequency was set from 100 kHz to 10 MHz with perturbation amplitude of 5 mV. The results were analyzed using Zview2 software. Prior to the measurements the samples were exposed to Hank's solution for 0.5, 41 and 184 h, respectively.

2.3 Corrosion morphology

After the potentiodynamic polarization tests, the surface morphology of some selected samples was examined by scanning electron microscopy (XL-30FEG Philips).

3 Results and discussion

3.1 Open-circuit potential measurements

The OCP versus time curves for the Ti6Al4V without and with deposited films are shown in Fig. 1. The OCP of the alloy with films was found more noble (positive) in comparison to the bare Ti6Al4V. This means that the corrosion resistance of the TiN and TiN/Ti films is higher than that of the bare Ti6Al4V substrate. However it was noted that the samples with TiN and TiN/Ti films exhibited different corrosion behavior. The alloy with TiN/Ti composite film showed higher OCP, and hence higher stability in comparison to the ones with TiN film. This suggests that the TiN/Ti film was more compact and more corrosion-resistant than the TiN film.

3.2 Potentiodynamic polarization tests

The potentiodynamic polarization curves for the alloy without and with deposited films in Hank's solution are shown in Fig. 2. The corrosion current density of the films was much lower than that of the bare alloy, which clearly implies that compact films of TiN and TiN/Ti act as effective barriers for corrosive species. Therefore the corrosion resistance of Ti6Al4V alloy was greatly improved.

After potentiodynamic polarization, the TiN and the TiN/Ti films exhibited localized breakdown and rapid repair at all potentials and were never completely destroyed, but the bare Ti6Al4V substrate failed at potentials around 300 mV.

From the polarization curves in Fig. 2, one can calculate the free corrosion potential, the corrosion current density and the polarization resistance as shown in Table 4. The

Table 2 Deposition parameters of TiN

Sample	Total pressure (Pa)	N_2 partial pressure (Pa)	Arc current (A)	Arc voltage (V)	Target–substrate distance (cm)	Deposition time (min)	Negative pulse bias (V)
Ti6Al4V	1	0.8	60	19	20	10	400

Table 3 Chemical composition of Hank's solution

Component	Concentration (g L^{-1})
NaCl	8.00
KCl	0.40
$CaCl \cdot 2H_2O$	0.18
$MgSO_4 \cdot 7H_2O$	0.06
$NaH_2PO_4 \cdot 2H_2O$	0.06
$NaHCO_3$	0.35
KH_2PO_4	0.60
$MgCl_2 \cdot 6H_2O$	0.35
Glucose	1.00

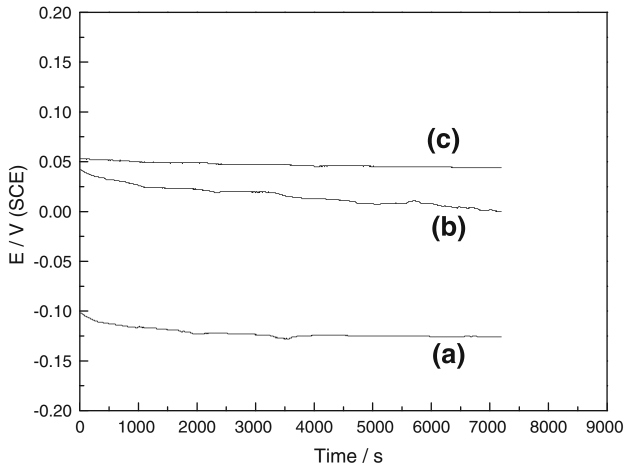

Fig. 1 OCP potential against time for Ti6Al4V without (**a**) and with TiN (**b**) and TiN/Ti (**c**) in Hank's solution at 37 °C and pH 7.4

corrosion potential of the samples with deposited films is more positive than that of the bare Ti6Al4V, indicating again that TiN/Ti6Al4V and TiN/Ti/Ti6Al4V are more stable in Hank's solution. The free corrosion potentials of the samples without and with deposited films in Hank's solution, determined by potentiodynamic polarization tests, (Fig. 2) are significantly different from those shown in Fig. 1. The reason may be that the polarization tests were started at a cathodic potential about 250 mV below the free corrosion potential. The passive film, if any, which existed on the surface of the samples, was probably removed because the negative potential is highly reducing. Furthermore, the polarization curves exhibited the characteristics of a direct transition from the immunity region to the passive region. The corrosion potential in these curves is defined by the intersection of the activation polarization anodic curve related to the formation of the passive film with the activation cathodic curve of oxygen reduction. This intersection takes place at potentials lower than where there is already a well-formed passive film on the surface [9].

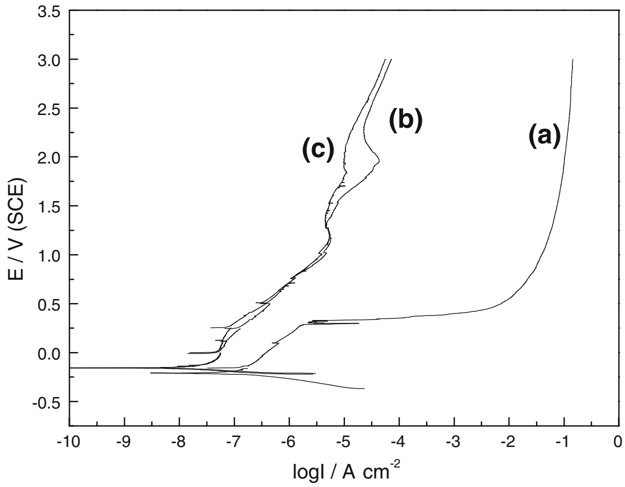

Fig. 2 Potentiodynamic polarization curves of Ti6Al4V without (**a**) and with TiN (**b**) and TiN/Ti (**c**) in Hank's solution at 37 °C and pH 7.4

Corrosion current density, to which the corrosion rate is normally proportional, is an important parameter for evaluating the kinetics of corrosion reactions. The corrosion rates of the samples with TiN and TiN/Ti films, given in Table 4, were respectively approximately 84.2 and 84.9% lower than that of the bare substrate.

It can also be observed that the polarization resistance of both the samples with deposited films was higher than that of the Ti6Al4V alloy. All these results indicate that the TiN and TiN/Ti films provide effective protection to Ti6Al4V alloy in Hank's solution. This may be attributed to the fact

Table 4 Electrochemical parameters obtained from potentiodynamic polarization curves in Fig. 2 for the uncoated and the coated Ti6Al4V in Hank's solution at 37 °C and pH 7.4

Specimens	E_{corr} (V)	I_o (A cm^{-2})	R_p (Ω cm^2)
Ti6Al4V	−0.208	2.19E−7	1.19E5
TiN/Ti6Al4V	−0.154	4.00E−8	6.53E5
TiN/Ti/Ti6Al4V	−0.156	3.29E−8	7.92E5

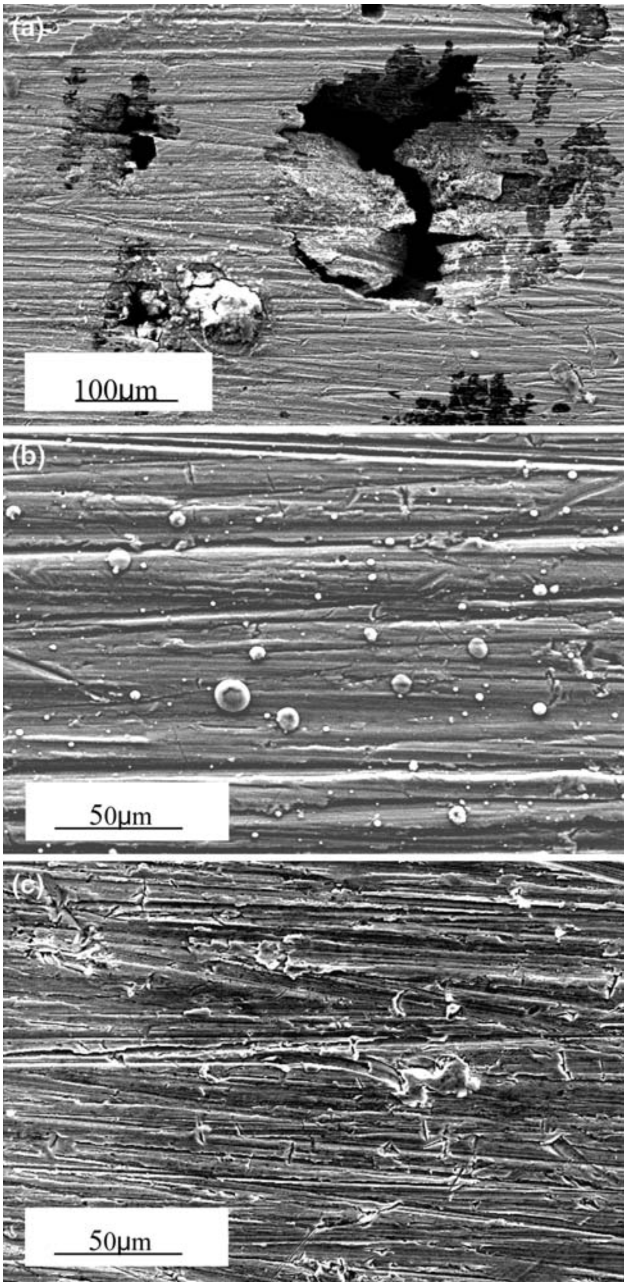

Fig. 3 SEM micrographs of the surface of Ti6Al4V without (**a**) and with TiN (**b**) and TiN/Ti (**c**) in Hank's solution after potentiodynamic polarization

that the protective layers formed on the surface of the alloy via surface treatment are essentially inert and resistant to the environment. The surface of the coated samples consisted of TiN, which possesses excellent corrosion resistance by developing a thin surface layer of TiO_2. This layer forms readily and imparts good corrosion resistance and adherence to the TiN layer. Furthermore, the nitrogen incorporated in TiN was found to combine with oxygen to form oxynitrides. These oxynitrides, along with TiO_2 impede the dissolution of the TiN film, thus enhancing the corrosion resistance [7].

The TiN/Ti film has lower corrosion current density and higher polarization resistance than the TiN film, and hence better corrosion resistance, possibly because it has a different microstructure and composition. The intermediate Ti film may also lower the residual stress of the system. It has been suggested that TiN grain boundaries may act as diffusion paths to the substrate surface for corrosive reagents, which in turn influences the corrosion process. Again, composite films can help in reducing this effect [10]. However, in the present study the enhancement of corrosion resistance by the composite TiN/Ti films compared with TiN is fairly small, which implies that it is mainly the outer TiN film which is acting as an efficient barrier to corrosion, and increasing the resistance to charge transfer at the corrosion interface. When this film is destroyed the Ti film may still give protection.

Figure 3 shows the surface morphology of Ti6Al4V samples without and with deposited films after potentiodynamic polarization tests. Some big local pitting is evident as marked on Fig. 3a, for the bare alloy. The pits generally appear to be irregular in shape and depth. From Fig. 3b and c, the surfaces of the TiN/Ti6Al4V and TiN/Ti/Ti6Al4V are completely inhomogeneous, characterized by grooves and ridges, which are related to their smaller current densities and narrow regions of second active–passive transitions as shown in Fig. 2. However, no evident pitting is observed on the surface, indicating that the TiN and the Ti/TiN films were compact, and could therefore provide good protection to the substrate.

3.3 Electrochemical impedance spectroscopy

In general, the impedance at high frequencies in a Bode plot represents the response of a surface film, thus providing information concerning that film, while that at low frequencies provides information about the process related to the reaction at the substrate/solution interface [6].

The Bode plots, (experimental data and theoretical circuit fitted curves), for samples of TiN/Ti6Al4V and TiN/Ti/Ti6Al4V taken after immersion for 0.5 h (1), 41 h (2) and 184 h (3) in Hank's solution at pH 7.4 and 37 °C are presented in Figs. 4 and 5, respectively. The Bode diagrams can be interpreted by a simple equivalent circuit with a single time constant composed of a resistor and a constant phase element (CPE), as shown in Fig. 6a. However, the resistance values of the barrier layer (R_1) calculated from the model shown in Fig. 6a were widely spread, and thus we turned to a simplified equivalent model, shown in Fig. 6b [3]. The calculated results based on this simplified model are given in Table 5 with fitting errors less than 1.1% for the samples.

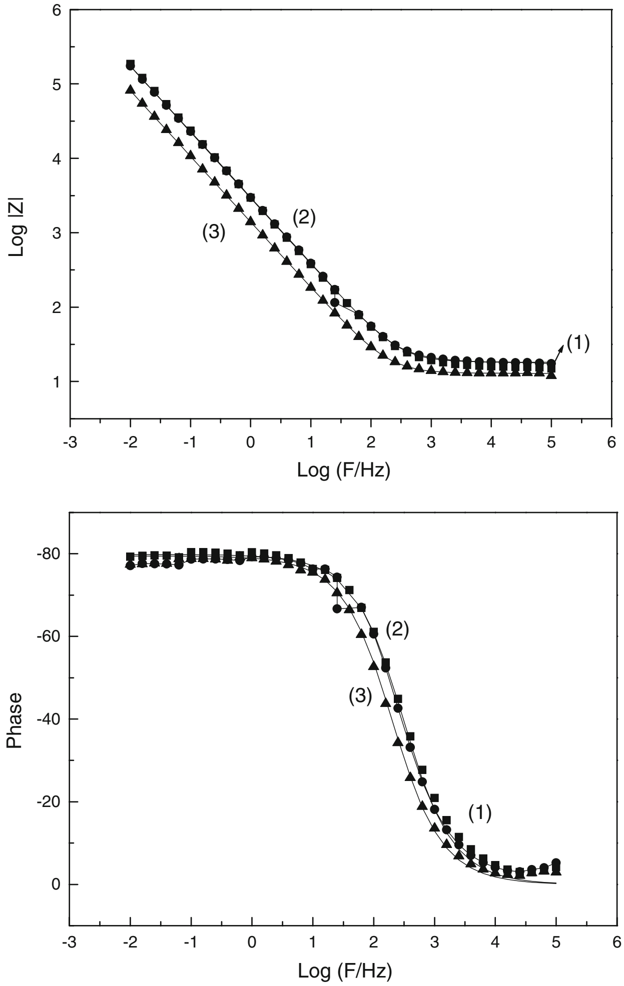

Fig. 4 Bode plots of TiN/Ti6Al4V in Hank's solution for immersion periods of 0.5 h (1), 41 h (2) and 184 h (3) at 37 °C and pH 7.4: (*symbols*) experimental data; (*lines*) model data

A constant phase element (CPE) is usually used instead of a capacitance to account for the non-ideal capacitance response due to the almost complete absence of pure capacitance in the real electrochemical process:

$$Z_{(\mathrm{CPE})} = 1/[Y_0(j\omega)]^n \qquad (1)$$

where Y_0 is a constant and ω is the angular frequency, n is a mathematical expression where $0 \leq n \leq 1$. If $n = 0$ the impedance is entirely resistance, while it is capacitance if $n = 1$. And $0 < n < 1$ represents deviation from the ideal capacitance, which is related to the surface roughness [6].

As seen in Figs. 4 and 5, the wide peak with a maximum near 90° suggests the presence of a compact film on the surface acting as an efficient barrier to corrosion, which increases the resistance to charge transfer at the interface. Figure 4 shows that no significant changes in the impedance and phase shift of the TiN/Ti6Al4V occurred over the entire frequency range during the 41 h test, which suggests that at short exposure time the film was stable. However, the impedance and the phase shift decreased slightly with increasing immersion time from 41 to 184 h, which implies that the TiN film became somewhat less protective and more conductive due to the penetration of solution into the film through small defects/pores after long immersion times. The impedance also decreased in Fig. 5 for times between 0.5 and 41 h. This was followed by a small

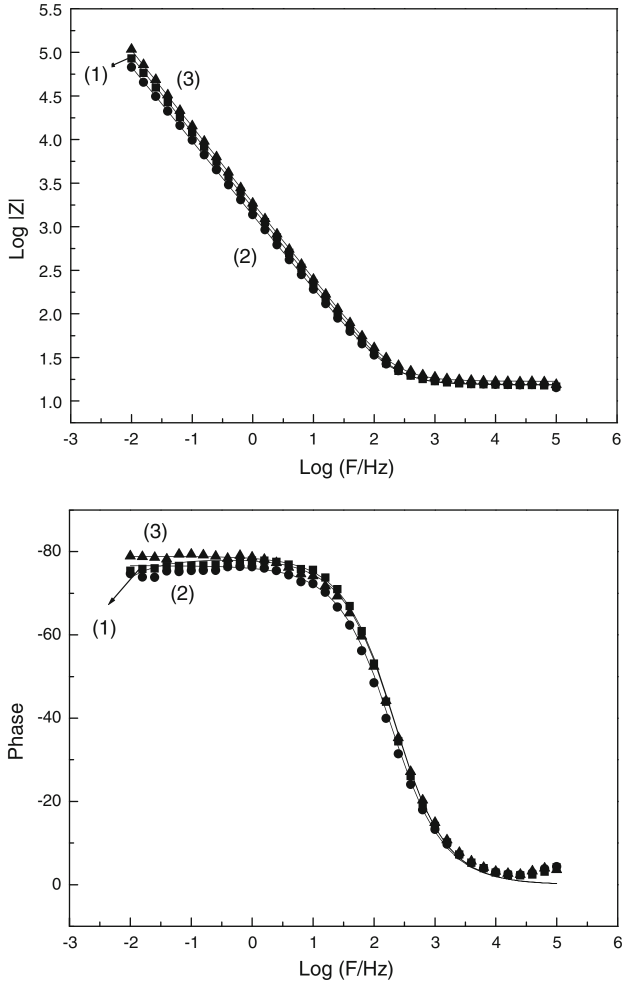

Fig. 5 Bode plots of TiN/Ti/Ti6Al4V samples in Hank's solution for immersion periods of 0.5 h (1), 41 h (2) and 184 h (3) at 37 °C and pH 7.4: (*symbols*) experimental data; (*lines*) model data

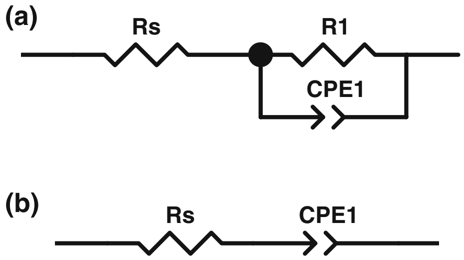

Fig. 6 Equivalent circuits: **a** equivalent circuit for one time constant; **b** simplified version of equivalent circuit (**a**). R_s-solution resistance; R_1-resistance of barrier layer; CPE1-constant-phase element

Table 5 Impedance parameters of TiN/Ti6Al4V and TiN/Ti/Ti6Al4V in Hank's simulated body fluid (equivalent circuit Fig. 6b)

Immersion time (h)	TiN/Ti6Al4V			TiN/Ti/Ti6Al4V		
	R_s (Ω cm^2)	CPE (μF cm^{-2})	n	R_s (Ω cm^2)	CPE (μF cm^{-2})	n
0.5	16.10	65.59	0.89	15.26	123.91	0.87
41	18.16	67.14	0.89	15.51	154.66	0.85
184	12.87	141.87	0.88	16.86	106.57	0.88

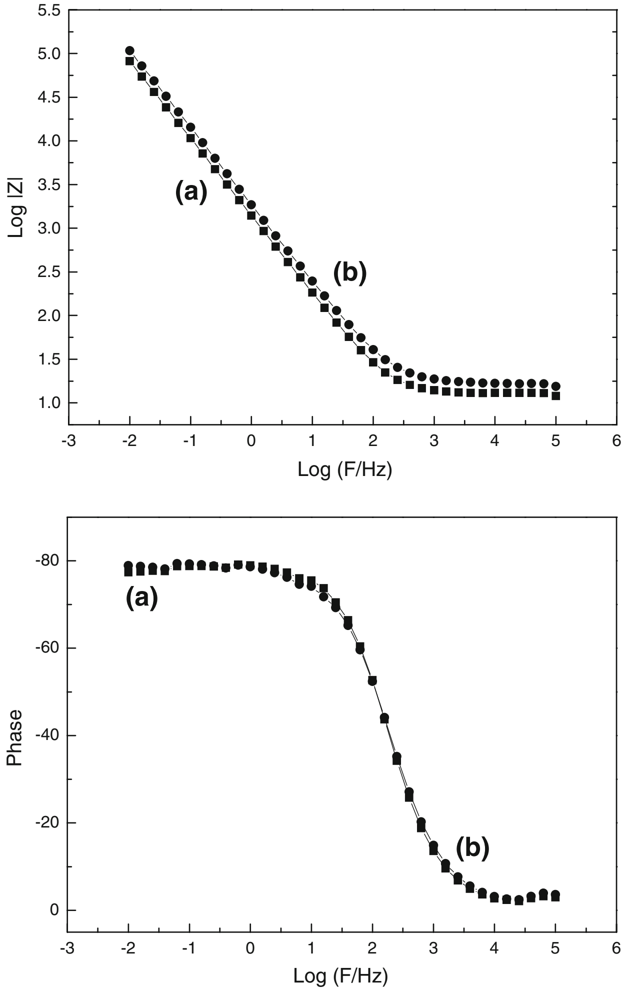

Fig. 7 Bode plots of TiN/Ti6Al4V (**a**) and TiN/Ti/Ti6Al4V (**b**) samples in Hank's solution for an immersion period of 184 h at 37 °C and pH 7.4

increase between 41 and 184 h immersion. This, together with an increase in the phase angle, indicates that corrosion product formed within defects/pores in the film which hindered further inward penetration of electrolyte.

The results for TiN/Ti6Al4V in Table 5 show that the capacitance of the barrier layer increased slightly with increasing exposure time, which again indicates that electrolyte penetrated the TiN film through defects and/or pores in the film. This resulted in an increase in the total area exposed to the electrolyte and lowered the corrosion resistance of the samples. For the TiN/Ti/Ti6Al4V samples, the capacitance of the barrier layer increased after 41 h immersion and then decreased after 184 h. The increase may have been caused by electrolyte penetration into the TiN/Ti film which changed its microstructure. The decrease may have been caused by formation of corrosion product within small defects/pores in the film which hindered further electrolyte penetration. In this study 600 grit SiC papers were used as the final surface preparation for the specimens, therefore, the surface of the samples was a little rough, which has an effect on the value n. The values of n for the samples with TiN and TiN/Ti films in Hank's solution were within the range 0.85–0.90, which indicates a non-ideal capacitance interface.

Figure 7 compares the Bode plots of the TiN/Ti6Al4V and TiN/Ti/Ti6Al4V films after 184 h of immersion in Hank's solution at 37 °C and pH 7.4. The impedance of TiN/Ti/Ti6Al4V was a little higher than that of TiN/Ti6Al4V. This implies that the TiN/Ti film formed on Ti6Al4V is more resistant than the TiN layer to Hank's solution. However, the corrosion resistance of the TiN/Ti film was only marginally greater than that of the TiN film, which may be because the characteristics of the TiN coating dominated for short-term exposures. This is in good agreement with the results of potentiodynamic polarization tests. In summary, few changes are observed for the two kinds of films after 184 h of immersion.

4 Conclusions

The corrosion behavior in Hank's simulated body fluid of Ti6Al4V alloy with TiN and TiN/Ti films prepared by AIP were evaluated and compared with the bare alloy. The alloy with deposited films showed higher corrosion potential and polarization resistance as well as lower corrosion current density than the bare alloy, indicating the two films can provide effective protection for Ti6Al4V. The corrosion resistance of the TiN/Ti film was only slightly superior to that of the TiN film and it is thought that the characteristics of the TiN film dominated in both cases for short-term experiments. No evident pitting was observed on the surface of either of the films after potentiodynamic polarization tests but they were observed on the bare alloy, which means the films can provide effective protection for the substrate. The impedance and phase shift obtained from EIS tests decreased slightly with increasing immersion time, which implies that the protection conferred by the TiN and TiN/Ti films was somewhat reduced after long-term immersion.

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