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Short Communication

Corrosion Resistance of Passive Film Formed on TA10 Dental Implant in Simulated Body Fluid

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The passive behavior of TA10 dental implant was systematacially studied by measuring open circuit potential (OCP), potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Mott-Schottky (MS) curves in simulated body fluid (SBF) for different immersion times. The results showed that the OCP of TA10 dental implant is positively shifted with the extension of immersion time, and stabilizes at about 35 mV_{SCE} after immersing for 1 day; the typical metal passive polarization curve could be observed in SBF with a wide passive potential range, the maintaining passivity and the self-corrosion current density of the TA10 implant decreases with the extension of immersion time and the self-corrosion current density decreased to 0.07 $\mu A/cm^2$ after 3 days of immersion; the EIS impedance modulus of the passive film is about 10^5 $\Omega \cdot cm^2$ order of magnitude at the initial stage of immersion and increases sharply with extension of immersion times and finally stabilizes at about 3×10^6 $\Omega \cdot cm^2$ after 3 days of immersion; the passive film is characterized by n-type semiconductor and the number of defects decreases with the extension of immersion time, a stable corrosion resistant passive film of TA10 implant could be formed after 3 days of immersion.

Keywords: TA10; Dental; Passive film; Implant; EIS

1. INTRODUCTION

Titanium (Ti) and its alloy implants have been widely used in oral prosthesis treatment. Due to its good mechanical properties, excellent corrosion resistance and biocompatibility, Ti and its alloy implants are comprehensively applied as oral implant materials [1-5]. In the dental implant environment, the corrosion resistance of Ti and its alloy implants passive films is the key factor to determine its durability. Due to the appropriate temperature, humidity, pH and other reasons in the oral planting environment, Ti and its alloy implants may be corroded, resulting in the precipitation of Ti and other ions, which would have a certain impact on the implant itself and the body [6-8].

There have been a large number of reports on the corrosion behavior of Ti and other dental materials in oral environment [9-12]. The formation process of passive film is related to many factors [12-15]. However, the formation process and corrosion resistance of Ti implant passive film in planting environment has not been studied in detail. Therefore, TA10 dental prosthesis implant was taken as the research object in this paper, and the passive film formation and its corrosion resistance mechanism in simulated body fluid (SBF) environment were discussed. The results could provide certain reference for the use of Ti and other dental implant materials in clinical.

2. MATERIALS AND METHODS

2.1 Samples and solutions

The dental implant material selected for this project is TA10, the chemical composition is Mo 0.27, Ni 0.74, Ti balance. The TA10 implant was mechanically cut into samples with a dimension of 5 mm×5 mm×3 mm as electrochemical test samples. Before testing, the samples were polished step by step with 200, 400, 600 and 1200 # silicon carbide sandpaper, and then one side of the samples was welded with a copper wire, and the other sides were sealed with epoxy resin, the electrochemical test area was 5 mm×5 mm. Subsequently, the sample was degreased by ultrasound in acetone, rinsed with ethanol, and then blow-dried at room temperature, and stored in a dryer for further experiment and analysis.

The corrosion solution was a simulated body fluid (SBF) [16] with the composition of 0.9 wt.% NaCl which was prepared by analytical pure chemical reagent. A thermostatic water bath was used in the experiment, and the temperature was controlled at 36.5°C.

2.2 Electrochemical measurement

Solartron 1287A potentiostat/current analyzer and Solartron 1255B frequency response analyzer were used for electrochemical testing in SBF at 36.5°C. CorrWare software was used to analyze the passive film corrosion resistance of TA10 dental implant. The standard three-electrode system was selected for the test, the testing sample was the working electrode (the test area was 1 cm^2), saturated calomel was the reference electrode, and platinum plate was the auxiliary electrode.

Electrochemical measurements include measuring open circuit potential (OCP), potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Mott-Schottky (MS) curves. The OCP was used to measure the spontaneity of the corrosion reaction with immersion times, indicating the corrosion tendency, and the test time was 7 days, during which the potential reached a stable state. In the potentiodynamic polarization test, the potential was scanned from -250 mV to +2000 mV (vs OCP) at a scanning rate of 1 mV/s. EIS was carried out within the frequency range of 100 kHz-10 mHz and the disturbance signal amplitude was 10 mV [17]. The function of capacitance *C* with applied potential *E* could be obtained by measuring MS of the sample. The capacitance is measured at a potential interval of 50 mV from -1.2 V_{SCE} to 2.0 V_{SCE} at 1 kHz. All electrochemical measurements were repeated three times to ensure the repeatability, and the representative curves were presented in the results section.

3. RESULTS AND DISCUSSION

3.1. Open circuit potential

Figure 1 shows the OCP of TA10 dental implant immersion in SBF for different times (0 h, 0.5 h, 6 h, 12 h, 1 d, 2 d, 3 d, 4 d, 5 d, 6 d, 7 d), it can be seen that with the extension of immersion time, the OCP moves to the positive direction. In the early stage of immersion, the OCP is relatively negative, at about 0.35 V_{SCE}; the OCP increases sharply within 12 h of immersion, showing that corrosion resistance of passive film is greatly improved; then the increasing of OCP is in a slow moving speed within 12-24 h of immersion and reaches approximately at 30 mV_{SCE} after 1 day of immersion; and then the OCP is stabilized in the following 7 days fluctuating at around 25 mV_{SCE}, this indicates that a stable passive film may have been formed [18]. Based on Sanchez [19], the variation of OCP with time of passive alloys demonstrates the following functional relationship:

$$E = A \cdot \exp(-t/a) + B \cdot \exp(-t/b) + C \qquad (1)$$

where *A*-*C*, *a*, and *b* are all constants. The variation curves were fitted according Eq. (1), and the fitting results are shown in Fig. 1, which show that the relationship in Eq. (1) is suitable and the passive film formation is in accordance with the exponent function law.

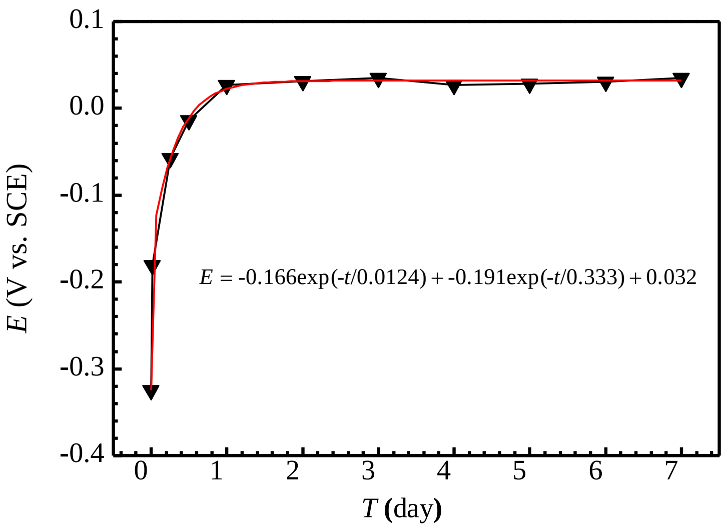

Figure 1. OCP of TA10 dental implant immersion in SBF at 36.5°C for different times (0 h, 0.5 h, 6 h, 12 h, 1 d, 2 d, 3 d, 4 d, 5 d, 6 d, 7 d).

3.2 Polarization curve

The potentiodynamic polarization curves of the TA10 dental implant after immersion in SBF at 36.5°C for different times is shown in Fig. 2. It can be seen that the polarization curves with a wide passive interval (0 V_{SCE} - 1.5 V_{SCE}) show typical passive behavior after different immersion times. With the extension of immersion time, the self-corrosion potential of the TA10 dental implant moves to positive direction and the whole curve moves to the up-left. The maintaining passivity current density and the self-corrosion current density after immersion for 30 min, 1 d and 3 d is 6.31, 3.16, 1.86 μA/cm^2 and 0.22, 0.14, 0.07 μA/cm^2, respectively. This indicates that with the extension of immersion time, the passive film corrosion resistance of TA10 dental implant increases, and a stable passive film could be formed after immersion in SBF. In general, when the self-corrosion current density of the alloy is less than 0.1 μA/cm^2 [20,21], it can be considered that a relatively stable and corrosion-resistant passive film is formed, that is to say after three days immersion a compacted passive film has been formed.

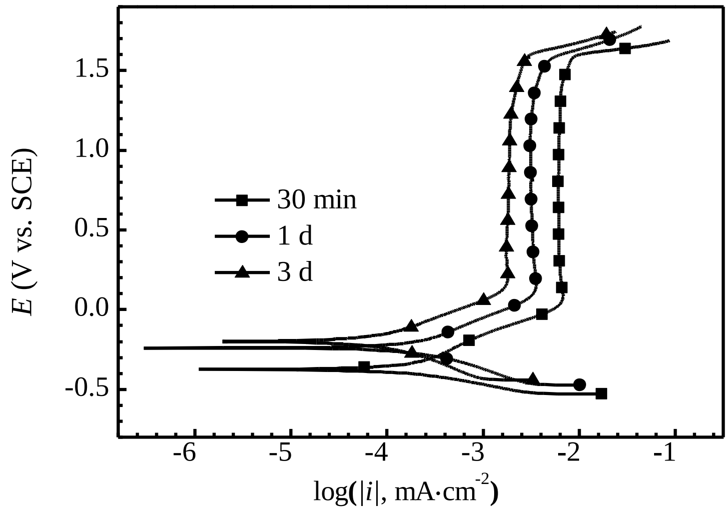

Figure 2. Polarization curves of TA10 dental implant immersion in SBF at 36.5°C for different times (0.5 h, 1 d, 3 d).

3.3 EIS

The EIS of TA10 dental implant immersion in SBF at 36.5°C for different times (0.5 h, 6 h, 12 h, 1 d, 2 d, 3 d, 4 d, 5 d, 6 d, 7 d) is shown in Fig. 3. It can be seen from the Nyquist plots in Fig. 3(a) that one capacitive reactance arc could be observed, with the increasing the immersion time, the radius of arc increase rapidly, indicating the passive film is forming. The impedance modulus |Z| at 0.01Hz is widely used to indicate the corrosion resistance of passive films [22-24]. It can be also seen that the impedance modulus |Z| at 0.01Hz of Bode plots (Fig. 3(b)) gradually increases with the increasing immersion times. The impedance modulus |Z| at 0.01 Hz of TA10 dental implant after immersion in SBF at 36.5°C for different times is shown in Fig. 4, it can be seen that in the early stage of immersion (0.5 h), |Z| is in the range of 2.1×10^5 Ω·cm^2 magnitude; as the extension of immersion time, |Z| increases to 1.4×10^6 Ω·cm^2 after immersion for 1 d; |Z| increases to 3×10^6 Ω·cm^2 after immersion for 3 d and then tends to be stable. Thus, it can be judged that at least 3 days is needed for TA10 dental implant to form a stable passive film in SBF. Those findings are in accordance with OCP and polarization results.

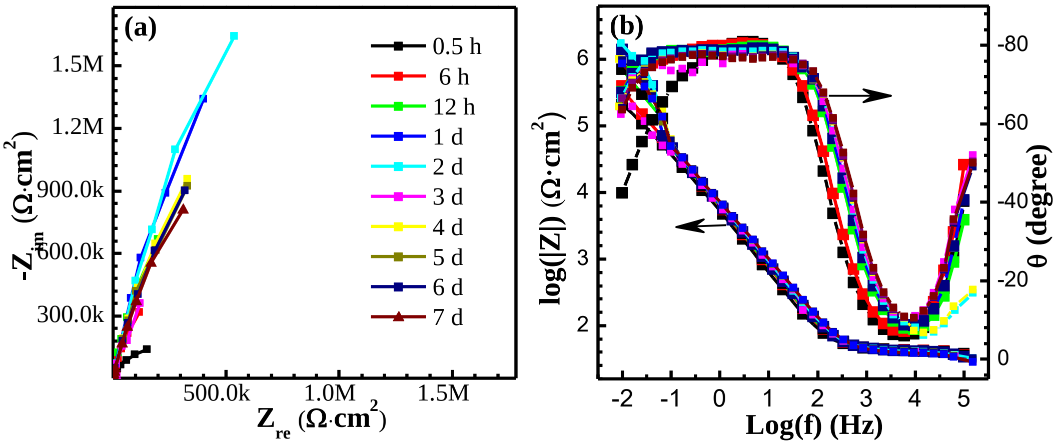

Figure 3. The (a) Nyquist and (b) Bode diagrams of TA10 dental implant after immersion in SBF at 36.5°C for different times (0.5 h, 6 h, 12 h, 1 d, 2 d, 3 d, 4 d, 5 d, 6 d, 7 d).

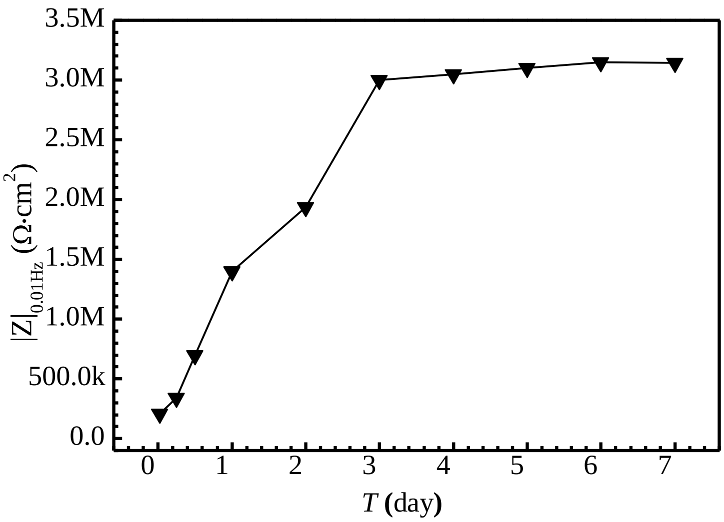

Figure 4. The impedance modulus |Z| at 0.01 Hz of TA10 dental implant after immersion in SBF at 36.5°C for different times (0.5 h, 6 h, 12 h, 1 d, 2 d, 3 d, 4 d, 5 d, 6 d, 7 d).

3.4. Mott-Schottky

The semiconductor characteristics of passive films formed on the surface of titanium and its alloy implants in simulated implantation environment can usually be described by Mott-Schottky (M-S) theory, The relationship between space charge capacitance and potential follows the following relationship [25,26]:

n type: $\frac{1}{C^2}=\frac{2}{\varepsilon\varepsilon_0 e N_D}(E-E_{fb}-\frac{kT}{e})$ (2)

P type: $\frac{1}{C^2}=-\frac{2}{\varepsilon\varepsilon_0 e N_A}(E-E_{fb}-\frac{kT}{e})$ (3)

where C is the space charge layer capacitance of the passive film; E is the applied potential; ε is the semiconductor dielectric constant, and ε_0 is the relative dielectric constant of Ti-oxide. *e* is the electric quantity, e=1.602×10^{-}19 C; N_D and N_A is the electron donor and acceptor concentration respectively; E_{fb} is the voltage intercept corresponding to the straight line segment of M-S curve; k is Boltzmann constant, k=1.38×10-23 J/k; T is the thermodynamic temperature. Then, the space charge layer capacitance at different potentials can be measured, and the semiconductor type of passive film can be determined by plotting with potentials. A positive slope presents n-type semiconductor characteristics and otherwise is p-type.

Figure 5 shows the M-S curves of TA10 implant electrodes after immersion in SBF for different times. When the electrode potential is higher than that of the flat-band, the fitting line of the M-S curves show positive values, indicating that the formed passive films of TA10 dental implant present n-type semiconductor characteristics after immersion in SBF for different times. According to Eq. (2), the N_D is 2.53, 2.15 and 1.98 after immersion for 30min, 1 d and 3 d, respectively. It can be seen that the N_D in TA10 implants decreases with the extension of immersion time, indicating that the stability of the passive film increases with the extension of immersion time.

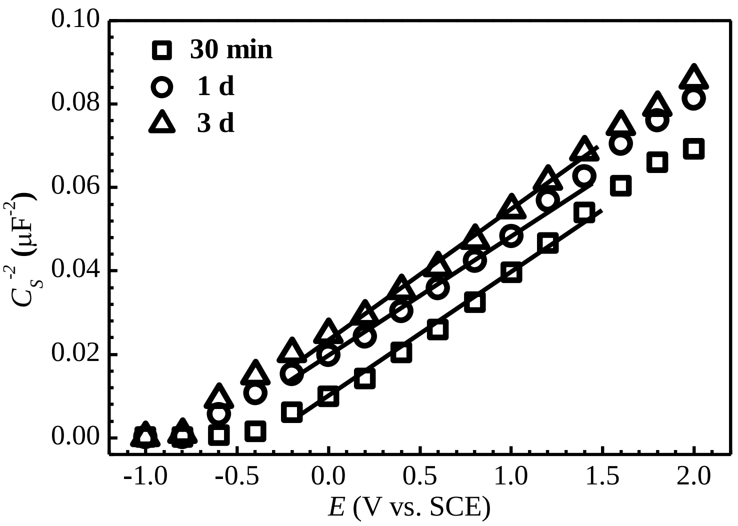

Figure 5. MS curves of TA10 implant immersion in SBF at 36.5oC for different times (0.5 h, 1 d, 3 d).

Furthermore, the variation film thickness on the surface of TA10 dental implant after immersion in SBF for different times could also be used to evaluate its corrosion resistance [27]:

$$d=\left[\frac{2\varepsilon\varepsilon_0(E-E_{fb}-\frac{\kappa T}{e})/e}{eN_D}\right]^{1/2} \quad (4)$$

where the parameter in Eq. (3) are the same as Eqs. (2) and (3). It can be concluded from the increasing of N_D that the thickness of passive film is enhanced with the extension of immersion time, and then tends to maintain a stable corrosion resistance.

4. CONCLUSION

(1) With the extension of immersion time, the OCP of TA10 dental implant moves to the positive direction. OCP increases sharply within 12 h, then increasing in a slow speed within 12-24 h and then tends to be stable at about 30 mV_{SCE} after 1 day immersion.

(2) The maintaining passivity current density and the self corrosion current density decreases with extension of immersion times, the corrosion resistance of TA10 dental implant passive film increases.

(3) The TA10 dental implant passive film is characterized by n-type semiconductor and the number of defects decreases with the extension of immersion time, a stable corrosion resistant passive film could be formed after 3 days of immersion.

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CONFLICTS OF INTEREST
The authors declare no conflict of interest.

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