The electrochemical behavior and characterization of the anodic oxide film formed on titanium in NaOH solutions

Abstract Titanium dissolution and passivation were studied in NaOH aqueous solution using open-circuit potential, potentiodynamic and potentiostatic techniques. Potentiodynamic data showed that the active-passive transition involves active metal dissolution followed by formation of a poorly conducting passive oxide film that passivates the electrode. The critical current density varied with pH as \( \frac{\mathrm{d} \log j_m}{\mathrm{d} \mathrm{pH}} = -0.098 \) in the pH range 11.00–14.00, while the passivation potential is changed according to the following two features: at pH 10.55–13.00, \( \frac{\mathrm{d} E_m}{\mathrm{d} \mathrm{pH}} = -0.06 \) V; and at pH 13.50–14.00, \( \frac{\mathrm{d} E_m}{\mathrm{d} \mathrm{pH}} = -0.40 \) V. The apparent activation energy, \( E^a \), was calculated from the slope of the Arrhenius plot and was found to be 12.6 kJ mol\(^{-1}\). Current-time transients showed that the growth of titanium oxide passive film is a diffusion-controlled process. XPS measurements indicated that the passive oxide film consists mainly of TiO\(_2\) and a mixture of suboxides of Ti\(_2\)O\(_3\) and TiO.

Keywords Titanium electrode · Passive film · Potentiodynamic data · Open-circuit potential · X-ray photoelectron spectroscopy

Introduction

Titanium and titanium alloys possess good mechanical properties, a high strength-to-weight ratio and excellent corrosion resistance as a result of the native oxide film (~20 Å thick) that spontaneously forms on the surface of the metal in air and aqueous solutions. Hence, they are increasingly used not only for industrial applications [1] but also for medical applications [2]. In recent years, much research [3, 4, 5, 6] has been conducted on different kinds of NaOH-treated titanium substrates for biomaterial applications. Therefore, it is interesting to study the passivation as well as the electrochemical behavior of Ti in NaOH solutions.

Few works have been published on the electrochemical behavior and passivation of Ti in alkaline media [7, 8, 9, 10]. The corrosion behavior of Ti in carbonate-bicarbonate buffer solution of pH 9.7 was studied by El Sayed and Leach [7]. They found that the changes in the impedance and corrosion rate with potential are both due to change of cation valency and to oxide non-stoichiometry. Prusi and Arsov [9] reported the growth kinetics and optical properties of titanium oxide on a Ti surface in KOH solutions under open-circuit potential conditions.

The purpose of the present investigation is to study the passivation behavior of a Ti electrode in NaOH solutions as well as to characterize the passive oxide film. The influence of various parameters, including sweep rate, electrolyte concentration, solution temperature and pH, on the anodic dissolution as well as on the passivation of the Ti electrode was studied.

Experimental

The working electrode employed in the present study was made of pure titanium (99.99%) sheets axially embedded in Araldite holders to offer a Ti exposed surface area of 2.3 cm\(^2\). Prior to each experiment, the working electrode was mechanically polished with different grades of emery paper, i.e., 600, 800, 1000 and finally 1200, and then the polished electrode was rinsed with acetone and distilled water. Finally, the electrode was activated in 1 M HF for 1 min followed by generous washing with double-distilled water, and then dipped in a conventional three-electrode cell. The oxide film was removed when necessary by gentle hand polishing on 0.05 µm alumina. A platinum plate (2.0 cm\(^2\)) was used as a counter electrode. All potentials were measured against a Ag/AgCl electrode. To avoid contamination, the reference electrode was connected to the working electrode through a bridge with a Luggin capillary filled with the test solution. The capillary tip was put very close to the electrode surface to minimize the ohmic drop of the
solution. Solutions were freshly prepared from doubly distilled water and pure grade chemicals and purged with argon gas for 1 h before the experiment. The electrolyte was exchanged after each measurement in order to avoid build-up of soluble titanium species, which are known to enhance the stability of the oxide under open-circuit conditions. Solutions of different pH values were prepared by mixing 1 M NaOH with appropriate amounts of 5 M H$_2$SO$_4$. All measurements were conducted at constant temperature with the help of a water thermostat.

Electrochemical measurements were performed using a potentiostat-galvanostat (EG&G model 273A) connected to a personal computer. Potentiodynamic measurements were carried out by sweeping the potential from $-1.5$ V to 2.0 V. Potentiostatic anodization was carried out for 1 h at different applied potentials. Potentiostatic current-time transients at constant potentials were recorded in the following way. The Ti electrode was held at the starting potential of $-1.5$ V for 60 s to attain a reproducible Ti surface, and then the electrode was scanned potentiodynamically from $-1.5$ V in the positive direction with a sweep rate of 5 mV s$^{-1}$ to a potential limit at which the current-time transients were recorded for 100 s.

X-ray photoelectron spectroscopy (XPS) was carried out using an ESCA-3200 (Shimadzu) operated at a chamber pressure less than $5 \times 10^{-6}$ Pa, using Mg K$_x$ radiation. The source was run at 6 kV and 30 mA from the magnesium anode. All measurements were conducted at a take-off angle of 45$^\circ$ with respect to the sample surface. The binding energy was calibrated with the line position of the C(1s) peak at 284.6 eV. The surface morphology as well as the thickness of the oxide film was examined using a scanning electron microscope (SEM) (FE-SEM, model S-4500, Hitachi, Tokyo, Japan).

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**Results and discussion**

**Open-circuit potential**

Titanium electrodes exposed to the atmosphere after mechanical and chemical polishing are covered spontaneously by an oxide film, being predominately titanium dioxide in a dense modification of rutile TiO$_2$ [10]. As soon as a Ti electrode is immersed in NaOH solutions, at open-circuit conditions, the process of dissolution of the natural oxide film of TiO$_2$ begins first. Simultaneously, self-passivated film formation also begins. These two processes are recorded on the open-circuit potential (OCP) versus time curves at various concentrations of NaOH, as shown in Fig. 1. The results show that, firstly, the corrosion potential slowly decreased, showing minimum potential values at approximately $-1070$, $-1310$ and $-1350$ mV in 0.5, 1.0 and 2.0 M NaOH, respectively. This could be attributed to the slow dissolution of naturally formed titanium oxide film as mentioned before. After that, the corrosion potential gradually rose to more noble potential values and finally achieved steady-state potential values at approximately $-715$, $-735$ and $-805$ mV in 0.5, 1.0 and 2 M NaOH, respectively, as a result of the self-passivation. The pseudo-like plateau observed at about $-1.3$ V, when the concentration of NaOH is increased, might be due to the high dissolution power on the Ti oxide. When the solubility product of the oxide is achieved, the potential starts to rise again. It is worth noting that the stronger the NaOH, the longer the time needed to achieve the steady-state potential and the less noble the steady-state potentials, as shown in Fig. 1.

The open-circuit stability of the passive film in alkaline solution is investigated not only because of its obvious relevance to practical corrosion but also because it allows us to determine the formation rate of the passive film of the Ti electrode. For example, the steady-state potential of the Ti electrode is achieved after 1.9, 2.7 and 6.4 h in 0.5, 1.0 and 2.0 M NaOH, respectively. The broadening in the curve at high NaOH concentrations indicates the competition between dissolution and the formation of the passive oxide film. Generally speaking, the data in Fig. 1 reveal that a shorter time is required for the steady-state potentials to attain in NaOH when compared to the reported data for Ti in acid medium [11].

**Potentiodynamic polarization curves**

Figures 2, 4, 7 and 10 illustrate the potentiodynamic $E/j$ anodic polarization curves for a Ti electrode in NaOH solution at various NaOH concentrations, pH values, sweep rates and solution temperatures, respectively. The potential sweep was initiated at $-1.5$ V, where a considerate cathodic current (point a in Fig. 2) is observed and ended at 2.0 V. The cathodic current approaches zero value, and thereafter several characteristic features in the anodic region were observed. These features could be defined as: (1) an active dissolution region between points b and c, where the anodic current increases exponentially with potential; (2) a region where the current increases linearly with potential between c and d; (3) the region of the anodic current peak d; (4) a region in which the anodic current decreases towards a low value, d–e, corresponding to the passivation of the electrode; and (5) the passive range between e and f.