Surface characterization of the commercially pure titanium after hydrogen charging and its electrochemical characteristics in artificial seawater

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ABSTRACT

The surface film on hydrogen-charged commercially pure titanium and its influence on the electrochemical behavior in artificial seawater was studied in detail using surface characterization techniques and electrochemical measurements. The results revealed that with the increase in charging current density, the original surface film underwent three stages of evolution. When the charging current density was $< 20\,mA/cm^2$, the surface film just expanded and bulged; when the current density exceeded $30\,mA/cm^2$, the surface film was significantly destroyed and began to fall off; when the current density reached to $50\,mA/cm^2$, the surface film fully peeled off and was replaced by a new layer of loose film. Accordingly, the composition of the surface film transformed from titanium oxides to a mixture of titanium oxides and titanium hydrides, and finally to entirely titanium hydrides. Under the influence of hydrogen charging, the corrosion resistance of the surface film in artificial seawater sharply decreased, showing a significant increase in anodic current density, decrease in surface film resistance, as well as a tendency toward early failure of the surface film at a lower potential.

1. Introduction

Titanium and its alloys are widely used in the aerospace, automotive, chemical, and biomedical industries owing to their excellent corrosion resistance, bio-compatibility, high specific strength, and low density [1–3]. Some studies indicate that the good resistance to corrosion is attributable to the very stable surface film, mainly composed of TiO_2 [4–6]. Even though the oxide film is very thin, it can act as a strong barrier when the titanium material is in contact with corrosive media. Moreover, even if the film is broken down, the newly exposed surface of titanium can be quickly re-passivate to form a new film. In summary, many interesting and unknown features concerning the surface film attract attention. Thus, research efforts are increasingly devoted to investigating the nature of the surface film and its influence on the titanium substrate under various conditions [7–10].

Generally, hydrogen exerts a significant influence on almost all types of metallic materials, and titanium and its alloys are no exception [11–13]. Although the content of hydrogen in titanium materials is strictly controlled before use, many types of titanium equipment are still attacked by hydrogen atoms during service, because the equipment may be in a cathodic polarization condition or exposed to environments that can act as sources of hydrogen. For example, pure titanium is recommended as the insert material used in chimney in coal-fired power

stations by the International Committee on Industrial Chimneys (ICIC), that means that pure titanium will work in a strong acidic media composing of a mixture of sulfuric acid, nitric acid and hydrochloric acid. Therefore, hydrogen atoms can still permeate the surface film and contact the titanium substrate, which may lead to the formation of hydrides on the surface. Liu et al. [14] found that titanium dihydride (TiH_2) formed on the surface could induce radical changes to the properties of the film. This conclusion was consistent with that of another study [15], which further indicated that even small concentrations of hydrogen, not necessarily sufficient to form titanium hydrides, might also result in failure when trapped inside the material. Moreover, the work conducted by Chen [16] pointed out that hydrogen existed in passive films in the form of protons, and notably improved the ratio of OH^-/O^{2-} through reacting with O^{2-} in the film. This means that the invasion of hydrogen can distinctly alter the composition and deteriorate the performance of the surface film, which may introduce uncertainty regarding the service of titanium materials in certain key components [3]. Thus, attention should be paid to the properties of the surface film on titanium in the presence of hydrogen, as well as the subsequent effects on the corrosion resistance of titanium.

The present work focused on the effect of hydrogen charging on the surface characteristics of commercially pure titanium and its subsequent electrochemical behavior in artificial seawater. Specifically,

scanning electron microscopy (SEM), laser scanning confocal microscopy (LSCM), scanning Kelvin probe force microscopy (SKPFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were applied to analyze the surface structure and composition of hydrogen-charged titanium. Meanwhile, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Mott–Schottky measurements were performed to study the electrochemical behavior of the charged specimens in artificial seawater.

2. Experimental

2.1. Sample preparation and hydrogen charging

The experimental material was commercially pure titanium (TA2) with 99.99% Ti, whose microstructure was totally composed of the α phase. The pre-charging specimen was coated with epoxy, leaving an exposure area of 10 mm × 10 mm as the working surface. Meanwhile, the thickness of the charged specimen was 3 mm. Subsequently, the specimen was sequentially ground to 4000 grit emery paper and cleaned in distilled water and ethyl alcohol, in turn.

Hydrogen charging experiments were performed in a mixture solution consisting of phosphoric acid and glycerin with a volume ratio of 1:2 [17] at room temperature (~25 °C). During this process, the specimen acted as the cathode, and a platinum mesh served as the anode. To obtain samples with different hydrogen contents, the specimens were charged for different hydrogen charging times (0, 25, and 50 h) and current densities (0.5, 10, 20, 30, 40, and 50 mA/cm^2). Then, the specimens were quickly cleaned with distilled water and alcohol for the following experiments.

2.2. Surface characterization

After hydrogen charging, the surface morphology and roughness of the specimen were carefully examined using a FEI QUANTA 250 SEM and a Keyence VK-X250 LSCM, respectively. Meanwhile, XRD and XPS were also used to analyze the surface composition of the specimen. XRD was performed using a MAC Science-M21X analyzer over a range of 10°–90° at a scanning rate of 4°/min, to determine the main crystalline phases of the surface film. XPS was carried out on the surface using a Thermo ESCALAB 250Xi device with an Al Ka (1486.6 eV) X-ray source. The binding energy was adjusted for the charging effect by referencing the C1s peak (284.8 eV). The XPS data were fitted using the software package XPS-Peak 4.1.

2.3. SKPFM measurements

SKPFM was applied to obtain information of the Volta potential distribution across the surface in air, which provides clear evidence concerning compositional inhomogeneity with submicrometer resolution [18]. Thus, the surface film after hydrogen charging was also analyzed using an atomic force microscope (Brucker Multimode VIII) in

the SKPFM mode. A PFQNE-AL probe of nominal tip radius 5 nm from Brucker was used for the SKPFM measurements. In this part, the local Volta potential difference was measured using amplitude modulation (AM) mode, which is a two-path scanning process with topographical information obtained in the first path and the corresponding potential data acquired in the second path. A lift height of 120 nm was used to measure the local Volta potential differences. The scan area was set as 30 μm × 30 μm with a scanning rate of 0.301 Hz. Usually, the Volta potential map is obtained according to the contact potential difference (V_{CPD}) between the sample and the tip; the difference V_{CPD} was defined as

$$V_{CPD} = (\phi_{Sample} - \phi_{Tip})/e \qquad (1)$$

where φ_{Sample} and φ_{Tip} are the work functions of the sample and tip, respectively, both of which are directly related to the Volta potential in ultrahigh-vacuum, and e signifies the fundamental charge.

2.4. Electrochemical measurements

Electrochemical measurements were done on a Princeton 2273 electrochemical workstation utilizing a conventional three-electrode cell, in which Pt foil was used as the counter electrode, a saturated calomel electrode (SCE) was the reference electrode, and the charged specimen was the working electrode. It should be noted that all the potentials were measured and quoted with respect to the SCE if not explicitly mentioned in this paper. The corrosive media was artificial seawater, whose composition was as follows (g/L): 26.726 NaCl, 2.260 MgCl$_2$, 3.248 MgSO$_4$, 1.153 CaCl$_2$, 0.721 KCl, and 0.198 NaHCO$_3$. The pH was adjusted to approximately 8.10 (close to the pH of seawater) using a 0.01 mol/L NaOH solution.

Prior to the tests, the specimens were maintained in the corrosive environment for 2000 s to reach a steady open-circuit potential (OCP). Then, EIS measurements were carried out from 100 kHz to 10 mHz with an AC amplitude of 10 mV. The EIS data were fitted using the software package Zsimpwin. Potentiodynamic polarization measurements were conducted from −0.5 V (vs. OCP) to 6 V at a sweep rate of 1 mV/s. It is worth noting that when the current density exceeded 10^{-2} A/cm^2, the passive film was considered to be destroyed and the measurement process was manually stopped. Finally, the Mott–Schottky curves were acquired by measuring the frequency response at 1 kHz during a 50 mV/s negative potential scan, and the scanning potential was varied from 0 to 3 V. All the electrochemical tests were repeated three times at ambient temperature.

3. Results

3.1. Morphology observation and composition analysis

Fig. 1 shows the surface morphologies of the specimens that were uncharged and charged with 0.5 mA/cm^2 for 25 and 50 h, respectively. There are almost no changes on the specimen surfaces, and all the films
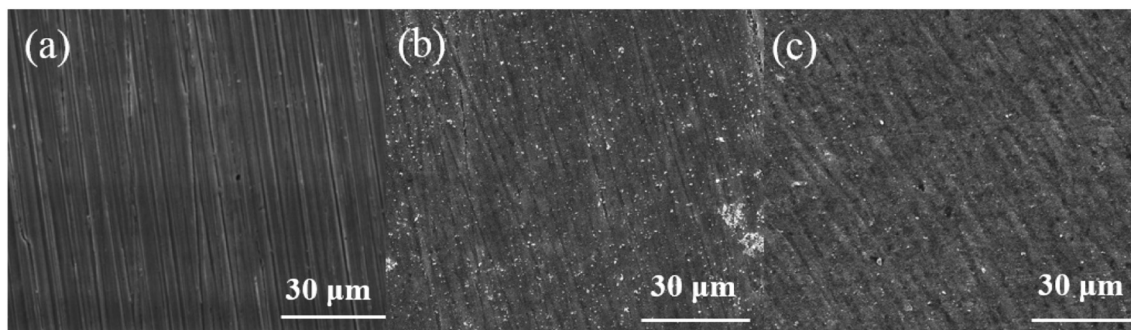

Fig. 1. Surface morphologies of the (a) uncharged and charged TA2 specimens at 0.5 mA/cm^2 for (b) 25 h and (c) 50 h.