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Steam-induced changes in surface characteristics and corrosion resistance of spark-anodized titanium

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ABSTRACT

Titanium was spark-anodized in 1 M phosphoric acid solution. Surface characteristics and corrosion resistance of spark-anodized titanium were investigated before and after the steam exposure at 180 °C. It was found that spark-anodizing of titanium produced a layer of poorly crystallized TiO_2 film with the incorporation of phosphate anions. The oxide film exhibited a porous microstructure with many craters and micro-projections on the surface. After the steam exposure for 48 h, the crystallinity of anodic TiO_2 increased greatly. The original dense and smooth micro-projection surface became very loose and rough, and fine $Ti(OH)PO_4$ crystals formed and congregated there. A phase transition mechanism has been proposed based on the experimental observations. The corrosion behavior investigation has shown that the steam exposure could reduce the corrosion resistance of spark-anodized titanium greatly.

1. Introduction

Titanium and its alloys are attractive materials for the offshore oil and gas industry because of their high strength to weight ratio and good corrosion resistance [1]. However, they still suffer from pitting and crevice corrosion in some aggressive environments, for example in hot chloride solutions, which restricts their use in certain offshore applications [2]. The good corrosion resistance of titanium and its alloys under normal conditions is attributed to the natural TiO_2 film, approximately 3–5 nm in thickness, formed on the surface. It has long been thought that their corrosion resistance can be further improved by any surface treatments that can thicken the surface TiO_2 film [3]. The frequently-used techniques to thicken the TiO_2 film include thermal spraying, thermal annealing and electrochemical anodization [3,4]. Among these techniques, anodization of titanium has attracted great attention because it is simple to perform and the fabricated TiO_2 films exhibit enough thickness, good adhesion and varied structures [4,5]. The anodization treatment performed at a voltage higher than the breakdown voltage is known as spark-anodizing or micro-arc oxidation [5,6].

After the anodization treatment, titanium alloys usually exhibit improved corrosion resistance [7]. However, the protective anodic TiO_2 films may undergo structural transformation and performance degradation under certain conditions [8,9]. For instance, anodic TiO_2 nanotubes were found to transform into nanowires after a long-term immersion in water [8]. When exposed to a hydrothermal environment at 180 °C, these nanotubes collapsed completely after only 2 h [9]. For spark-anodized titanium, there is a shortage of studies on its surface characteristic changes in harsh environments [10].

In the present study, spark-anodizing of titanium was performed in 1 M phosphoric acid solution. Then, the spark-anodized titanium samples were exposed to steam at 180 °C for 48 h. The high temperature steam was chosen to roughly simulate the harsh environment likely to be encountered by titanium alloys in the offshore gas applications. Steam-induced changes in surface morphology, phase composition and corrosion resistance of spark-anodized titanium were investigated and discussed.

2. Materials and methods

2.1. Preparation and characterization of samples

A commercially pure titanium (ASTM grade 2) plate, 1.5 mm in thickness, was cut into circular samples with a diameter of 15 mm using an electric discharge machine. The circular samples were ground with 1000-grit sandpapers and cleaned ultrasonically in acetone and distilled water in turn. Subsequently, the titanium sample and a platinum plate were connected to the anode and the cathode respectively. Anodization was carried out in 1 M phosphoric acid solution using a DC power supply. The anodizing process lasted for 2 min in the potentiostatic mode at the voltages of 200 and 300 V, respectively.

For the subsequent steam exposure, the spark-anodized titanium samples were first placed on a support to avoid their direct contact with the liquid water, and then the support together with the samples was put into a 100 ml Teflon-lined autoclave containing 5 ml distilled water. The autoclave was sealed and kept at 180 °C for 48 h. After the

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exposure, the samples were taken out and dried at 40 °C for 24 h. For comparison, a few anodized titanium samples were put into the same autoclave containing no water and heated with the same temperature and duration.

Before and after the exposure of spark-anodized titanium, its surface morphologies were observed by scanning electron microscopy (SEM) (JSM-6340 F, JEOL, Japan) at the operating voltage of 5 kV. The energy dispersive X-ray (EDX) analyses were performed at the operating voltage of 15 kV, the working distance of 15 mm and the magnification of 10000 using the built-in EDX unit in the JSM-6340F. The surface chemical composition and the elemental chemical states were characterized using X-ray photoelectron spectroscopy (XPS) (Kratos Axis Ultra, UK). During the collection of the XPS data, the pressure in the sample analysis chamber of the XPS instrument was lower than 10^{-9} Torr. An Al Kα (1486.6 eV) monochromatic X-ray source was used with the emission of 10 mA and the anode HT of 15 kV. The calibration of the binding energy scale was performed using the C 1 s line (285 eV) from the carbon contamination layer as a reference. The surface phase composition was analyzed by thin-film X-ray diffraction (TF-XRD) (XRD-6000, Shimadzu, Japan). The TF-XRD measurements were performed in the range of 20–60° in 2θ using Cu Kα ($\lambda = 0.15405$ nm) radiation as the source at the rate of 2°/min and with the glancing angle of 1° against the incident beam on the sample surface.

2.2. Corrosion test

The corrosion resistance of spark-anodized titanium before and after the exposure was evaluated by performing an anodic polarization test in 3.5 wt.% NaCl solution at room temperature using a potentiostat/galvanostat (PGSTAT302N AUTOLAB, Eco Chemie, the Netherlands). The experimental setup for the electrochemical measurements consisted of a three-electrode glass cell. A standard calomel electrode was used as the reference electrode which contacted with the solution through a bridge tube. The titanium sample was used as the working electrode. The counter electrode consisted of two platinum sheets positioned symmetrically relative to the working electrode. The surface area of each titanium sample exposed to the electrolyte was 1.0 cm^2. The anodic polarization curves were recorded for a potential scan ranging from −0.5 to 1.0 V and the scan speed was 10 mV/s.

3. Results and discussion

Fig. 1 shows surface morphologies of spark-anodized titanium before and after the steam exposure at 180 °C for 48 h. The spark-anodized titanium before the exposure exhibited a porous surface with many craters, as shown in Fig. 1a. At a higher magnification (Fig. 1b), it can be seen that a micro-projection with smooth surface was formed around the crater. Fig. 1a and b present the typical surface morphology of spark-anodized titanium. When the applied anodization voltage exceeds the breakdown limit (about 150 V for titanium in 1 M phosphoric acid solution [11]), sparking will occur during the anodization process. The sparks initiated at weak points of the oxide film and then spread over the whole sample surface quickly with audible cracking, copious gas evolution and local oxide overgrowth. This violent electrochemical reaction resulted in lots of microprojections and craters where sparks were generated. After the steam exposure at 180 °C for 48 h, the original smooth micro-projection surface became very rough, as evidently shown in Fig. 1c. At a higher magnification (Fig. 1d), it can be observed that many block-shaped oxide particles formed and congregated on the micro-projection surface. The surface structure of the micro-projection became relatively loose and the original crater was almost filled up. Besides, the average surface area of the micro-projection increased due to the formation and growth of oxide particles.

Fig. 2 shows the XPS spectra from surfaces of spark-anodized titanium before and after the steam exposure. From the survey spectra in Fig. 2a, it can be seen that before and after the exposure, the samples

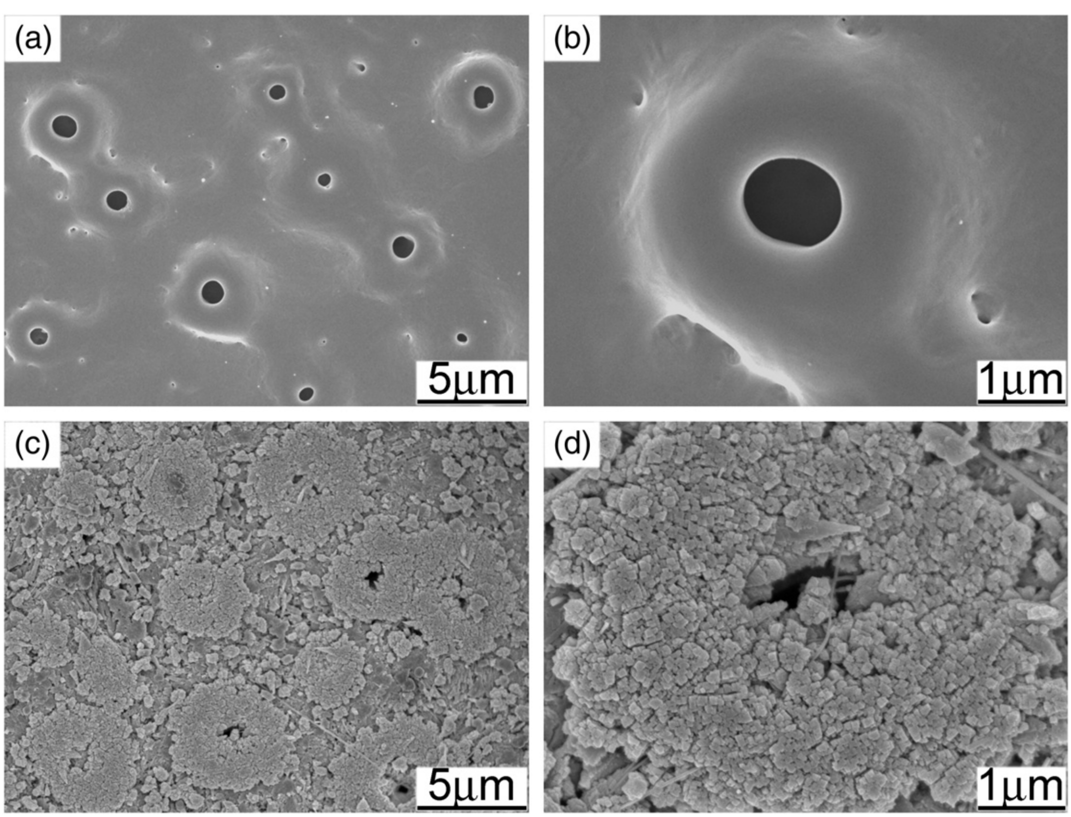

Fig. 1. Surface morphologies of spark-anodized titanium before (a, b) and after (c, d) the steam exposure at 180 °C for 48 h.