



Effect of surface mechanical attrition treatment on corrosion resistance of commercial pure titanium



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ABSTRACT

We report on the effects of surface mechanical attrition treatment on the corrosion behavior of commercial pure titanium. The corrosion resistance before and after treatment were investigated by studying potentiodynamic polarization curves and by electrochemical impedance spectroscopy. The potentiodynamic polarization curves for a sample treated by surface mechanical attrition and for an untreated commercial pure titanium sample at room temperature showed that the corrosion potential of the former ranged from -1.11 to -1.06 V, whereas that of the latter was -1.23 V. The corrosion current density for the treated sample ranged from -5.02×10^{-4} to -4.98×10^{-4} A.cm⁻², and that for the untreated sample was -4.56×10^{-4} A.cm⁻². A comparison of current densities at the same polarized potential showed a significant reduction in dissolution current of the treated sample. This indicates a lower corrosion rate for the sample treated by surface mechanical attrition. Surface mechanical attrition treatment was therefore confirmed to have beneficial impacts on corrosion behavior in 3.5 wt.% NaCl solution.

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1. Introduction

Titanium and its alloys have proven to be important engineering alloys for advanced applications in aerospace, automotive, chemical and biomedical industries because of their high corrosion resistance [1–5]. Titanium has a remarkable corrosion behavior because of the very stable oxide film formed on its surface [6]. However, this film is unstable in reducing or complexing media, such as hydrochloric acid and solutions that contain chloride ions, which limits its industrial application [7–9].

In general, passive films formed on titanium and its alloys consist mainly of amorphous titanium dioxide. The formation of a stable passive oxide film on titanium and its alloys may reduce their corrosion [10,11]. A high-surface grain boundary density is beneficial for the formation of a passive film [12].

Most material failures occur on the surface and therefore, controlling the surface properties can effectively improve the overall material behavior [13]. Many efforts have focused on surface hardening to improve corrosion resistance. Grain refining has been shown to be an effective method to improve surface properties [12–15].

Surface mechanical attrition treatment (SMAT) can be used to apply repeated impacts on a sample surface and refine grains on the material surface [16,17]. But few investigations have been carried out to predict the effect of SMAT on corrosion behavior when using a 3.5 wt.% NaCl solution (the equivalent concentration of sea water). Very few of

these have investigated the influence of processing time on corrosion protection. Also, none have evaluated the corrosion protection mechanisms and characterized the passive layers formed on material surfaces in 3.5 wt.% NaCl solution. The purpose of this work was to study the microstructure and properties of refined grains on the surface of commercial pure titanium as induced by SMAT. Attention was focused primarily on evaluating the corrosion protection mechanisms. The effect of SMAT treatment on the corrosion behavior was also investigated and analyzed. Samples were processed under different SMAT conditions to form different refined grain surface layers. Electrochemical measurements were conducted in 3.5 wt.% NaCl solution to investigate the corrosion behavior of commercial pure titanium before and after treatment. Commercial pure titanium was analyzed by X-ray diffraction (XRD) for phase analysis and calculation of grain size. Scanning electron microscopy (SEM) was carried out to characterize the surface microstructure. For comparison, the same measurements were also conducted on commercial pure titanium.

2. Experimental

The material used in this study was commercial pure titanium with the following nominal composition (wt.%): C 0.02, Fe 0.10, O 0.15, N 0.02, H 0.0011 and a balance of titanium.

The surfaces of rectangular specimens (100 × 100 × 2 mm) were ground using 360–1200[#] SiC abrasive papers; polished using 2.5 μm diamond pastes until the surfaces reached a highly reflective level; cleaned ultrasonically with acetone, alcohol, and distilled water; and dried in air.

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SMAT may cause severe plastic deformation of the material surface. In SMAT, the sample surface to be treated is peened with a large number of impacts over a short time using a high frequency system (50 kHz). SMAT was conducted for 15, 30, and 45 min using a large quantity of 8-mm-diameter GCr15 balls and a vibration amplitude of 50 kHz. After SMAT, the sample surface was electropolished slightly in 5% HCl + C2H5OH solution at room temperature to remove the impurities and surface contaminants, and to eliminate the effects of contamination on corrosion performance [18]. The final samples were termed SMATx, where x = 15, 30 or 45 min.

Microstructures were examined using a G2 pro scanning electron microscope. X-ray diffraction (XRD) analysis of the surface layer was carried out using a Philips PW 1830/00 diffractometer. X-ray photoelectron (XPS) analysis was performed on a PHI5500 system using AlK α radiation.

Electrochemical experiments were carried out in three-necked flasks using an electrochemical potentiostat model PARSTAT 4000 (Princeton Applied Research, NJ, USA) to identify the corrosion behavior. A saturated calomel electrode (SCE) was used as the reference electrode, the samples as the working electrode, and a platinum coil as the counter electrode. The temperature of the three-necked flask was maintained at 27 ± 0.1 °C. Potentiodynamic polarization tests were initiated after 1 h immersion of the samples in a 3.5 wt.% NaCl solution, when a stable open circuit potential can be obtained at a potential scanning speed of 3 mV/s from -2000 mV to 1000 mV. Electrode impedance spectroscopy (EIS) tests were conducted at an open circuit potential value to characterize the corrosion behavior of these samples. The electrode response was analyzed from ~ 0.01 Hz to 100 kHz using a 10 mV amplitude alternating current voltage signal. The EIS tests were recorded at the open circuit potential developed by the samples after 600 s of immersion in the 3.5 wt.% NaCl solution. All electrochemical tests were repeated three times to ensure reproducibility of the measurements, and reproducibility of the data is expressed in terms of the corresponding standard deviation.

3. Results

3.1. Potentiodynamic polarization curve studies

To investigate the corrosion behavior before and after SMAT, potentiodynamic polarization tests were carried out on commercial pure titanium samples, in 3.5 wt.% NaCl solution at pH = 6.0 (Fig. 1).

On the cathodic branch, the main reaction is hydrogen evolution reaction. The chemical equation may be [19]:

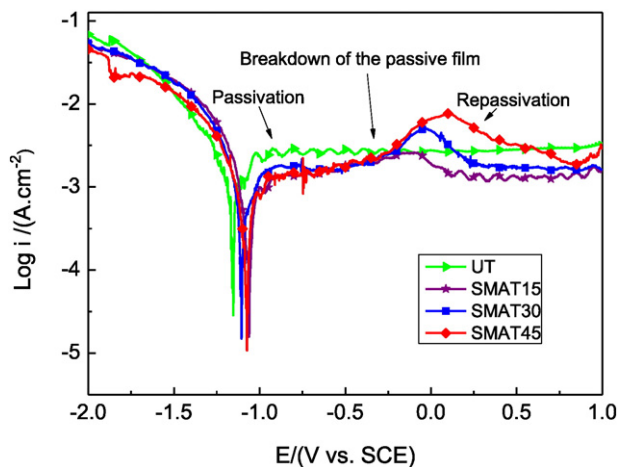
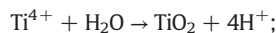
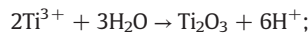
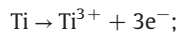
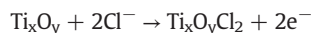


Fig. 1. Potentiodynamic polarization curves for samples before and after SMAT after 1 h immersion in 3.5 wt.% NaCl solution at 27 °C. Scanning rate: 3 mV s^{-1} .

On the anodic branch, the curves describe typical behavior for metals that undergo passivation when exposed to a certain level of electric current because of the formation of a passive oxide film over the sample surface, which inhibits corrosion evolution. The formation of the passive film can be represented by the following chemical reactions [20]:



The series of reactions produces $\text{Ti}^{3+}/\text{Ti}^{4+}$ ions, which form a stable passive film of TiO_2 and Ti_2O_3 . The $\text{TiO}_2/\text{Ti}_2\text{O}_3$ film protects the material from further corrosion. The presence of aggressive ions, such as chloride, sulfate and fluoride in solution, accelerates the anodic process [21]. According to Liu, Cl^- can migrate across the passive oxide film in parallel with oxide ions [22], as represented by the following chemical reaction:



A wide passive region from -1.0 to -0.25 V_{SCE} with current density ~ 1 $\mu\text{A cm}^{-2}$ was observed after a short active dissolution for the SMAT samples. In contrast, a narrow passive region existed for the untreated samples from -1.10 to -1.15 V_{SCE} . Corrosion resistance behavior is exhibited in the region in which the samples are passive. The current increases for SMAT samples at a potential up to -0.25 V_{SCE} , according to Oliveira et al. and Tavares et al., which indicates that the passive film is breaking [1,23]. However, the current range is set rapidly as per the metal's repassivation. For the SMAT samples, the SMAT15 sample translated directly into the passive region from the Tafel region from -1.10 to 1 V_{SCE} , and exhibited a typical self-passivation characterization. However, the SMAT30 and 45 experience several active-passive transitions from -1.10 to 0.14 V_{SCE} and then tend to passivation again. This indicates the formation of a passive film that is not sufficiently protective under immersion into the electrolyte, and in the active-passive region the corrosion rate increased [24]. According to Geetha et al. [25], the phenomenon of metal repassivation also plays an important role in the alloy's corrosion behavior. Titanium alloys show a faster repassivation phenomenon than that from stainless steel. This provides excellent corrosion resistance for SMAT30 and 45 samples [26–28]. In the passive region, the SMAT sample passive current densities were lower than for the untreated sample. The decrease in current density resulted because the passivating oxide film dominated over the dissolution rate on the bare surface [29–32]. By comparing the current densities at the same polarized potential, a significant reduction in dissolution current of the SMAT sample can be observed. This represents a reduction in SMAT sample corrosion rate. A comparison of the SMAT samples shows that the SMAT15 sample has no active-passive transitions, and that the current density always maintains a lower value. However, the SMAT30 and 45 samples have active-passive transitions, and in this region, the current density increased. This phenomenon may occur because the SMAT processing time is too long and the substrate surface has many more micro-cracks, which reduces the corrosion resistance.

The corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic and cathodic Tafel slopes (β_a and β_c) of the materials were determined by Tafel analysis of anodic and cathodic branches of the polarization curves using EC-Lab software (see Table 1). Data show

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