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Electrochemical corrosion behavior of platinum-coated lanthanum doped titanium-zirconium-molybdenum alloy

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ABSTRACT

Electrochemical corrosion behavior of platinum coated (Pt-coated) lanthanum doped titanium-zirconium-molybdenum alloy (La-TZM alloy) was studied in this paper. La-TZM alloy plates were fabricated using powder metallurgy and rolling technique, and platinum was coated on their surfaces by using electroplating. Corrosion behavior of Pt-coated La-TZM alloy samples were investigated in neutral and alkaline medium while the Cl^- concentrations keep invariant, which was quantitatively analyzed using potentiodynamic polarization, scanning electron microscope and energy spectrum techniques. Results show that the Pt-coating can improve the corrosion resistance of the La-TZM alloy. Pt-coating on La-TZM alloy can effectively hinder the matrix alloy electrochemical corrosion during different corrosion mediums. In addition, the Pt-coating on La-TZM alloy in a neutral medium is more corrosion resistant than that in an alkaline medium. Pt-coating can effectively hinder the Cl^- destroys the corrosion formed on the surface passivation film, OH^- and Cl^- double erosion promoted La-TZM alloy intergranular corrosion increased during the electrochemical corrosion processes.

1. Introduction

Titanium-zirconium-molybdenum (TZM) alloy contains 0.5–0.8 wt% Ti, 0.08–0.1 wt% Zr and 0.016–0.02 wt% C in Mo matrix, which has high melting point, excellent high-temperature properties, good thermal conductivity, low coefficient of linear expansion and low vapor pressure [1–3]. TZM alloy has been widely used in aerospace, power generation, high temperature structural materials and military, chemical industries and nuclear reactors due to their high rigidity, low temperature ductility, excellent anti-radiation properties and high liquid metal corrosion resistance [3–6]. But, the comprehensive performance of TZM alloy should be put forward higher requirements due to TZM alloy with increasing the applications in special conditions of high temperature, high pressure, and strong erosion.

Currently, mechanical properties and high temperature oxidation resistance of rare earth lanthanum doped TZM (La-TZM) alloy have been studied [7–14]. The related researches on the corrosion of TZM alloy mainly focus on the corrosion-resistant coating for the mode of preparation and coating systems, doping Al, Si, B and other alloying elements to improve the corrosion resistance of molybdenum alloys [15–18]. However, the study of the law of La-TZM alloy electrochemical corrosion behavior and the corrosion process are not systematic enough under extreme conditions [11,19]. Their corrosion resistances should be further studied especially in different corrosion mediums.

Our previous studies [7–9,12,13,20–24] have shown that La-TZM alloy has desirable mechanical properties at high temperature and high pressure, due to the grain refinement of lanthanum oxide particles resulting in an oxide coating on the substrate hind oxygen intruding matrix effectively. In addition, Pt-coated La-TZM alloy which can effectively hinder oxygen erosion the matrix, and enhance its oxidation resistance during the high temperature oxidation experiments and no cracks or defects appear on platinum coating surface. In this paper, the electrochemical corrosion behavior of the Pt-coated La-TZM alloy in neutral and alkaline

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Table 1
Compositions of La-TZM alloys (wt%).

Sample	Ti	Zr	Stearic acid	$La(NO_3)_3$	Mo
La-TZM	0.50	0.10	0.25	1.99	Balance

medium was investigated. It is essential to study the corrosion resistance and anti-corrosion mechanism of the Pt-coated La-TZM alloy in order to explore whether it can have more applications. The Pt-coated has improved La-TZM alloy corrosion resistance, which may expand the applications of La-TZM alloys.

2. Experimental investigation

2.1. Fabrication of La-TZM alloy plate

La-TZM alloy plates were fabricated using powder metallurgy and rolling. Table 1 lists compositions of the alloy. A stearic acid and ethanol solution containing lanthanum nitrate was used, along with TiH_2 and ZrH_2 powders, to obtain La-doped Mo. The La-TZM alloy compacts were processed with mixing, ball-milling (in a ball-milling machine, revolving speed 240 r/min, milling for 2 h), stirring, vacuum-drying (in an oven, at 70 °C for 4 h), compacting (at 21 MPa for 5 s) and multi-stage sintering (passing into protective hydrogen, subsection sintering: maintaining a temperature of 300 °C, 900 °C and 1200 °C for 2 h each, and finally sintering at 1900 °C for 4 h). Finally, 0.5 mm-thick × 10 mm-width × 10 mm-length plates were fabricated by hot-rolling, warm-rolling and caustic washing processes.

2.2. Coating preparation

A dense, well-adhered and uniform Pt coating was obtained through electroplating in the study, the average thickness is 7 μm. The La-TZM alloy plates serve as the cathode, the Pt electrode material serve as electroplating electrode. The medium is acidic solution (H_2PtCl_6, K_2SO_4 and K_2SO_3). During the electroplating, the current density is 6.5 mA/dm^2, temperature is 20 °C and the time is 15 min.

2.3. Electrochemical test

Electrochemical corrosion characteristics of the La-TZM and Pt-coated La-TZM alloy samples were tested using the electrochemical workstation Princeton 4000 as shown in Fig. 1. A saturated calomel (Ag/AgCl saturated with KCl) electrode was used as a reference electrode and a platinum piece was used as an auxiliary electrode. The Pt-coated La-TZM alloy and La-TZM alloy samples were used as the working electrode, placed in a three-electrode system electrolyte. By three-electrode connection method, the Pt-coated La-TZM alloy and La-TZM alloy samples were placed in an acidic medium (Cl^- content 3.5%), and then in alkaline (Cl^- content 3.5%, OH^- content 1 mol/L), Tafel and AC impedance plots were obtained through dynamic potential sweep measurements.

Electrochemical etching parameters were set as follows: (1) room temperature; (2) initial potential 500 mV; (3) termination potential 2.0 V; (4) scanning speed 0.5 mV/s; (5) number of scans 1; (6) termination potential holding time for 0 s. Before electrochemical impedance spectroscopy (EIS) test, the working electrode was kept into the test solution soak for 1 h in order to adapt the system to achieve a stable corrosion potential, and the scanning frequencies range from 100 KHz to 10 mHz, and sine wave excitation signal amplitude was 5 mV with automatic mode.

2.4. Corrosion characterization

Electrochemical corrosion characterization of samples were analyzed using a JSM-6460LV scanning electron microscope (SEM, JEOL, Japan). The SEM images of the sample surface and cross-sectional characterization were obtained for electrochemical corrosion morphology, microstructure and composition. Energy dispersive spectra (EDS) analyzer was used to obtain the surface composition.

3. Results and discussion

3.1. Electrochemical corrosion characteristics of Pt-coated La-TZM alloy

3.1.1. Polarization curves

Table 2 and Fig. 2 show the corrosion rate and polarization curves of the Pt-coated La-TZM alloy and La-TZM alloy in neutral and alkaline mediums. Table 2 shows that the Pt-coated La-TZM alloy and La-TZM alloy exhibit a greater corrosion rate in an alkaline medium compared to that in the neutral medium. The corrosion rate of the La-TZM alloy is much higher than that of the Pt-coated La-TZM alloy in neutral and alkaline mediums. For an alkaline medium, the presence of both OH^- and Cl^- leads to double the corrosion rate and surface pitting, which leads to intergranular corrosion, thus corrosion rate of La-TZM alloy is accelerated. However, the corrosion potential significantly increases and the corrosion current density significantly reduces for the Pt-coated La-TZM alloy, which shows good corrosion resistance in alkaline medium. The Pt coating can effectively hinder the Cl^-, which destroys the corrosion formed on the surface passivation film, then improves the corrosion resistance of the alloy.

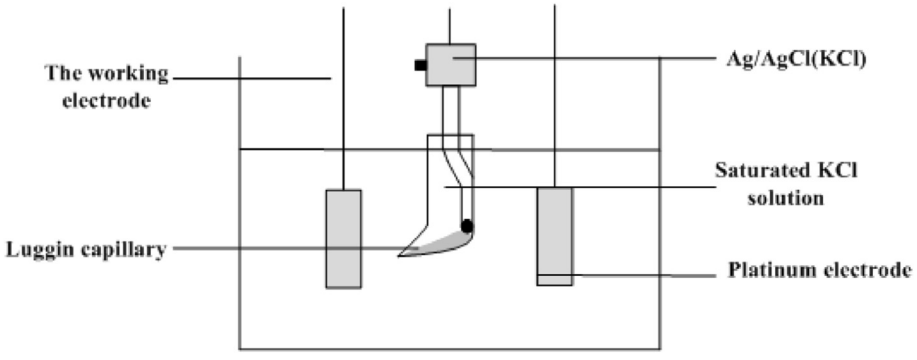

Fig. 1. Schematic diagram of three-electrode system.