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Influence of concentrations of chloride ions on electrochemical corrosion behavior of titanium-zirconium-molybdenum alloy

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ABSTRACT

Titanium-zirconium-molybdenum (TZM) alloy was fabricated by using powder metallurgy and rolling techniques. Electrochemical corrosion behavior of the alloy was studied quantitatively using potentiodynamic polarization and scanning electron microscope. Effect of different chloride ions concentrations on corrosion resistance and electrochemical corrosion mechanism on TZM alloy was investigated. Results show that pitting corrosion and intergranular corrosion of TZM alloy mainly occurs in sodium chloride solution. Corrosion generates firstly in the form of pitting corrosion around second phase particles and increases with corrosive media Cl⁻ concentration increasing, and then the intergranular corrosion occurs along grain boundaries and defects. Cl⁻ corrosion can effectively destroy the passive film formed on the sample surface. As the Cl⁻ concentration of corrosive media increases, the corrosion rate of TZM alloy increases until 1.0 mol/L and then decreases. TZM alloy exhibits good corrosion resistance when the concentration of Cl⁻ in corrosive media is 0.5 mol/L.

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1. Introduction

Titanium-Zirconium-Molybdenum (TZM) alloy, formed by adding a small amount of Ti, Zr and trace elements of C in Mo matrix, has been widely used in aerospace, power generation, nuclear reactor, military and chemical industries due to its excellent properties such as high melting point, high strength and low coefficient of linear expansion [1–4]. TZM alloy is regularly used in special conditions of high temperature, high pressure and strong erosion along with the broadening of application fields. Therefore, the performance of TZM alloy puts forward higher requirements. There are some investigations of the TZM alloy related to high temperature oxidation resistance, physical properties and mechanical properties [5–10]. However, there are few reports on the corrosion behavior of TZM alloy up to date.

Researchers have tested the polarization behavior of

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http://dx.doi.org/10.1016/j.jallcom.2017.03.025 0925-8388/© 2017 Elsevier B.V. All rights reserved. molybdenum alloys in aqueous solution, and analyzed the oxide film formed on its surface [11,12]. The molybdenum alloy exhibits good corrosion resistance. Some studies show that surface passivation film of molybdenum alloys in aqueous solution is mainly composed of Mo and MoO₂ [13,14]. However, some researchers have argued that the passivated form of molybdenum alloy is a chemical adsorption and the surface passivation film is a dense film which is composed of MoO₂ and MoO(OH)₂ [15,16]. Currently, 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 [17-20]. However, the theories of electrochemical corrosion behavior and the corrosion process of TZM alloy are not established systematically under extreme conditions, and there has been few studies on the corrosion behavior of TZM alloy in solutions with different concentrations of Cl⁻.

Based on previous studies [5,7,9,21–25], this study further investigated the electrochemical corrosion behavior of TZM alloy in different Cl^- concentrations, and explored the electrochemical



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corrosion ability and mechanism of corrosion process of the alloy under different concentrations of Cl⁻.

2. Experimental

2.1. Fabrication of TZM alloy

TZM alloy was fabricated by using powder metallurgy. Table 1 lists the compositions of the alloy. Graphite was mixed with TiH_2 and ZrH_2 powders, to obtain TZM alloy. The TZM alloy compacts were fabricated subjected to the processes of 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 150 MPa for 30 s) and multi-stage sintering (passing into protective hydrogen, sintering at 1900 °C for 4 h). Finally, 0.5 mm thick - 10 mm width TZM alloy sheets were fabricated by hotrolling, warm-rolling and caustic washing processes.

2.2. Preparation of TZM alloy electrochemical corrosion sample

The TZM alloy sheets were cut into 10 mm \times 10 mm \times 0.5 mm samples. Firstly, we immersed samples in the acetone on ultrasonic vibration clean instrument oscillating oil removal, and made sure that the sample surfaces were free of oil and impurities; Secondly, water sandpapers of 240 #, 400 # and 600 # were used to pre-grind the working surface and cross-sectional samples to remove the sample surface oxide layer and wire cutting marks, and to prevent the appearance of crevice corrosion during electrochemical corrosion experiments. Then the samples were washed in distilled water and alcohol and through a high temperature conductive adhesive with bonding wire the back of sample. The samples were placed in an Φ 15 mm PVC pipe, to ensure that there was no space between the test sample surface and the transverse cross-section of PVC pipe aligning. The gap between the sample and the PVC pipe was filled with denture powder and then exposed to the outside of the PVC pipe copper wire with silicone encapsulation.

2.3. Test of electrochemical corrosion

Electrochemical corrosion characteristics of the TZM alloy were investigated by using an 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 TZM alloy samples were used as the working electrode, placed in a threeelectrode system electrolyte. By three-electrode connection method, TZM alloy samples were placed in different neutral mediums (Cl⁻ concentration: 0.5 mol/L, 0.7 mol/L, 1.0 mol/L and 1.5 mol/L). The TZM alloy samples were dynamic potential sweep measurements, from which we obtained Tafel and AC impedance (Nyquist) plots.

The electrochemical etching parameters were set as follows: constant test at room temperature; initial potential 500 mV; termination potential 2.0 V; number of scans 1; termination potential holding time for 0 s, the scanning speed 0.5 mV/s. Before the 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

Compositions of TZM alloy (wt%).	

Sample	Ti	Zr	С	Мо
TZM	0.50	0.10	0.06	Balance

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

The corrosion characterization was tested by using a JSM-6460LV scanning electron microscope (SEM). The sample surface was analyzed for electrochemical corrosion morphology, micro-structure and composition.

3. Results and discussion

3.1. Tafel curves

Fig. 2 shows the corrosion polarization curves of the TZM alloy in different Cl⁻ concentrations. In the figure, it can be seen that the overall polarization curve shows that there is significant difference in the corrosion rate of the alloy under the four Cl⁻ concentrations although the differences of TZM alloy passivation characteristics at different Cl⁻ concentrations are not significant. The corrosion rate increases with increasing the Cl⁻ concentrations from 0.5 mol/L to 1.0 mol/L. However, the corrosion rate is significantly reduced with a further increase in Cl⁻ concentration. When the Cl⁻ concentration increased to 1.5 mol/L, the corrosion rate with the minimum value and the alloy corrosion rate are similar with that of the Cl⁻ concentration 0.5 mol/L. The corrosion rate of the alloy reaches a maximum when the concentration of Cl⁻ is 1.0 mol/L, the corrosion rate of TZM allov increases and then decreases with growth of Cl⁻ concentration from 0.5 mol/L to 1.5 mol/L. It can be also seen that the corrosion current density of TZM alloy increases and then decreases with growth of Cl⁻ concentration, which indicates that the rate of dissolution of the surface passivation film increases and then decreases with the growth of Cl⁻ concentration. The corrosion current density has a sudden downward trend when Cl⁻ reaches 1.5 mol/L, then the dissolution rate of TZM alloy surface passivation film is reduced, which discourages further erosion of Cl⁻ on the substrate.

In addition, the anodic current density increases which accelerates the chemical dissolution of the alloy substrate surface when Cl⁻ concentration in the range of 0.5–1.0 mol/L, resulting in the increase of the corrosion current density gradually. The alloy forms at the surface passivation film adsorption Cl⁻ increases with more passivation film through the central plains and some defects. The role of the alloy matrix forms soluble compound in the current action. Meanwhile, Cl⁻ easily forms a colloidal dispersion in the passivation film, which significantly improves electron and ion conductivity of the passivation film and the passivation film on the destruction of the protective effect of the matrix. The passivation film formed on the surface of the TZM alloy ruptures when it reaches a critical concentration rupture of Cl⁻, which results in the further corrosion and pitting of the alloy matrix. Whereas the anode current density is reduced to slow the anode reaction when the concentration increases to 1.5 mol/L, which leads to the alloy surface passivation film mitigating damage and reduces the degree of corrosion of the alloy matrix.

Fig. 3 shows the comparison of corrosion current density and pitting potential of TZM alloy in different Cl⁻ concentrations. In Fig. 3 (a), the corrosion current density of TZM alloy increases and then decreases with increasing the Cl⁻ concentration. The alloy corrosion tendentiousness and the corrosion current density are proportional to an integer under the same conditions, which indicates that the corrosion tendency of the alloy firstly increases and then decreases. However, for the corrosion current density, the pitting potential exhibits opposite trend with the increase of Cl⁻ concentration. At low concentration, the Cl⁻ concentration of alloy Download English Version:

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