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ARTICLE

Electrochemical Corrosion Behavior of Titanium-Zirconium-Molybdenum Alloy

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Abstract: Titanium-zirconium-molybdenum (TZM) alloy and rare earth lanthanum doped La-TZM alloy were fabricated using powder metallurgy and rolling technique. Their electrochemical corrosion behavior was studied quantitatively using potentiodynamic polarization, scanning electron microscope and energy spectrum techniques. Their corrosion behavior was investigated in neutral, acidic and alkaline medium, while keeping the Cl^- concentrations invariant. The results show that the corrosion resistance of the tested TZM alloy is better than that of the La-TZM alloy in neutral and alkaline media, while in an acidic medium, the La-TZM alloy is better. It is also found that the alloys are more corrosion-resistant in an acidic medium than in a neutral medium, and are the least corrosion-resistant in an alkaline medium. Finally, we find that Cl^- effectively destroys the passivation film formed on the corrosion surface; OH^- and Cl^- double erosion promoted these two types of alloy intergranular corrosion increased.

Key words: titanium-zirconium-molybdenum alloy; corrosion; polarization curves; electrochemical properties

A Titanium-Zirconium-Molybdenum (TZM) alloy formed by adding a small amount of Ti and Zr and trace elements of C in an Mo matrix has a high melting point, high strength, low coefficient of linear expansion and excellent high-temperature properties[1-4]. This alloy is widely used in the aerospace, power generation, nuclear reactor, military and chemical industries. The high temperature oxidation resistance, physical properties and mechanical properties of the alloy have been studied in detail[2, 5-7]. However, to date, there are few reports on the corrosion behavior of TZM alloys[8-9]. It is essential to study the corrosion resistance of the alloy in order to explore whether its scope of application can be further enhanced.

Our previous studies[6,10-12]have shown that a TZM alloy doped with the rare earth metal lanthanum (La-TZM) 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 which hinders oxygen intruding matrix effectively. The molybdenum oxide layer generated on the TZM alloy expanding outward and extremely volatile, causes the alloy matrix to gradually erode due to the presence of molybdenum oxide. In the present paper, the effect of Cl^- content in neutral, acidic and alkaline media on the electrochemical corrosion properties of the alloys (TZM and La-TZM) were investigated.

1 Experiment

Two kinds of TZM alloys were prepared: TZM alloy and La-doped TZM alloy. Table 1 lists the composition of the

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Table 1 Composition of TZM alloys (wt%)

No.	Ti	Zr	C	Stearic acid	La_2O_3	$La(NO_3)_3$	Mo
1	0.50	0.10	0.06	0.00	0.00	0.00	Bal
2	0.50	0.10	0.06	0.00	1.00	0.00	Bal
3	0.50	0.10	0.00	0.25	0.00	1.99	Bal

Note: 1-TZM, 2- La_2O_3-TZM, 3- $La(NO_3)_3$-TZM. Mole percent of La_2O_3 is equal to that of $La(NO_3)_3$, as well as those graphite and stearic acid

alloys. 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 TZM and La-TZM alloy compacts were fabricated using 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 21 MPa for 5 s) and multi-stage sintering (passing into protective hydrogen, subsection sintering: maintaining each of the temperature 300, 900 and 1200 °C for 2 h, and finally sintering at 1900 °C for 4 h). From the TZM and La-TZM alloys, 0.5 mm thick square plates measuring 10 mm on a side were fabricated by hot-rolling, warm-rolling and caustic washing.

The electrochemical corrosion characteristics of the alloys were investigated 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 as an auxiliary electrode. The TZM alloy and La-TZM alloy samples were used as the working electrode, and placed in a three-electrode system electrolyte. By a three-electrode connection method, the TZM alloy, La_2O_3-TZM and $La(NO_3)_3$-TZM alloy sample was placed in an acidic medium (Cl^- content 3.5%, H^+ content 1 mol/L), and then in neutral and alkaline (OH^- content 1 mol/L) The dynamic potential sweep measurements were performed to obtain Tafel plot. The electrochemical etching parameters were set as follows: constant test 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; automatic mode.

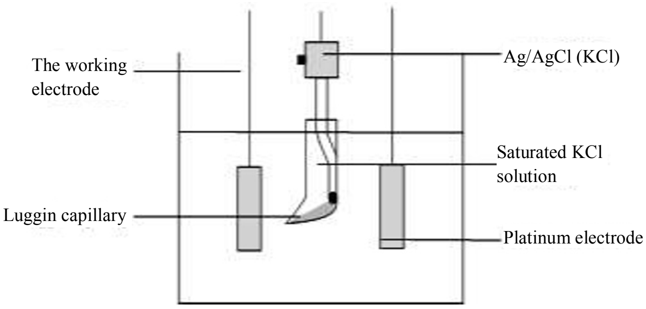

Fig.1 A typical schematic diagram of three-electrode system sulfuric acid and ethanol solution, which were electrolytic polished and thinned to micro perforated by double-jet

The corrosion characteristics were observed using a JSM-6460LV scanning electron microscope. The sample surface was analyzed for electrochemical corrosion morphology, microstructure and composition. The TEM samples were tested on JEM-200CX transmission electron microscopy. The two alloy samples were sliced, polished and mechanically thinned to 30~50 μm in 5%.

2 Results and Discussion

2.1 Microstructure of TZM alloy and La-TZM alloy

Previous studies[13-16] have shown that the mechanical properties of the TZM alloy doped with the rare earth metal Lanthanum (La-TZM) are superior to those of the TZM alloy (room temperature tensile strength 1341 MPa; elongation 7.5%, DBTT as low as 120 °C).

The TEM images of the TZM alloy and La-TZM alloy are shown in Fig.2. Fig.2a shows that the doping element is evenly distributed within the crystal and forms a distinct dislocation pinning. Fig.2b shows small (submicron and nanoscale) lanthanum oxide grains, mainly ellipsoidal and globular in shape, disperse in the alloy matrix. Comparing Fig.2a and 2b, since the fine sub-micron and nano-scale lanthanum oxide particles have high strength, the dislocations occur in front of lanthanum oxide particles bending. The lanthanum particles can significantly improve the yield strength of rare earth oxide doped lanthanum TZM alloy by hindering dislocation loops from moving. And therefore the mechanical properties of rare-earth doped La-TZM alloy are superior to those of TZM alloy.

2.2 Electrochemical corrosion characteristics of TZM alloy and La-TZM alloy

Table 2 and Fig.3 show the corrosion rate and polarization curves of the TZM alloy and La-TZM alloy in acidic, neutral

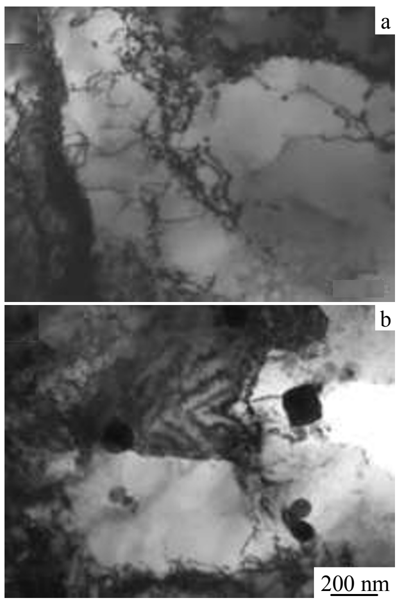

Fig.2 TEM images of TZM alloy (a) and La-TZM alloy (b)