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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 ℃ 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 ℃ for 2 h, and finally sintering at 1900 ℃ 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.

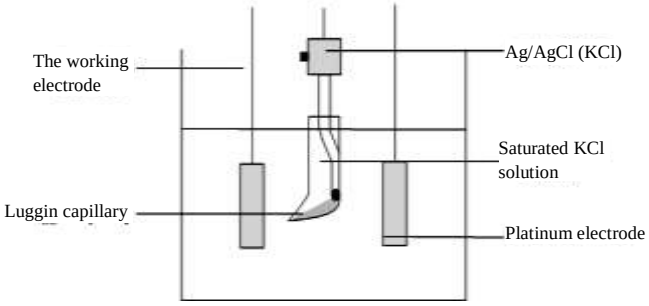

Fig.1 A typical schematic diagram of three-electrode system sulfuric acid and ethanol solution, which were electrolytic polished and thinned to micro perforated by double-jet

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 ℃).

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

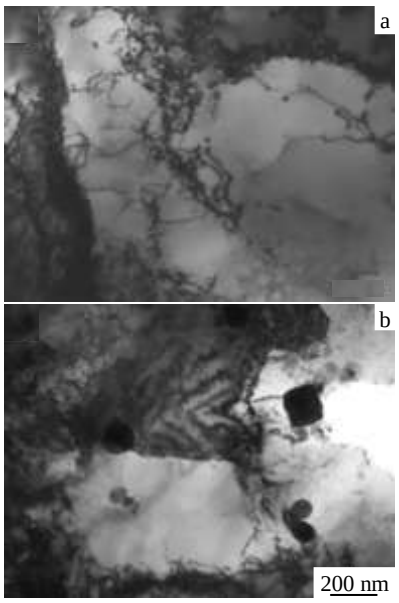

Fig.2 TEM images of TZM alloy (a) and La-TZM alloy (b)

Table 2 Electrochemical test results of TZM alloy and La-TZM alloy in different mediums

Sample	Mediums	Corrosion potential, E_{corr}/V	Corrosion current density, I_{corr}/ A·cm^{-2}
TZM	Acidic	–0.3828	3.96×10^{-6}
	Neutral	–0.4150	5.49×10^{-6}
	Alkaline	–0.8246	1.49×10^{-5}
La_2O_3-TZM	Acidic	–0.2949	3.23×10^{-6}
	Neutral	–0.4487	9.85×10^{-6}
	Alkaline	–0.9028	2.04×10^{-5}
$La(NO_3)_3$-TZM	Acidic	–0.3562	3.31×10^{-6}
	Neutral	–0.4278	7.17×10^{-6}
	Alkaline	–1.033	2.13×10^{-5}

and alkaline media. Table 2 shows that the TZM alloy and La-TZM alloy exhibit a greater corrosion rate in the alkaline medium, while their corrosion rate in the acidic medium of the least. For the alkaline medium, the presence of both OH^- and Cl^- leads to the double rate of corrosion and surface pitting. It also causes intergranular corrosion, so for both TZM alloy and La-TZM alloy, the corrosion rates are accelerated. Compared with the alkaline medium, the corrosion rates for both alloys are slow in neutral and acidic media, because the two types of alloys using powder metallurgy have good corrosion resistance in acidic medium, making the alloy corrosion rate in the acidic medium the slowest.

Fig.3 shows the polarization curves of the two alloys in different media. It can be seen that the corrosion rate of La-TZM alloy is faster in neutral and alkaline media. The corrosion rate of the TZM alloy is faster in the acidic medium. Therefore, TZM alloy has better corrosion resistant Cl^- and OH^- ability, and La-TZM alloy has better corrosion resistant H^+. In neutral and alkaline media, firstly, the doping element in the La-TZM alloy makes it more prone to pitting corrosion, pitting spread and more intergranular corrosion. Secondly, the rare earth element La on the internal grain boundaries can enhance free oxygen adsorption, and pinning effect is apt to consume oxygen. Cl^- and OH^- constantly corrode the internal matrix when the oxide film forms oxide. In the acidic medium, SO_4^{2-} weakening La element for oxygen adsorption and pinning effect. Meanwhile, the sulfuric acid corrosion resistance is stronger in La doped TZM alloy.

2.3 Corrosion surface microstructure of TZM alloy and La-TZM alloy

Fig.4a and 4b show the SEM images of TZM alloy corrosion surface and Fig.4c~4f are the La-TZM alloy corrosion surface in the acidic medium. It can be seen from Fig.4a, 4c, and 4e that the outermost surface layers of TZM alloy corrosion have fallen off, and the net corrosion layer has already occurred. In comparison, the outermost surface layer of La-TZM alloy corrosion has not yet started to fall. This implies that the corrosion resistance of the La-TZM alloy is stronger than that of the TZM alloy in acidic media. It is the same conclusion as that drawn from the above electrochemical test analysis. The two alloy mesh surface morphologies are similar. The lines become widened gradually into grooves and troughs, crossing one another and dividing the corrosion surface into small pieces. New pits occur in the grooves, troughs and then spread to the depths of the alloy matrix.

Fig.5a and 5b show the SEM images of TZM alloy corrosion surface, and Fig.5c~5f show SEM images of the La-TZM alloy corrosion surface in the neutral medium. It can be seen that the corrosion surface of the La-TZM alloy is characterized by wide grooves, cracking, pitting and greater corrosion at depth. In comparison, the extent of corrosion in the TZM alloy is much less. The same conclusion can be also drawn from the above electro-chemical test analysis. The corrosion mechanism in the La-TZM alloy is mainly characterized by surface pits at the grain boundaries, leading to intergranular corrosion. The residual corrosion layer on the surface shows a large number of scattered uniform corrosion pores. When the corrosion layer loses its binding force, it separates and falls off from the matrix. Inside the grooves of matrix deeper corrosion appears. The corrosion degree of TZM alloy is slight. The surrounding alloying elements still have a tendency to crack. There occurs small amount of pitting, and the corrosion traces extend around from the added alloying elements.

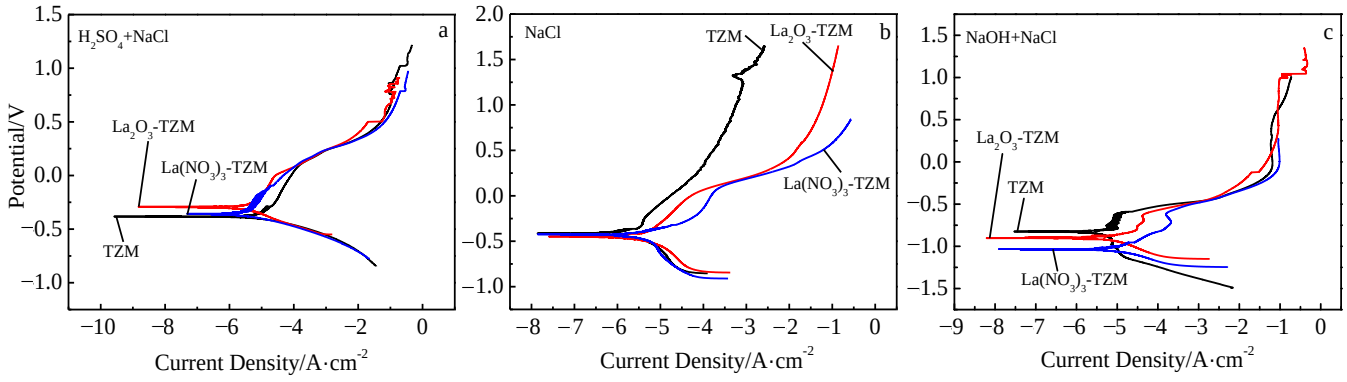

Fig.3 Tafel curves of TZM and La-TZM in different mediums: (a) acidic medium, (b) neutral medium, and (c) alkaline medium

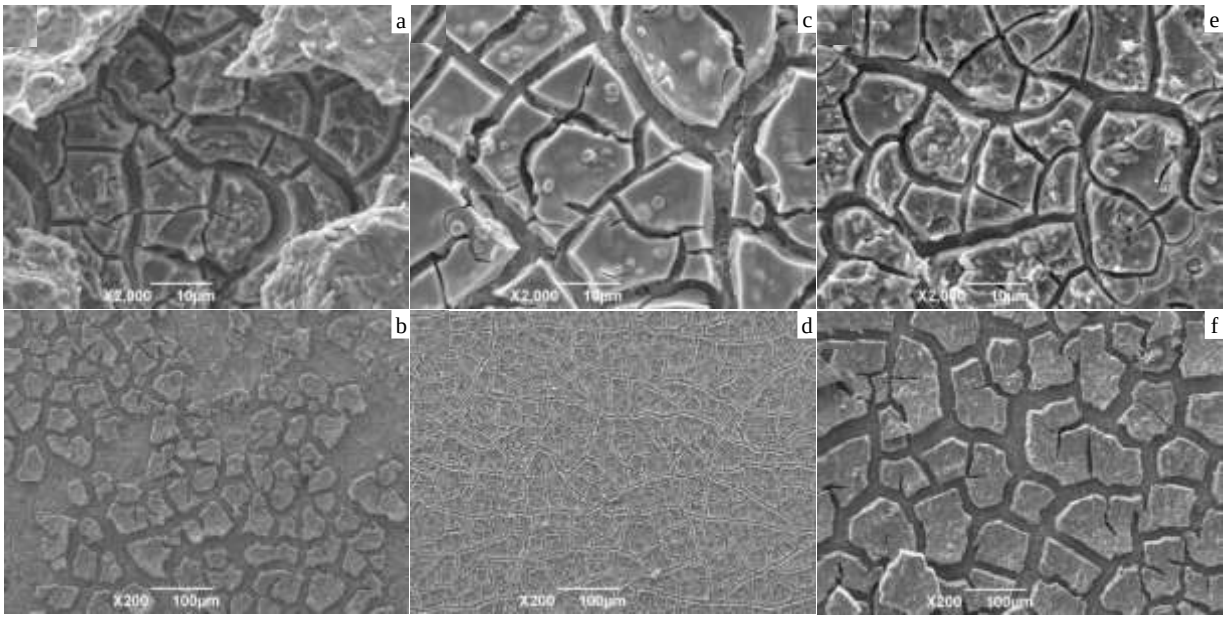

Fig.4 SEM images of the TZM alloy and La-TZM alloy corrosion surface in the acidic medium: (a, b) TZM alloy, (c, d) La_2O_3-TZM alloy, and (e, f) $La(NO_3)_3$-TZM alloy

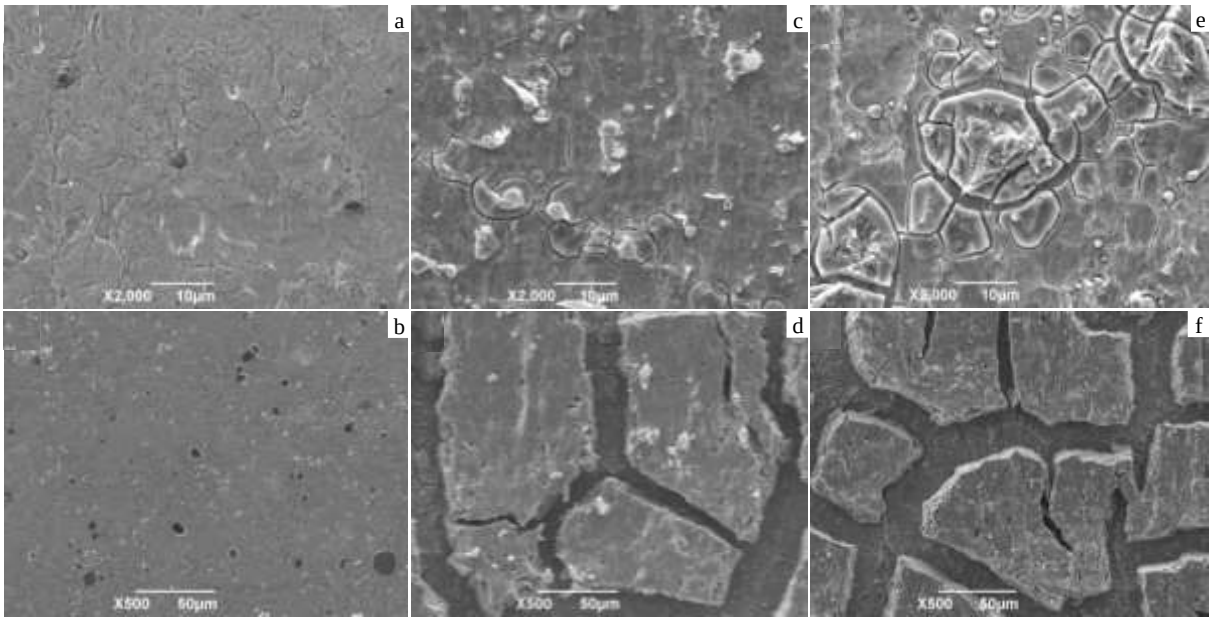

Fig.5 SEM images of the TZM alloy and La-TZM alloy corrosion surface in sodium chloride solution: (a, b) TZM alloy, (c, d) La_2O_3-TZM alloy, and (e, f) $La(NO_3)_3$-TZM alloy

Fig.6 shows the SEM images of TZM alloy and La-TZM alloy corrosion surface in the alkaline medium. It can be seen that the corrosion grooves of the La-TZM alloy are significantly wider and deeper than those in the TZM alloy. This implies that the corrosion resistance of the TZM alloy is stronger than that of La-TZM alloy in the alkaline medium. This is the same conclusion as drawn from the above electrochemical test analysis. For both alloys, the surface morphology is similar. The surface is divided into a network of many corrosion sites, corroding into the matrix, and forming a corrosion groove. New pits appear in the body of the matrix in all directions.

Fig.7 shows the corroded surface microstructure and spectrum analysis of the La-TZM alloy. It can be seen from Fig.6f that the surface corrosion begins along the grain boundaries. This corrosion surface belongs to the typical morphology of intergranular corrosion, due to the large activity of grain boundaries, etching process produces

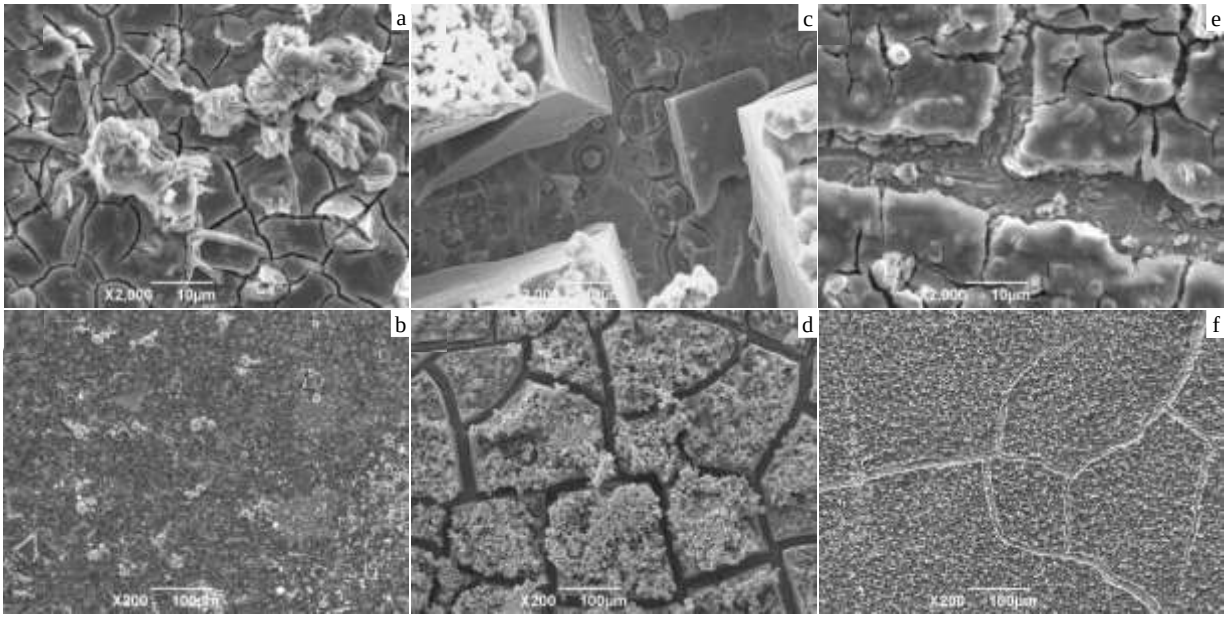

Fig.6 SEM images of the TZM alloy and La-TZM alloy corrosion surface in an alkaline medium: (a, b) TZM alloy, (c, d) La_2O_3-TZM alloy, and (e, f) $La(NO_3)_3$-TZM alloy

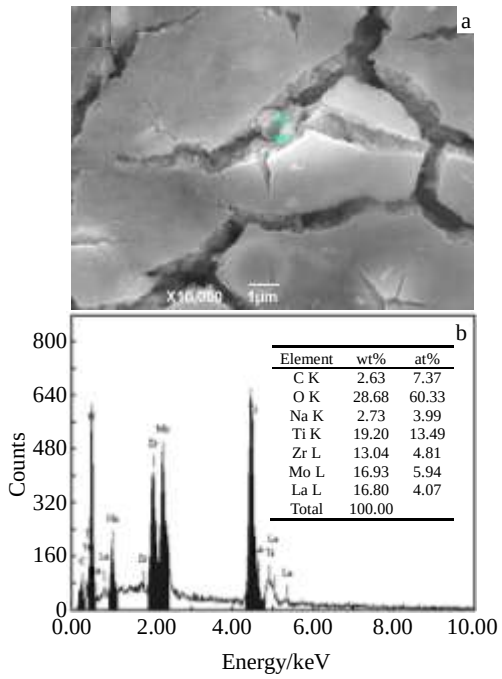

Fig.7 Surface corrosion morphology (a) and EDS spectrum analysis (b) of La-TZM alloy

localized corrosion from intergranular boundary or near the grain boundaries. Fig.7a shows a detail of the etched surface microstructure. It can be observed that the corrosion layer material has been seriously damaged. At the same time, the agglomerated-like corrosion products can be seen in the corrosion cracking area. Fig.7b shows that the oxygen content of corrosion material surface increases obviously, indicating that the most corrosion product is oxide. We could speculate that corrosion mechanism of action is under current role; due to oxidation-reduction, Mo alloy is oxidized into molybdenum oxide. Molybdenum oxide in the form of a thin film covers the surface of the alloy matrix, and some of molybdenum oxide will also grow into a reunion oriented structure in the electrolyte.

In summary, TZM alloy and La-TZM alloy corrosion microscopic structure of the surface are closely related with the corrosion potential and corrosion current density of the material. Material is fretted in a variety of corrosive media after a larger-rate corrosion. The microscopic changes in the structure of the alloy surface more greatly. With higher corrosion rate, the microstructure changes more obviously.

3 Conclusions

1) There are large differences in the corrosion rates in materials having different structures in various corrosive media. The corrosion rates of the tested TZM alloy and La-TZM alloy are maximum in an alkaline medium, followed by those in neutral and acidic media. The presence of OH^- and Cl^- in alkaline media intensifies the corrosion rate. Cl^- can destroy the passivation film formed on the surface effectively. TZM alloy and La-TZM alloy have a good resistance to acidic medium erodibility.

2) The corrosion rate of the TZM alloy is higher than that of La-TZM alloy in an acidic medium. The corrosion rate of the La-TZM alloy is higher than that of the TZM alloy in neutral and alkaline media. It can be concluded that the TZM alloy prepared by powder metallurgy has superior resistance to Cl^-

and OH^- ability to La-TZM alloy, i.e. TZM alloy is more suitable for neutral and alkaline conditions. La-TZM alloy possesses better acid erosion resistance than TZM alloys, namely La-TZM alloy is more suitable for acidic conditions.

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TZM 合金电化学腐蚀行为研究

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摘　要：采用粉末冶金和轧制工艺制备出 TZM 合金和稀土镧掺杂的 La-TZM 合金，通过动电位极化研究合金电化学腐蚀行为，扫描电子显微镜观察、能谱定量分析表征腐蚀产物显微结构特征。保持 Cl^-浓度不变分别探讨合金在中性、酸性、碱性介质中耐侵蚀能力。结果表明，TZM 合金在中性和碱性介质中抗腐蚀性能优于 La-TZM 合金，而在酸性介质中 La-TZM 合金抗腐蚀性能优于 TZM 合金，两类合金抗腐蚀性均表现为酸性介质强于中性介质，碱性介质最弱。Cl^-有效破坏腐蚀表面形成的钝化膜，OH^-和 Cl^-双重侵蚀促使两类合金晶间腐蚀加剧、粉末冶金制备的 TZM 合金及 La-TZM 合金对酸性介质具有良好的耐蚀性。

关键词：TZM 合金；腐蚀；极化曲线；电化学特性

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