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Electrochemical behavior and microstructural characterization of lanthanum-doped titanium-zirconium-molybdenum alloy

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Lanthanum-doped titanium-zirconium-molybdenum (La-TZM) alloy with high strength and high toughness was prepared by powder metallurgy and rolling process. The influence of OH^- concentrations (5%, 7% and 10%) on the electrochemical behaviors of La-TZM alloys was investigated by potentiodynamic polarization tests. Scanning electron microscopy (SEM) was used to characterize the microstructure and energy dispersive spectroscopy (EDS) was used to analysis the secondary phase. The electrochemical corrosion mechanism was analyzed comprehensively. The results reveal that the corrosion rate of La-TZM alloy first decreases and then increases with the increasing of OH^- concentration. The pitting corrosion firstly occurs around the secondary phase particles (La-Ti-Zr-O), and expands along the grain boundaries and defects as the potential increasing. The addition of rare earth element La affects the formation of passive film on the surface and reduces the corrosion resistance of the alloy. The micro galvanic couples between the secondary phase and the matrix accelerate the corrosion of the base material. Therefore, according to the environment, the corrosion resistance and the mechanical properties should be both considered in the process of strengthening alloy with additive elements.

1. Introduction

It is well known that corrosion greatly threatens the safety and practicability of metal materials, which plays an important role in industrial applications [1]. Usually, alloying elements are added to improve the mechanical properties of metal materials. With the improvement of mechanical properties, the application environment of metal materials is more and more severe. Therefore, much more attention has been paid to the research on the corrosion behavior of metal materials.

Titanium-zirconium-molybdenum (TZM) alloy is one of the widely used molybdenum-based alloy, which contains alloying elements titanium (Ti), zirconium (Zr) and carbon (C) [2]. The TZM alloy has extensive used in the aerospace, power generation, nuclear reactors and chemical fields because of its high mechanical properties [3–7]. Lanthanum-doped titanium-zirconium-molybdenum (La-TZM) alloy is a new type of molybdenum-based alloy, which is based on TZM alloy with adding a certain amount of rare earth element lanthanum (La). The presence of lanthanum oxide particles lead to better properties of La-TZM alloy than TZM alloy [8]. Some researchers have been carried out on the high temperature oxidation resistance [9,10], physical properties [11] and mechanical properties [12–14] of La-TZM alloy. The tensile strength and elongation were increased by 40% and 26% and reached 1295 MPa and 8.09%, respectively [14]. The addition of rare earth element La further expands the application of La-TZM alloy, and the wider application environment puts forward higher requirements for the corrosion resistance of La-TZM alloy.

W.A. Badawy et al. [15] investigated the corrosion and passivation behaviors of molybdenum in aqueous solutions. The passivation film was formed on the surface of molybdenum, and the passive film was unstable in alkaline solution. J.G. Gonzalez-Rodriguez et al. [16] studied the corrosion performance of Mo-22Si and Mo-25Si alloys in 0.5 M sodium chloride (NaCl) and 0.5 M sodium hydroxide (NaOH) solutions. They found that Mo-

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22Si alloy developed a passive film in 0.5 M NaOH solution, whereas Mo-25Si alloy was passivated only in 0.5 M NaCl, pH = 10 solution. And the Mo-22Si alloy showed the most corrosion resistant in 0.5 M NaCl, pH = 7 and 0.5 M NaOH solutions. Y.L. Zhou et al. [17] reported the corrosion resistance of Ti–Mo alloys increased with Mo content and Ti–Mo alloys showed better corrosion resistance than commercial pure Ti. Both Ti–10Mo and Ti–20Mo alloys exhibited a passive behavior. However, few studies focus on the corrosion behavior of La-TZM alloy.

In our research group's previous work, the corrosion behavior of TZM and La-TZM was compared in neutral, acidic and alkaline medium, while keeping the Cl^- concentrations invariant. It was found that the two alloys were more corrosion resistant in an acidic medium than in a neutral medium, and the least corrosion resistant in an alkaline medium due to the double erosion of OH^- and Cl^- [18]. In this paper, the influence of OH^- concentrations on electrochemical corrosion behavior of La-TZM alloy is particular studied. The effect of La on corrosion resistance and microstructures of La-TZM alloy are also observed. The corrosion mechanism of La-TZM alloy, which is related to the secondary phase particles is investigated. This work will provide the necessary theoretical support for the application of La-TZM alloy in alkaline condition, and give a reference for the selection of the doped elements in the preparation of molybdenum-based alloy.

Table 1
Design composition of La-TZM alloy (wt.%).

Sample	TiH_2	ZrH_2	Fructose	$La(NO_3)_3$	Mo
$La(NO_3)_3$-TZM	0.54	0.11	0.25	1.99	balanced

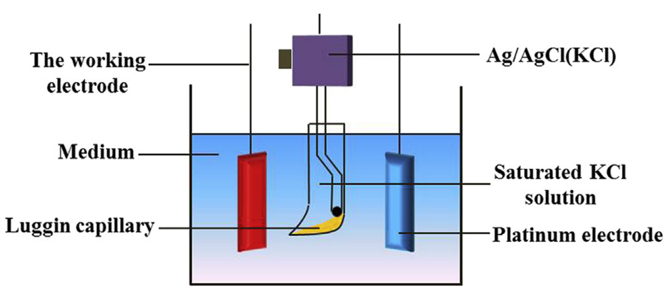


Fig. 1. A typical schematic diagram of three-electrode system.

Table 2
Chemical composition of La-TZM alloy (wt.%).

Element	La	Ti	Zr	C	O	Fe	Ni	Mo
wt.%	0.983	0.650	0.073	0.027	0.44	0.013	0.007	balanced

2. Experimental

2.1. Preparation of La-TZM alloy samples

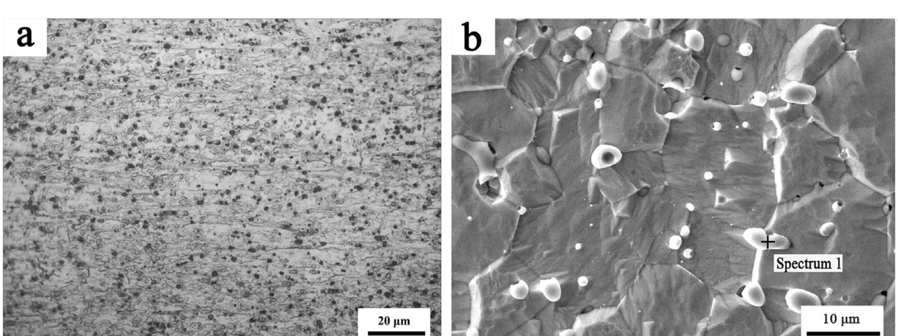
The La-TZM alloy is prepared by powder metallurgy process, and the design composition is shown in Table 1. Lanthanum nitrate and fructose were dissolved in absolute ethanol respectively, then the liquid blenders were mixed with commercial molybdenum powder (Jinduicheng Molybdenum Group Co., Ltd.), TiH_2 powder (Xi'an Baode Powder Metallurgy Co., Ltd.) and ZrH_2 powder (Xi'an Baode Powder Metallurgy Co., Ltd.) by liquid-solid doping method. Through mixing, ball milling, stirring, vacuum drying, pressing forming and high temperature sintering, the La-TZM alloy plate was obtained. The relative density of the sintered samples is 98.36%. Three square La-TZM alloy sheets with a thickness of 0.5 mm and a side length of 10 mm were prepared by rolling, alkaline washing and wire cutting.

The oil and impurity of the samples were cleaned by acetone through ultrasonic cleaning instrument. Three 10 mm × 10 mm surfaces were selected from each sample as the test surfaces at random, then grinded with 240#, 400#, 600# and 800# abrasive papers to eliminate cutting marks and oxide layer. Copper wires were connected with the back of the samples through high temperature conductive adhesive. The samples were then placed in Φ15 mm PVC tubes. The test surfaces of the samples were flush with the cross sections of the PVC tubes, and the interspace between the samples and the PVC tubes were filled with epoxy resin. Finally, the test surfaces were polished, washed with deionized water and alcohol and then dried in time. The samples were used as the working electrodes in electrochemical tests.

2.2. Electrochemical test

Electrochemical tests were performed using an electrochemical workstation PARSTAT4000A Instruments (ametek, America) controlled by a computer and software. The three-electrode method was used in the experiments, as shown in Fig. 1. The electrochemical measurements were conducted using a thin platinum plate as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the La-TZM alloy sheet as the working electrode. All the potentials described in the paper were relative to the SCE.

The potentiodynamic polarization curves (PC) and electrochemical impedance spectroscopy (EIS) measurements were carried out in NaOH solutions with different concentrations



Elements of spectrum 1	Mass %	Atom %
O	28.01	68.2
Ti	19.61	15.95
Zr	1.86	0.79
Mo	7.02	2.85
La	43.5	12.2
Total	100	100

Fig. 2. Microstructure of La-TZM alloy and component analysis of the secondary phase particle. (a)Microstructure; (b) EDS of the secondary phase particle.