Journal of Alloys and Compounds 686 (2016) 1037–1043

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Pt-plating effect on La-TZM alloy high temperature oxidation behavior

Ping Hu [a, b, *], Fan Yang [a, b], Rui Song [a, b], Kuai-She Wang [a, b, **], Bo-Liang Hu [a, b], Wei-Cheng Cao [c], Dong-Xin Liu [c], Xuan-Qi Kang [d], Alex A. Volinsky [e]

[a] School of Metallurgy Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China
[b] State Local Joint Engineering Research Center for Functional Materials Processing, Xi'an, 710055, China
[c] Jinduicheng Molybdenum Co., Ltd., Xi'an, 710068, China
[d] Xi'an Taijin Industrial Electrochemical Technology Co., Ltd., Xi'an, 710016, China
[e] Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA

ARTICLE INFO

Article history:
Received 22 April 2016
Received in revised form
18 June 2016
Accepted 20 June 2016
Available online 25 June 2016

Keywords:
La doped
La-TZM alloy
Pt plating
High temperature oxidation

ABSTRACT

Pt coating on La-TZM alloys can effectively hinder the matrix alloy oxygen corrosion during high temperature oxidation processes. Doping powder metallurgy was used to prepare La-TZM alloy plates (doped with lanthanum), and electroplating was utilized to deposit a platinum coating on the plate surface. After high temperature treatment of the Pt-coated La-TZM alloy samples at different times and temperatures, scanning electron microscopy and energy dispersive spectra analysis of the sample surface and cross-sections were performed to observe the microstructure and composition changes. Differential thermal analysis of the Pt-coated La-TZM alloy specimens after high temperature treatment was performed to assess the high temperature oxidation resistance of the coated matrix alloy. The results show that the oxidation resistance of the TZM alloy can be enhanced, expanding its temperature application range.

1. Introduction

TZM alloys (contains 0.5–0.8 wt% titanium, 0.08–0.1 wt% zirconium, 0.016–0.02 wt% carbon and molybdenum balance) are molybdenum-based alloys widely used in aerospace, power generation and nuclear reactors such as key parts in aircrafts, turbines and fusion reactors due to their high strength, high melting point, high rigidity, high corrosion resistance, low coefficient of linear expansion, good mechanical properties at high temperatures, and good thermal conductivity [1–3]. However, TZM alloy applications are greatly limited due to poor oxidation resistance at high temperatures [4–6]. Moreover, the poor oxidation resistance of TZM alloy especially limit the application of melting glasses as electrode materials. Studies have shown that TZM alloy oxidation rates are very slow and the alloy surface generates less volatile MoO_2 when the temperature is below 400 °C. The oxidation weight gaining increases rapidly by generating volatile MoO_3 when temperatures were between 400 °C and 750 °C. A sharp decline in weight gain and severe loss of the oxide due to the volatile MoO_3 was observed when the temperature was above 750 °C [7].

Many protecting methods have been created to protect TZM alloy such as brush coating, pack cementation coatings, physical vapour deposition coatings, electroplate coatings, etc. The necessary surface properties of coating layers including strong bonding with TZM alloy, uniform coatings of structure and oxidation stability under extreme environments [8]. In the coating processes, the electroplating is an attractive method to protect the surface of alloys for the strong bond strength between coating materials and substrate due to the interdiffusion reactions. Furthermore, the electroconductibility of alloy materials can be enhanced by electroplating high conductivity materials such as Au, Pt, Ti alloys, etc.

Our previous studies have shown that lanthanum-doped La-TZM alloys can increase the oxidation reaction initiation temperature by 50–100 °C in air, effectively slowing the oxidation rate [9]. However, the anti-oxidation properties of the lanthanum-doped La-TZM alloy at elevated temperatures remained limited, requiring further studies for improvements. In this paper, a rare-earth doped lanthanum La-TZM alloy plate was prepared by powder metallurgy and rolling processes, then, Pt coating was electroplated. Pt-coated La-TZM alloys were prepared to study the anti-oxidation coating behavior at high temperature.

* Corresponding author. School of Metallurgy Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China.
** Corresponding author. School of Metallurgy Engineering, Xi'an University of Architecture and Technology, Xi'an, 710055, China
E-mail addresses: huping1985@126.com (P. Hu), wangkuaishe888@126.com (K.-S. Wang).

http://dx.doi.org/10.1016/j.jallcom.2016.06.183
0925-8388/

2. Experimental procedure

2.1. Preparation of the La-TZM alloy plate

Lanthanum doped TZM alloys were prepared by the powder metallurgy process with the composition listed in Table 1. Liquid-solid mixing and ball-milled processes were used to prepare the La-TZM alloy, and the preparation process of the 0.5 mm thick La-TZM alloy plates is described in the previous publication [9]. The prepared La-TZM alloy plates were wire cut into 10 × 10 × 0.5 mm and 4 × 4 × 0.5 mm squares for the coating process and thermal analysis.

2.2. Coating preparation

In this study, Pt was electroplated on the La-TZM alloy plates. Ingredients of the acidic bath were H_2PtCl_6 (Chloroplatinic acid), K_2SO_4 and K_2SO_3, and the solution pH was adjusted to 1 using H_2SO_4. The Pt electrode material was used as electroplating electrode. Current density, temperature and time were strictly controlled during electroplating. As a result, a uniform, dense and well-adhered Pt coating with average thickness of 6 μm was obtained.

2.3. High temperature oxidation experiments

The TZM alloys are usually used in extreme high temperature above 1000 °C, even 1400 °C. According to the oxidation behavior and the application environment, the specimens (10 × 10 × 0.5 mm squares) were placed in a heating furnace under the air for the high temperature oxidation tests at 400 °C, 600 °C, 800 °C, 1000 °C, 1200 °C and 1400 °C, respectively. For the lower temperature tests at 400 °C, 600 °C, 800 °C and 1000 °C, the holding time was 1 h, 2 h, 3 h and 4 h. For the higher temperature tests at 1200 °C and 1400 °C, the holding time was 15 min, 30 min and 45 min respectively. The sample mass was measured before and after oxidation with 0.0001 g accuracy using the analytical balance, allowing the calculation of the oxidation mass loss of the sample.

2.4. Sample characterization

JSM-6460LV scanning electron microscope (SEM, JEOL, Japan) was used for the samples surface, microstructure and cross-sectional morphology characterization after high temperature oxidation. Energy dispersive spectra (EDS) analyzer was used to obtain the surface composition.

2.5. Comprehensive thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetry (TG) experiments were conducted with the Pt-coated La-TZM alloy samples (4 × 4 × 0.5 mm squares) in air by using the STA449F3 differential thermal analyzer (DTA, NETZSCH, Germany). The temperature was varied from room temperature to 1300 °C with a 10 °C/min heating rate, with the flow rate of 20 ml/min. The DSC-TG curves were used to analyze the thermogravimetric loss and the reactions mechanism.

Table 1
Composition of the La-TZM alloy (wt%).

Ti	Zr	Stearic acid	$LaNO_3$	Mo
0.5	0.1	0.25	1.99	Balance

3. Results and analysis

3.1. Oxidation kinetics analysis

Fig. 1 shows the oxidation mass loss of the Pt-coated La-TZM alloy samples heated at 400 °C, 600 °C, 800 °C and 1000 °C for 15 min, 30 min, 45 min, 1 h, 2 h, 3 h and 4 h, respectively. For the samples heated at 1000 °C, 1200 °C and 1400 °C, the holding time was 15 min, 30 min and 45 min, respectively. Based on Fig. 1, the mass loss of the Pt-coated La-TZM alloy gradually increased with the holding time. Almost no mass loss happened when the oxidation temperature was below 600 °C, indicating no obvious oxidation. The mass loss showed a rising trend with the oxidation temperature increasing. The oxidation was apparent when the temperature rose to 800 °C, and held for 1 h. More mass was lost at 2 h, and the mass loss was about 60% after 4 h, indicating that the substrate oxidized seriously. The mass loss was 13.31% when the temperature rose to 1000 °C after heating 15 min, reaching 44.53% after 1 h oxidation, while more than half of the substrate oxidized when the oxidation time was more than 2 h. As seen in Fig. 1, steep oxidation happens at high temperatures (1000–1400 °C, 15, 30, 45 min holding time), especially at 1400 °C after heating 45 min of 80% mass loss, indicating that the oxidation mass loss increases and oxidation was more severe as the temperature rises.

Table 2 shows the comparison of the oxidizing mass loss between the Pt-coated La-TZM and uncoated La-TZM alloy samples from the previous studies at 800 °C and 1000 °C under different holding times, the oxidation date of uncoated La-TZM alloy comes from the reference [9]. From the table it can be seen that the mass loss of the uncoated La-TZM alloy were 24.49% and 56%, while they were 2.24% and 13.31% for the Pt-coated La-TZM alloy heated at 800 °C and 1000 °C held for 15 min, decreased by 90.85% and 76.23% respectively. Then, the mass loss of the Pt-coated La-TZM alloy and uncoated La-TZM alloy were 6.64% and 40.81% while heated at 800 °C held for 30 min. When heated at 1000 °C, the mass loss of the Pt-coated La-TZM alloy and uncoated La-TZM alloy were 19.29% and 91.83% respectively held for 30 min. The mass loss of the Pt-coated La-TZM alloy were obvious lower than it of the uncoated La-TZM alloy. While the uncoated La-TZM alloy was nearly completely oxidized at 1000 °C for 30 min, the Pt-coated La-TZM seems started to be oxidized. This clearly demonstrates that the Pt coating can effectively hinder oxidation and the alloy matrix corrosion, increasing the anti-oxidation properties of the TZM alloy.

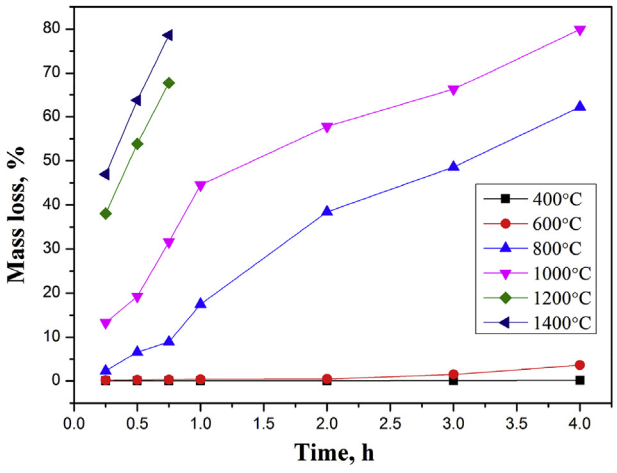

Fig. 1. Oxidation mass loss of the samples tested at different temperature.

Table 2
The mass loss of the alloy plates at 800 °C and 1000 °C.

Heating temperature (°C)	Holding time (min)	Mass loss (%)	
		La-TZM	Pt-coated La-TZM
800	15	24.49	2.24
800	30	40.81	6.64
1000	15	56	13.31
1000	30	91.83	19.29

3.2. Oxidation characterization of Pt-coated La-TZM alloy plates

3.2.1. Surface analysis of platinum coating

Fig. 2 shows SEM surface topography images and surface EDS elements analysis of the Pt-coated La-TZM alloy plates. As seen in Fig. 2a, the coating is uniformly distributed with round particulates on the substrate surface with no cracks or flaking and no hole defects. Fig. 2b shows the dense Pt coating exist on surface of the alloy plate, indicating good adhesion between the Pt coating and the substrate.

3.2.2. Surface morphology and EDS analysis of oxidation layer

Fig. 3 and Fig. 4 show the surface SEM images and EDS profiles of the Pt-coated La-TZM alloy plates oxidized at 400–1400 °C for different times, compared with the previous studies of the La-TZM alloy surface oxide layer morphology [9] (Fig. 5a and Fig. 5b). Fig. 3a, b and c show that the Pt-coated La-TZM alloy plate surface is not damaged by oxygen corrosion, and there are no hole defects when the oxidation temperature is below 600 °C as well as 800 °C for 15 min. Combined with EDS analysis (Fig. 4a and b), it shows that the O content is very small, thus no molybdenum oxides appear, and the surface topography is still intact. In Fig. 3d, e and f, the sample surface had white spots when the oxidation temperature was above 800 °C. Combined with the spectroscopy analysis (Fig. 4c), it shows that the Mo oxide was generated on the surface after oxidation, resulting in decreased surface conductivity. Fig. 3d shows a small amount of holes seen on the plate surface when the oxidation temperature is 800 °C, indicating that the matrix alloy has being corroded by oxygen at the surface. As seen in Fig. 4c, the energy spectra of O and Mo point to the Mo oxide generated at the hole. Oxidation in the lower temperature range of 400–800 °C showed that the alloy plate was remained stable until 4 h heating at 800 °C.

Fig. 3e and f show surface SEM images of the alloy plates oxidized at 1000 °C for 15 min and 4 h. The alloy plate surface was gradually corroded by oxygen with pronounced surface cracking. Lamella oxide coating appeared on the surface of the alloy with the smaller holes emerging when the oxidation time was 4 h. A comparison of different holding times show that the flocculent oxide particle began to appeared and attached closely on the surface of matrix when the holding time is 4 h, compared with the La-TZM alloy plate (Fig. 5a and b). The alloy plate without electroplated platinum has been oxidized completely after 15 min, indicating that the Pt coating significantly delayed and slowed the oxidation.

Fig. 3g and h show surface SEM images of the alloy plates oxidized at 15 min when the oxidation temperature was 1200 and 1400 °C. One can see that the number of flocculent oxide particles decreases with the holding time when the alloy was heated to higher temperatures. Eventually the flocculent oxide particles disappeared, leaving the lamellar oxide layer when the temperature reached 1400 °C and the holding time was 15 min. It shows that the oxidation aggravated with the heating temperature risen.

3.2.3. Cross-section morphology and EDS analysis

Fig. 6 shows the cross-sectional SEM and EDS surface scanning images of the original Pt-coated La-TZM alloy plate. From Fig. 6a and b, it can be seen that the coating on the unheated alloy plate has good adhesion with the matrix alloy, free of cracks and not peeling. As seen in Fig. 6a, the average thickness of the original coating is about 5.48 μm.

Fig. 7 show the cross-sectional SEM images of the Pt-coated La-TZM alloy plates unheated and oxidized at 400–1400 °C for different times. Fig. 7a and b show little change of samples after heating at 400 °C and 600 °C for 4 h, that the Pt coating still have good adhesion with the matrix alloy. As seen in Fig. 7c and d, the coating separated from the matrix gradually when heated at 800 °C for 15 min, and the loose oxide layer was obtained between the matrix and Pt coating after 4 h heating. The surface oxide appears as flaky lamella, compared with Fig. 3. It can be seen that the oxidation starts from the surface and propagates inward. Fig. 7e and f show the comparison of oxide layer thickness between Pt-coated La-TZM alloy plate and La-TZM alloy plate [9] heated at 800 °C for 4 h and 10 min respectively. The loose oxide layer thickness of La-TZM alloy is about 100 μm after heated at 800 °C for 10 min, while after 4 h heating at same temperature, the oxide layer thickness of Pt-coated La-TZM alloy is only 110 μm, indicating that the platinum coating improves the oxidation resistance of La-TZM alloy.

3.3. Thermogravimetric analysis

Fig. 8 shows the differential thermal analysis results of the Pt-coated and uncoated La-TZM alloys. TG curves show that the two samples have a small weight gain when heated to lower

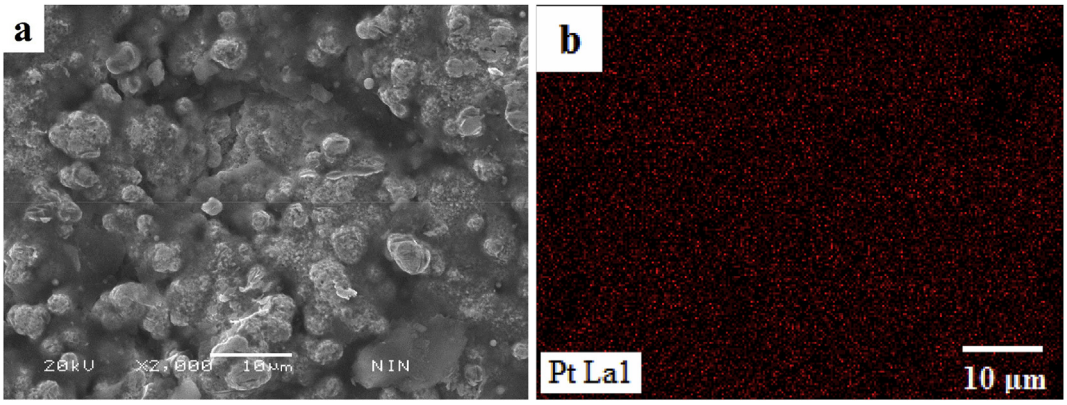

Fig. 2. (a) SEM and (b) EDS elements analysis images of the original sample Pt-coated surface.

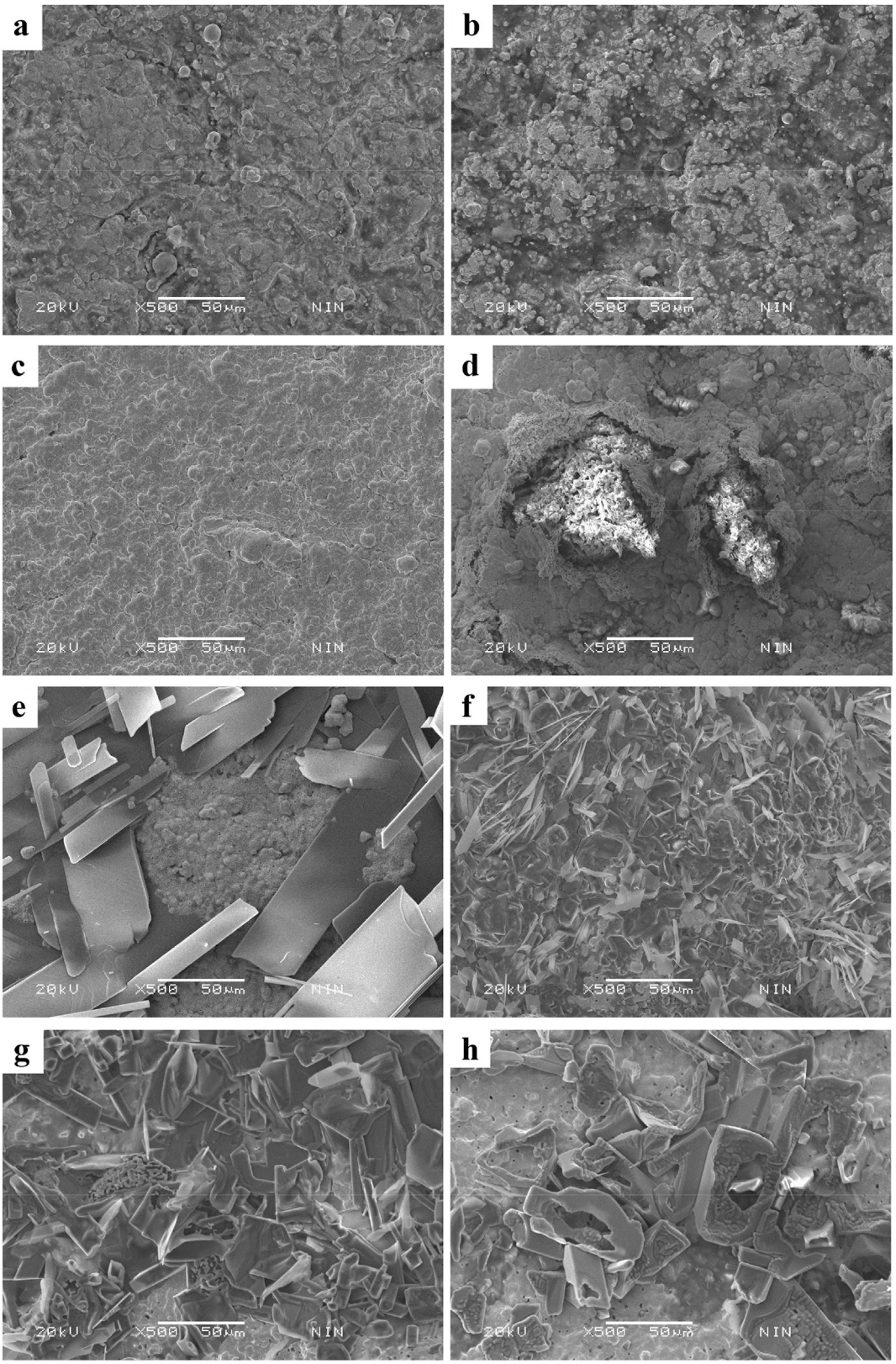

Fig. 3. SEM images of the Pt-coated La-TZM samples surface oxidized at different temperature and time: (a) 400 °C, 4 h; (b) 600 °C, 4 h; (c) 800 °C, 15 min; (d) 800 °C, 4 h; (e) 1000 °C, 15 min; (f) 1000 °C, 4 h; (g) 1200 °C, 15 min; and (h) 1400 °C, 15 min.

temperatures (400–800 °C), however, the Pt-coated La-TZM alloy weight gain was not as pronounced. There is a significant weight gain when 850 °C was reached, with a clear exothermic peak, corresponding to DTA and DSC curves. EDS analysis combined with

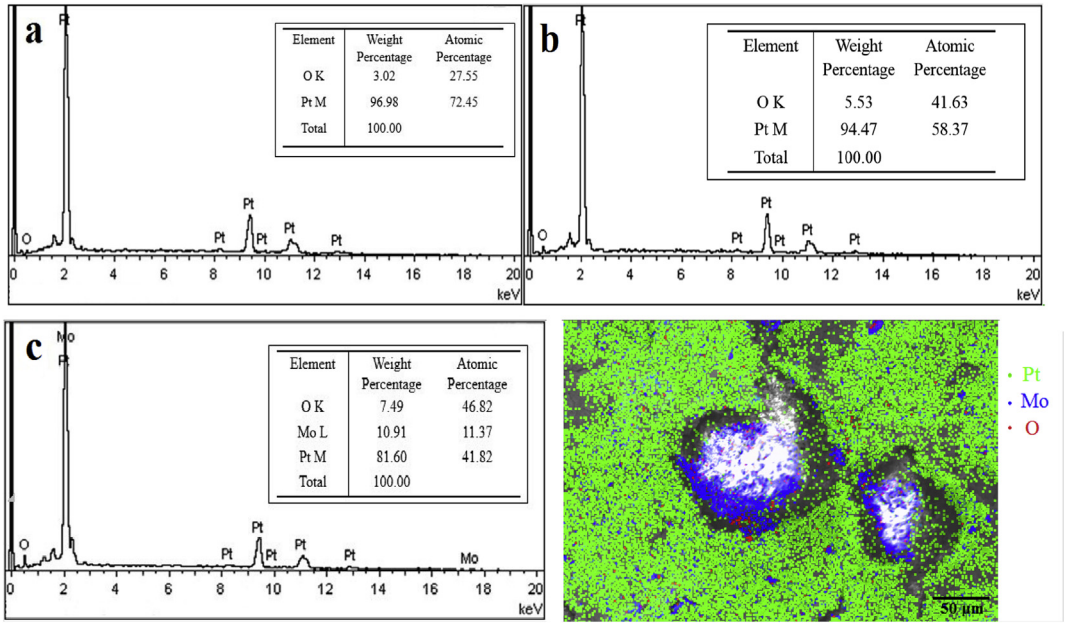

Fig. 4. Surface EDS profiles of the samples oxidized in 4 h at different temperature: (a) 400 °C; (b) 600 °C; (c) 800 °C.

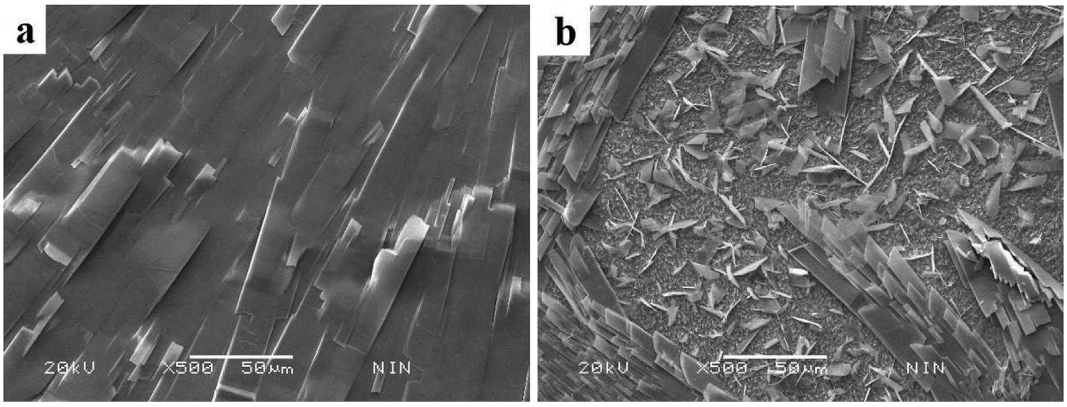

Fig. 5. SEM images of the La-TZM samples surface oxidized at: (a) 1000 °C, 10 min and (b) 1000 °C, 15 min [9].

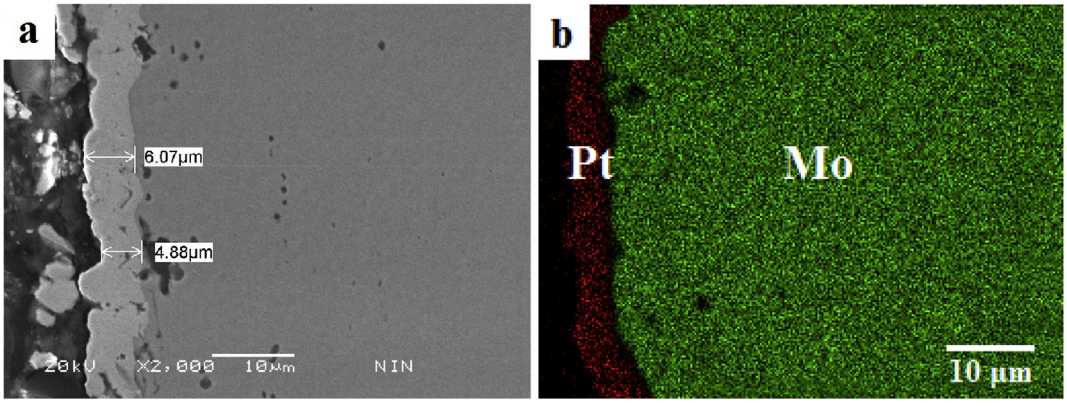

Fig. 6. Cross-sectional SEM and EDS images of the Pt-coated La-TZM alloy plate.

previous results shows that MoO_3 was previously generated and volatized at elevated temperatures. The DTA curve in Fig. 8a has a weak exothermic peak at 750 °C with a slightly obvious rising of TG curve, corresponding to the oxidation reaction in air, forming MoO_3. In Fig. 8b, the exothermic peak appears at 650 °C with a more obvious rising of TG curve, indicating that the oxidation

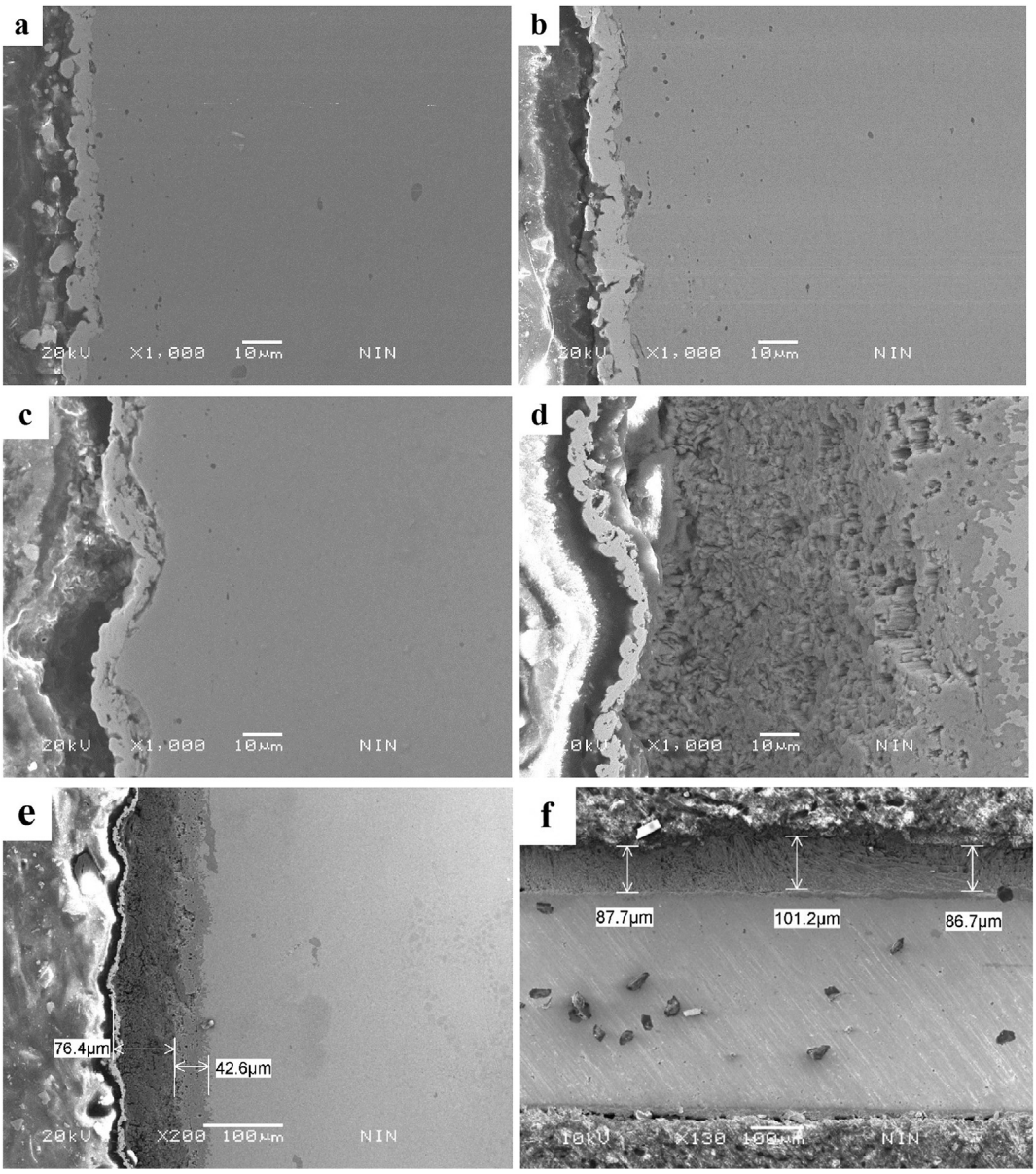

Fig. 7. Cross-sectional SEM images of Pt-coated La-TZM alloy plates heated at different temperature and different times: (a) 400 °C, 4 h; (b) 600 °C, 4 h; (c) 800 °C, 15 min; (d) and (e) 800 °C, 4 h and (f) La-TZM alloy plate heated at 800 °C for 10 min [9].

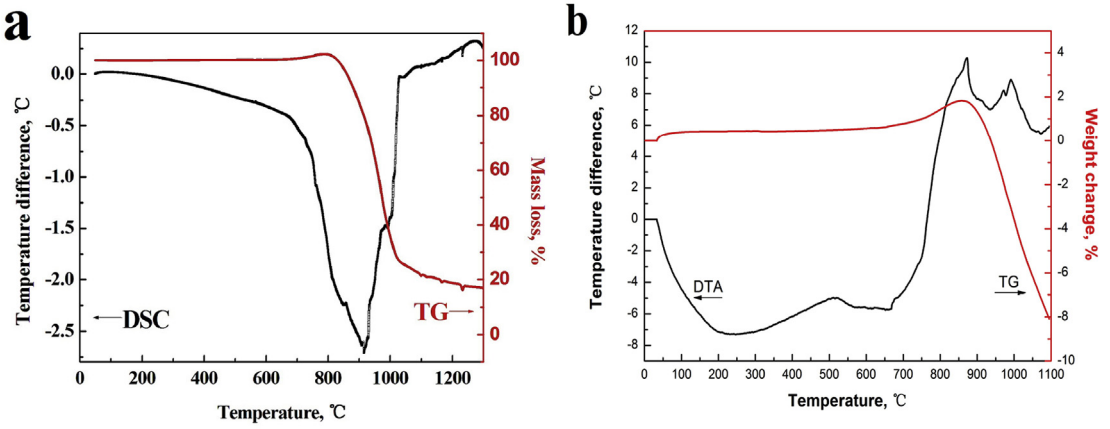

Fig. 8. TG-DTA/DSC curves of TZM alloy plates: (a) Pt-coated La-TZM alloy; (b) La-TZM alloy.

reaction has started at 650 °C. The matrix alloy was severely corroded by oxygen, and the MoO_3 generation temperature is 100 °C lower than for the Pt-coated La-TZM alloy. It can be concluded that the Pt coating can inhibit the La-TZM alloy surface oxidation, slowing the matrix alloy corrosion by oxygen, thus the Pt-coated La-TZM alloy has better anti-oxidation properties.

3.4. Oxidation mechanism

Pt-coated La-TZM alloy plates have a coating of Pt on all surface, enhanced its oxidation resistance during the high temperature oxidation experiments. The oxidation reaction almost no occurrence by the 400–600 °C heating and 800 °C heating within 15 min. Because of the disparity of the thermal expansion coefficient with molybdenum and platinum, while the Mo is 5.2×10^{-6}/K and the Pt is 9×10^{-6}/K, the Pt coating shows higher thermal expansion rate than the Mo matrix with the increase of temperature. As heating time goes on, the crack appeared on the surface of Pt coating at high temperature, causing the intrusion and corrosion of oxygen. With increasing oxidation temperature and time, the oxide expanded, fractured and was gradually volatized, causing the breaking and peeling of the Pt coating. The destruction of the coating caused the interior side of matrix to be oxidized gradually, leaving a small amount of La-TZM alloy matrix and residual Pt coating with oxidation above 1200 °C.

4. Conclusions

A dense platinum coating was electroplated on the La-TZM alloy plate surface and with none crack or defect observed by SEM. During the high temperature oxidation experiments, the obvious oxidation of the Pt-coated La-TZM alloy samples starting at 800 °C. With the increase of temperature and time, oxidation corrosion occurs gradually, occurring 80% mass loss of samples after 15 min heating at 1400 °C. That is because the Pt coating have a different thermal expansion coefficient with La-TZM alloy matrix, causing the cracking of the coating with the increase of heating temperature and time. Pt coating improves La-TZM alloy oxidation resistance due to the good binding between the coating and the substrate, which hinders oxygen invasion into the matrix, thus the Pt-coated La-TZM alloy oxidation resistance is largely improved. Compared with the La-TZM alloy, the Pt-coated La-TZM alloy plate prevents severe oxidation, increasing its starting temperature by 100 °C when heated in air, largely slowing the oxidation rate. This study of the oxidation behavior of the TZM alloy plates demonstrated that the Pt-coated La-TZM alloy has higher corrosion resistance, greatly expanding the TZM alloys applications.

Acknowledgments

This work was supported by the Science and Technology Coordinating Innovative Engineering Project of the Shaanxi province (2014KTCQ01-35), the Science and Technology Innovation Fund Project of the Western Metal Materials Co., Ltd. (XBCL-3-21), the Technology Transfer Projects in Colleges and Universities of Xi'an Science and Technology Plan (CXY1521(3)), Young Talent fund of University Association for Science and Technology in Shaanxi of China (2016), the Science and Technology Foundation of Xi'an University of Architecture and Technology (QN1505).

References

[1] G. Liu, G.J. Zhang, F. Jiang, X.D. Ding, Y.J. Sun, J. Sun, E. Ma, Nanostructured high-strength molybdenum alloys with unprecedented tensile ductility, Nat. Mater. 3544 (2013) 344–350.
[2] P. Hu, F. Yang, K.S. Wang, Z.T. Yu, J.F. Tan, R. Song, B.L. Hu, H. Wang, H.C. He, A.A. Volinsky, Preparation and ductile-to-brittle transition temperature of the La-TZM alloy plates, Int. J. Refract. Met. H. 52 (2015) 131–136.
[3] S. Majumdar, Formation of $MoSi_2$ and Al doped $MoSi_2$ coatings on molybdenum base TZM (Mo–0.5Ti–0.1Zr–0.02C) alloy, Surf. Coat. Technol. 206 (2012) 3393–3398.
[4] K. Babinsky, J. Weidow, W. Knabl, A. Lorich, H. Leitner, S. Primig, Atom probe study of grain boundary segregation in technically pure molybdenum, Mater. Charact. 87 (2014) 95–103.
[5] S.P. Chakraborty, S. Banerjee, K. Singh, I.G. Sharma, A.K. Grover, A.K. Suri, Studies on the development of protective coating on TZM alloy and its subsequent characterization, J. Mate. Process. Tech. 207 (2008) 240–247.
[6] S.P. Chakraborty, S. Banerjee, I.G. Sharma, A.K. Suri, Development of silicide coating over molybdenum based refractory alloy and its characterization, J. Nucl. Mater. 403 (2010) 152–159.
[7] G.R. Smolik, D.A. Petti, S.T. Schuetz, Oxidation and volatilization of TZM alloy in air, J. Nucl. Mater. 283–287 (2000) 1458–1462.
[8] J. Sik Park, J.M. Kim, Y. Son, Oxidation response of Al coated TZM alloys under dynamic plasma flame, Int. J. Refract. Met. H. 41 (2013) 110–114.
[9] F. Yang, K.S. Wang, P. Hu, H.C. He, X.Q. Kang, H. Wang, R.Z. Liu, A.A. Volinsky, La doping effect on TZM alloy oxidation behavior, J. Alloy. Compd. 593 (2014) 196–201.