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Effect of rare earth Eu on anti-passivation of metal oxide anode coating<sup>①</sup>ZOU Zhong(邹忠), LI Jie(李劫), DING Feng-qi(丁凤其), XIAO Jing(肖劲),  
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**[Abstract]** The anti-passivation effect of metal oxide anode coating doped with rare earth element Eu was discussed. The morphology and the composition distribution of the metal oxide coating anode before and after electrolysis were studied by SEM and EDX analyses. The results show that the erosion of the electrolyte at the defects is the main cause for the failure of the coating. The erosion rate of the electrolyte is anisotropic. In area with high density of defects, the erosion rate is very fast and the failure of the coating is very quick. Moreover, the life-time of the coating is prolonged by the doping of Eu.

**[Key words]** Eu doping; metal oxide anode coating; anti-passivation

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## 1 INTRODUCTION

The passivation of the Ti metal oxide anode coating gains much attention because it is closely related to the life-time and industry application of the anode<sup>[1]</sup>. The methods for improving bonding strength of Ti substrate and the coating include: 1) Roughening the surface of Ti substrate. The bonding strength of the substrate and the coating is improved by mechanical meshing and the passivation process is slowed down<sup>[2]</sup>; 2) Coating dense intermediate layer such as  $\text{Sb}_2\text{O}_3$ - $\text{RuO}_2$ ,  $\text{TiN}$ - $\text{TiFe}$ ,  $\text{RuO}_x$ <sup>[3~5]</sup>,  $\text{RuO}_2$ - $\text{TiO}_2$ <sup>[6]</sup>, on the surface of the Ti substrate to protect it from passivating, hence effectively prolonging the life-time of the anode system. The method for preparing the intermediate coating involves electrodeposition corrosion resistant metal on the substrate firstly, and then forming solid solution or compound by high temperature interfacial reaction<sup>[7]</sup>. Generally, these methods are all aiming at impeding the passivation of the Ti substrate and the dissolution of the oxide coatings<sup>[8]</sup>, while the studies for detailed failure mechanism of the anode is little. In this work the effect of the doping of rare earth element Eu on the anti-passivation of the metal oxide anode coating and the passivation mechanism are discussed.

## 2 EXPERIMENTAL

The preparation of the Ti base metal anode coating is divided into two steps: pre-treatment of Ti plate and preparation of electrocatalytic coating. The SnSb film was formed at 300 °C and the Ru-Eu surface coating was formed at 500 °C. The intensified

electrolysis was conducted following the standard experiment<sup>[9]</sup>. The composition of the electrolyte was  $\text{ZnSO}_4$  1.366 kg/mol,  $\text{H}_2\text{SO}_4$  1.534 kg/mol, and the intensified electrolysis was conducted at 34 °C.

## 3 RESULTS AND DISCUSSION

## 3.1 Mechanism of electrolysis failure

The life-time curve of the anode of Ru-Eu electrocatalytic layer with a SnSb base layer is shown in Fig. 1. After intensified electrolysis for 2000 s or so, the electric potential begins to decrease at first and then increase. It indicates that the coating begins to fall off and become unstable.

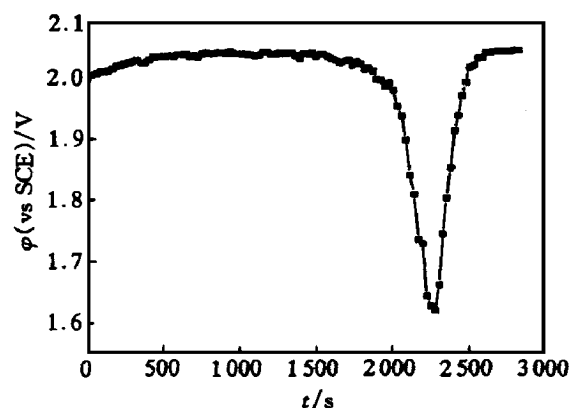
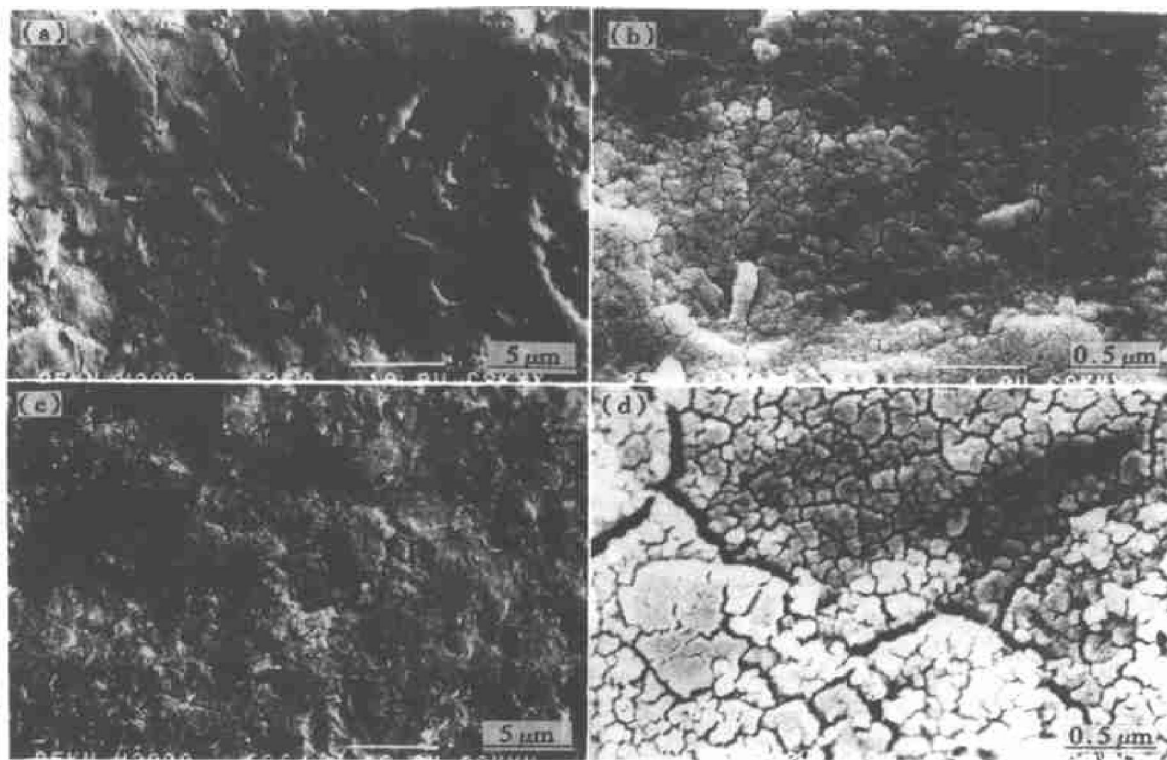


Fig. 1 Life-time curve of Ru-Eu coated anode formed at 500 °C  
(SnSb film was formed at 300 °C,  $J = 1 \text{ A/cm}^2$ )

By comparing the morphologies of the coating surface before and after electrolysis (as shown in Fig. 2), it can be seen that at low magnification the coating before electrolysis is smooth, flat and has no visi-

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**Fig.2** Morphologies of anode coated with Ru-Eu before and after electrolysis  
(a) and (b) —Before electrolysis; (c) and (d) —After electrolysis

ble crack, while after electrolysis it becomes rough and has local cracks. At high magnification, the coating before electrolysis has slight and homogeneous cracks, while after electrolysis the cracks are broadened and the propagation of the local crack is very apparent. The propagation of crack is shown in Fig.3. It seems that the electrolyte penetrates the coating along fine cracks, grain boundary and other area with high density of defects firstly. The erosion of the electrolyte intensifies with electrolyzing, and the coating becomes loose and falls off till the electrode fails. So the failure of the electrode accompanies with the erosion of the electrolyte and the passivation of the Ti substrate, at the same time the oxide in the



**Fig.3** Propagation of crack with electrolysis

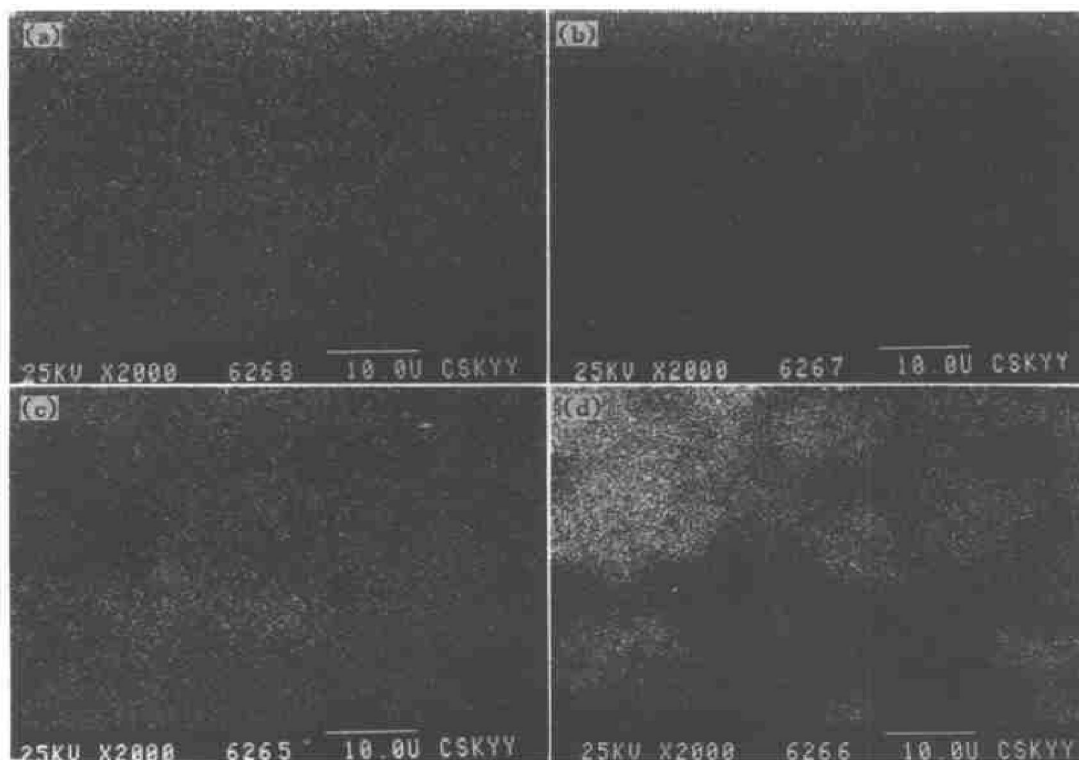
coating also dissolves and falls off.

The failure mechanism can be further analyzed by EDX area scanning of the electrode before and after electrolysis (as shown in Fig.4). Before electrolysis, the distribution of Ru element is homogeneous and dense, and that of Ti element is sparse but homogeneous, which indicates that there is a little Ti element in the coating. After electrolysis, there exists apparent Ru-poor area, in which the concentration of Ti element increases. It shows that in area with high rate of crack propagation, the dissolution of the oxide in the coating is more severe and the erosion of the electrolyte is more intensive, so leading to the increasing of Ti element. This result illustrates that the electrolyte penetrates in the coating preferentially along the area with high density of defects, and the erosion rate is anisotropic. So the failure of the coating is not homogeneous in the surface. In the area with high density of defects, the erosion rate is very fast and the area fails more quickly.

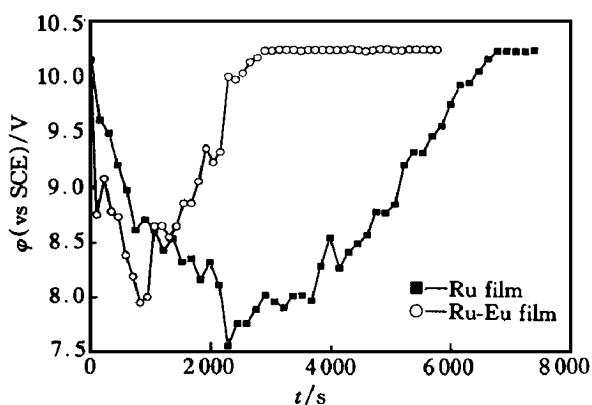
### 3.2 Effect of doping of Eu

In order to investigate the effect of the doping of rare earth element on the life-time of the coating, two electrodes were used for intensified electrolysis: the Ru-Eu coated anode doped with Eu at 500 °C and the pure Ru coated anode. The result is shown in Fig.5.

It can be seen in Fig.5 that the anode with Eu-doped coating has a better intensified electrolysis

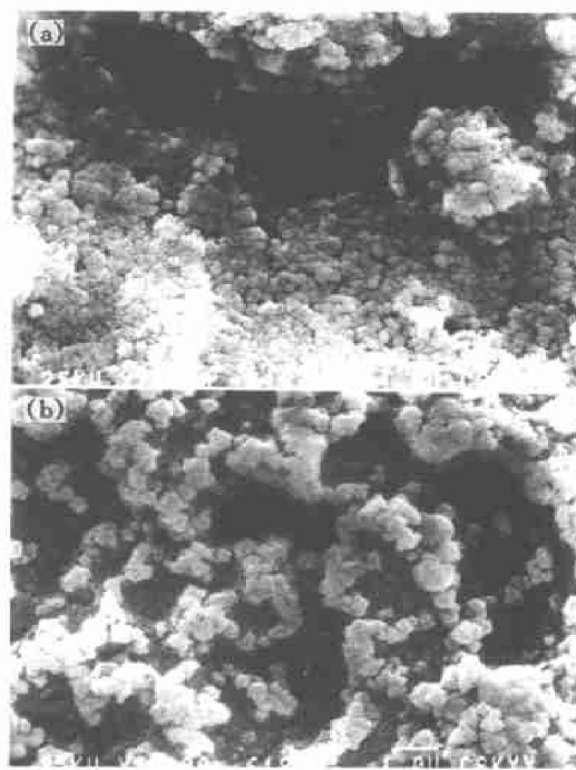


**Fig.4** EDX analyses of anode coated with Ru-Eu before and after electrolysis  
(a) and (b) —Ru and Ti elements before electrolysis ; (c) and (d) —Ru and Ti elements after electrolysis



**Fig.5** Effect of rare earth element Eu on life-time of coated anode in intensified electrolysis  
( $J = 1 \text{ A/cm}^2$ )

property compared with that of the pure Ru coating anode (it will take some time for the outmost layer of the anode to be stably polarized). Fig.6 shows the morphologies of the coatings before electrolysis. It indicates that the coating doping with Eu is flat and has homogeneous cracks, while the pure Ru coating is uneven and has conglomerated grains and local coarse cracks. The morphology difference of the two coatings determines their electrolysis property. And the improvement of surface morphology may be attributed to the influence of the doping of rare earth on the nucleation and growth of the coating.



**Fig.6** Morphologies of  $\text{RuO}_2$  coated anode doped with and without rare earth element Eu before electrolysis  
(a) —Doped with Eu ; (b) — Without Eu

#### 4 CONCLUSIONS

1) The morphology and the composition distribution of the metal oxide coating anode before and after electrolysis indicates that the erosion of the electrolyte along the defects in the coating is the main cause for the failure of the coating. The erosion rate of the electrolyte is anisotropic, in area with high density of defects the erosion rate is very fast and the failure of the coating is very quick.

2) The doping of rare earth can prolong the lifetime of the coating, which can probably be attributed to its effect on the nucleation and growth of the coating and the formation of beneficial crystal microstructures.

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