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## Degradation characteristics of Ti/ (IrO<sub>2</sub> + Ta<sub>2</sub>O<sub>5</sub>) coating anodes in H<sub>2</sub>SO<sub>4</sub> solution<sup>①</sup>

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**[Abstract]** The service life of Ti based IrO<sub>2</sub> + Ta<sub>2</sub>O<sub>5</sub> coating anodes over the whole composition range and prepared at different temperatures was studied by the accelerated electrolysis tests. The results show that as a result of incomplete decomposition, coatings obtained at low temperature are not stable. At the preparing temperature up to 450 °C, the stability of the resulting deposits increase dramatically, and is independent on temperature. However, at higher temperature, oxidation of Ti base occurred leading to a decrease in the adhesion of coatings which resulted in decreasing of the service life of anodes. The maximum durability was obtained for the anodes prepared at 450 °C. Resulting from the maximum solubility between the iridium and tantalum oxides, coatings with 70 %IrO<sub>2</sub> + 30 %Ta<sub>2</sub>O<sub>5</sub> (mole fraction) exhibited the maximum stability. A preferential dissolution of Ir on the non-close-packed planes of the rutile oxides was observed for the pure IrO<sub>2</sub> deposits while on the close-packed planes for the IrO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> mixed ones in electrolysis. This dissolution characteristic can interpret a low service life for the coating anodes with a low IrO<sub>2</sub> content since the close-packed planes orientations are dominant in these fresh samples. Two mechanisms for the degradation of Ti/(IrO<sub>2</sub> + Ta<sub>2</sub>O<sub>5</sub>) anodes were also proposed.

**[Key words]** oxide anodes; iridium oxide; tantalum oxide; degradation

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### 1 INTRODUCTION

Ti based IrO<sub>2</sub> coating anodes were widely used in electrochemical industry for their high electrocatalytic activity and stability<sup>[1]</sup>. In an extreme condition, such as high-speed electrodeposition, however, the stability of IrO<sub>2</sub> is no longer satisfied. Therefore, the modification of this type of coating is necessary. In the past ten years, lots of systematic investigation concerning the admixture of valve metals like Ti and Ta has been carried out<sup>[2~4]</sup>, and the mixture of IrO<sub>2</sub> + Ta<sub>2</sub>O<sub>5</sub> has been verified as the best binary combination for oxygen evolution in acid media<sup>[5]</sup>. The O<sub>2</sub> evolution activity and durability of the binary oxide have been studied extensively<sup>[2,6]</sup>. In our laboratory<sup>[7]</sup>, a close relationship between structure and electrocatalytic activity of Ti/(IrO<sub>2</sub> + Ta<sub>2</sub>O<sub>5</sub>) anodes in H<sub>2</sub>SO<sub>4</sub> solution has been proposed. Nevertheless, few works about the degradation characteristic of these anodes has been reported<sup>[8]</sup>, especially, the relationship between the deactivation behaviors and the crystal structure of the oxide coating has not been concerned.

In the present paper, the stability of IrO<sub>2</sub> + Ta<sub>2</sub>O<sub>5</sub> coatings and the variation of the structure after degradation have been emphasized, and two types of

the failure mechanism for the anodes with various composition and preparing temperature have also been discussed.

### 2 EXPERIMENTAL

#### 2.1 Preparation of electrodes

A conventional thermodecomposition technique was used to prepare the oxide coatings<sup>[9]</sup>. The titanium plate was degreased, and etched in 3.0 mol/L HCl solution, then rinsed with deionized water. The precursors were prepared by mixing the necessary amounts of H<sub>2</sub>IrCl<sub>6</sub>·6H<sub>2</sub>O and TaCl<sub>5</sub> in 1:1 (volume ratio) alcohol and isopropanol solutions in which the total metal concentration was kept about 0.2 mol/L. Then the substrates were painted with the coating solution with brushes. After dried at 100 °C, the titanium substrates were heated at an annealing temperature for 10 min. The entire procedure was repeated 10 times, then the sample was heated at the annealing temperature for 1 h.

#### 2.2 Material characterization

X-ray diffraction (XRD) was used to analyze the structure of the coating, the test was carried out on a D/MAX R3 type diffractometer equipped with Cu K<sub>α</sub> radiation and nickel filter. The texture coefficients of

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$\text{IrO}_2$  rutile crystal ( $C_i(hkl)$ ) can be calculated by using the measured integrated intensities from the equation<sup>[10,11]</sup>

$$C_i(hkl) = \frac{I(hkl)}{I^0(hkl)} \left[ \frac{1}{n} \sum_i \frac{I(hkl)}{I^0(hkl)} \right]^{-1} \quad (1)$$

where  $I(hkl)$  is a measured intensity of ( $hkl$ ) plane,  $I^0(hkl)$  is the standard intensity of the ASTM standard powder pattern diffraction data, and  $n$  is the total number of reflections.

Surface morphologies and chemical composition were investigated with a Cambridge S360 scanning electron microscopy (SEM), equipped with link X-ray energy dispersive analyzer (EDX). Oxides loading of  $\text{IrO}_2$  and  $\text{Ta}_2\text{O}_5$  in coatings was determined by using X-ray fluorescent (XRF). The test was conducted on a Philips PW2400 XRF Spectrometer.

### 2.3 Accelerated life tests

The service life test was carried out in a two compartment cell under galvanostatic conditions at 2 A/cm<sup>2</sup> using Ti plate cathodes. The electrodes was then anodically polarized in 0.5 mol/L  $\text{H}_2\text{SO}_4$  solution at 40 °C. The electrode service life was defined as the time at which the cell voltage increased significantly (about 5.0 V).

## 3 RESULTS AND DISCUSSION

### 3.1 Service life of electrodes

#### 3.1.1 Effect of oxide composition

It is generally accepted that<sup>[12,13]</sup> when the content of  $\text{IrO}_2$  was less than 30 % (mole fraction), the crystal phase of  $\text{IrO}_2 + \text{Ta}_2\text{O}_5$  deposits existed as  $\beta$   $\text{Ta}_2\text{O}_5$  as  $\text{IrO}_2$  dissolved in it. This type of anodes containing insufficient active component could not sustain a significant  $\text{O}_2$  evolution, and the service life was extremely low (less than 10 h). Fig.1 shows the dependence of service life and the dissolution rate of  $\text{IrO}_2$  in the oxide composition when the content of  $\text{IrO}_2$  is more than 30 %. The life, denoted as  $\tau$ , is normalized by the loading of  $\text{IrO}_2$  in the resulting coatings, and the dissolution rate  $\gamma$  is determined from the amount of  $\text{IrO}_2$  in coatings before and after degradation obtained by XRF tests. The standardized life initially increases and then decreases with  $\text{IrO}_2$  content at a maximum concentration of 70 %. This result is in a good agreement with the previous works<sup>[2,5]</sup>. It is clearly shown that, with increasing dissolution rate of  $\text{IrO}_2$ , the electrode service life decreases. Therefore, the deactivation of the resulting anodes is dominantly attributed to the dissolution of active component  $\text{IrO}_2$ . When the content of  $\text{IrO}_2$  was more than 30 %,  $\text{IrO}_2$  in  $\text{IrO}_2 + \text{Ta}_2\text{O}_5$  coatings was reported as (Ir, Ta)  $\text{O}_2$  rutile solid solution<sup>[12]</sup>. In our previous work<sup>[7]</sup>, the maximum stability of Ta in

rutile lattice for the coatings of 70 %  $\text{IrO}_2 + 30$  %  $\text{Ta}_2\text{O}_5$  has been found, which could probably interpret the highest corrosion resistance of the coating electrode for this composition. Resulting from the absence of stabilization by  $\text{Ta}_2\text{O}_5$ , coatings of 100 %  $\text{IrO}_2$  tends to be corroded significantly as shown in Fig.1. On the other hand, the coating adhesion of Ti/ $\text{IrO}_2$  deposit is also doubtful. Fig.2 shows the surface morphologies of the two electrodes after degradation. Corrosion and destruction of the coating occur on the whole surface in uniform for Ti/(70 %  $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ ) electrode. However, peeling-off of the coating is observed for Ti/ $\text{IrO}_2$  electrode, then Ti base is exposed to electrolyte and is anodically pass-

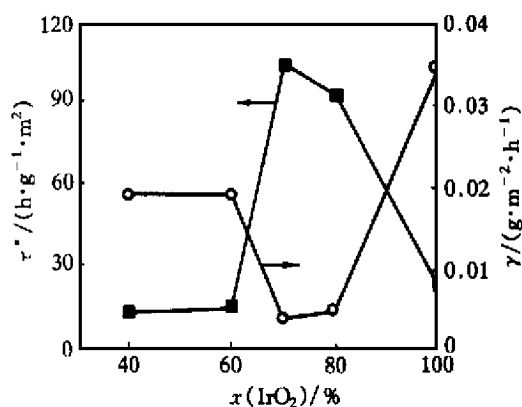


Fig.1 Standardized lifetime and  $\text{IrO}_2$  dissolution rate of Ti/( $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ ) electrodes prepared at 450 °C as a function of  $\text{IrO}_2$  content

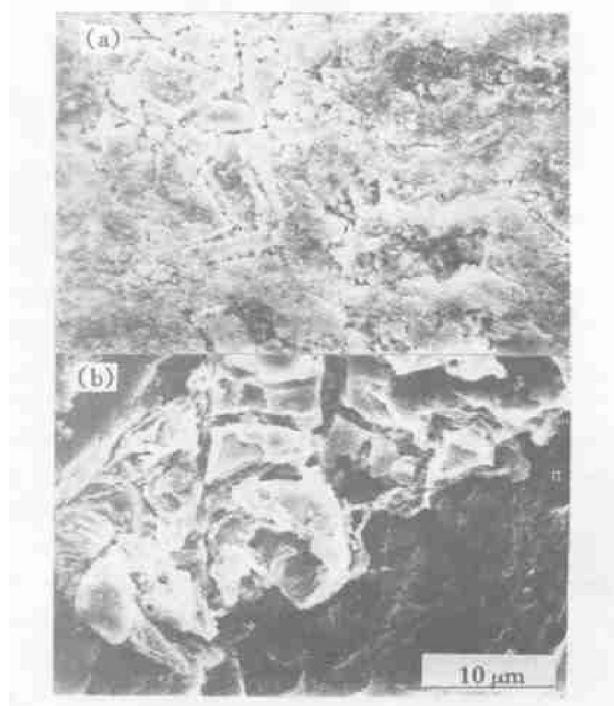


Fig.2 SEM images of electrodes after degradation

(a) — Ti/(70 %  $\text{IrO}_2 + 30$  %  $\text{Ta}_2\text{O}_5$ ) ; (b) — Ti/ $\text{IrO}_2$



vated. A similar result for the enhancement of adhesion of IrO<sub>2</sub> coating by Ta addition has been reported in literature [14].

### 3.1.2 Effect of calcination temperature

Fig. 3 shows the accelerated service life and IrO<sub>2</sub> loss rate of Ti/(70 % IrO<sub>2</sub> + 30 % Ta<sub>2</sub>O<sub>5</sub>) electrodes prepared at different temperatures. At less than 450 °C, corrosion of the binary oxides is severe, and the dissolution rate of the coating prepared at 350 °C is 3 orders of magnitude higher than that of 450 °C. It has been demonstrated that<sup>[1,15]</sup> at low temperature the chlorides of iridium and tantalum could not completely decomposed to the resulting oxides. The uncompleted decomposition products are thermodynamically unstable, and process a low activity for O<sub>2</sub> evolution, which results in an irreversible dissolution of coatings. When  $t \geq 450$  °C, the dissolution rate decreases significantly, and is independent on temperature. This result indicates a high stability for the coatings prepared at high temperature. However, when  $t \geq 500$  °C, the service life of electrode tends to decrease as shown in Fig. 3. This result can not be simply explained by the stability of coatings. Fig. 4 shows a SEM morphology for Ti/(70 % IrO<sub>2</sub> + 30 % Ta<sub>2</sub>O<sub>5</sub>) electrode prepared at 550 °C after deactivation. Similar to Fig. 2(b), coating detachment occurs in electrolysis. Vercesi<sup>[16]</sup> reported that when temperature was more than 550 °C, the oxidation rate of Ti base in air increased considerably, and a brittle or insulating interface would form between the coating and the base metal. TiO<sub>2</sub> rutile reflections were observed obviously for the electrodes prepared at this temperature<sup>[7]</sup>, and the deposits prepared at such temperature processed a compact morphology. Therefore, the formation of an inert insulating film resulted from the oxidation of Ti base was the main reason for the deterioration of coating adhesion.

### 3.2 Deactivation mechanism of anodes

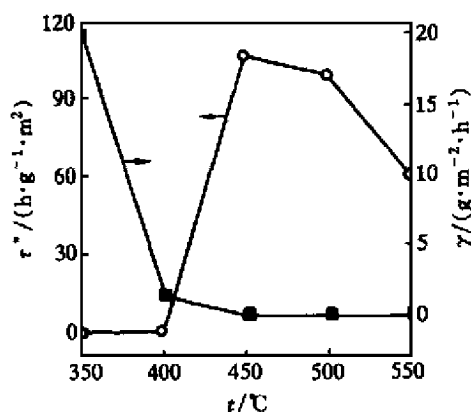


Fig. 3 Service life and IrO<sub>2</sub> dissolution rate of Ti/(70 % IrO<sub>2</sub> + 30 % Ta<sub>2</sub>O<sub>5</sub>) electrodes as a function of calcination temperature

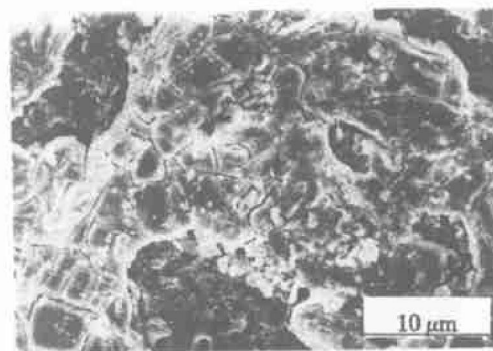
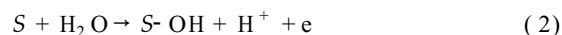


Fig. 4 Surface morphology of electrode of Ti/(70 % IrO<sub>2</sub> + 30 % Ta<sub>2</sub>O<sub>5</sub>) prepared at 550 °C after deactivation

From the above results, two reasons for the degradation of Ti/(IrO<sub>2</sub> + Ta<sub>2</sub>O<sub>5</sub>) anodes in electrolysis can be deduced. One is the dissolution of the active component of catalyst. Another is the coating detachment from the Ti bases. The former one results in thinning the deposit and decreasing in the active site gradually. When below a critical value of the active site, the mixed oxide can not sustain a high current density for O<sub>2</sub> evolution. The latter one leads to forming a  $\pi$ -p bond on the interface which decreases the conductivity of the whole electrode<sup>[17]</sup>.

The catalysis process for oxygen evolution on the surface of oxide electrodes can be written as<sup>[18]</sup>:



where  $S$  stands for surface active site. Generally, reaction (2) is the rate determining step. For an ideal catalysis circle, there is a same reaction rate for the three steps. When the step (2) is restricted, the accumulated intermediate product  $S-OH$  will be subject to decomposition or oxidation which results in a net loss of catalyst and decrease in the amount of oxygen evolution. The corrosion products of IrO<sub>2</sub> anode in the O<sub>2</sub> evolution, IrO<sub>3</sub> inert compound and IrO<sub>4</sub><sup>2-</sup> dissolvable ion, have been detected by Kotz, and a possible mechanism for O<sub>2</sub> evolution and the self-dissolution of IrO<sub>2</sub> electrode has been proposed<sup>[19]</sup>. It can be concluded from the present results that, this failure mechanism is dominated for the Ti/(IrO<sub>2</sub> + Ta<sub>2</sub>O<sub>5</sub>) anodes prepared at low and medium temperatures ( $t \leq 450$  °C).

Correa-Lozano et al<sup>[20]</sup> proposed that the nonstoichiometry of the active oxide was indispensable to keep its high activity for O<sub>2</sub> evolution. They found that, undergoing the oxygen evolution, the defectiveness of oxygen in SnO<sub>2-x</sub> lattice was filled by O gradually, which resulted in increase inner stress of Ti/(SnO<sub>2</sub> + Sb<sub>2</sub>O<sub>5</sub>) electrodes and the coating de-



tached layer by layer. The detachment of oxide coatings in electrolysis for the  $\text{Co}_3\text{O}_4$  containing oxide electrodes has also been reported by TANG<sup>[21]</sup>. This mechanism is suitable for the  $\text{Ti}/(\text{IrO}_2 + \text{Ta}_2\text{O}_5)$  anodes with low adhesion prepared at high temperature ( $t \geq 500^\circ\text{C}$ ).

In order to understand the corrosion and dissolution characteristics of the oxide anodes, the crystallite orientations of the coatings before and after degradation are tested. Fig. 5 shows the variations of texture coefficient ( $C_i(hkl)$ ) of various crystalline planes in the rutile crystals of 100 %  $\text{IrO}_2$  deposit after deactivation. It is shown that after failure a strongly preferential orientations of (101) is observed, which indicated that a significantly preferred dissolution on the other planes occurred. (101) plane is one of the most close-packed plane for Ir in the rutile structure, which is probably one of the main reasons of the high resistance for the crystal grains corresponding to this orientation. Richard<sup>[22]</sup> reported that, the electrogalvanized deposit with a (002) preferential orientation performed the highest corrosion resistance in the medium media, and the most close-packed structure for Zn in (002) plane was employed to interpret the above result.

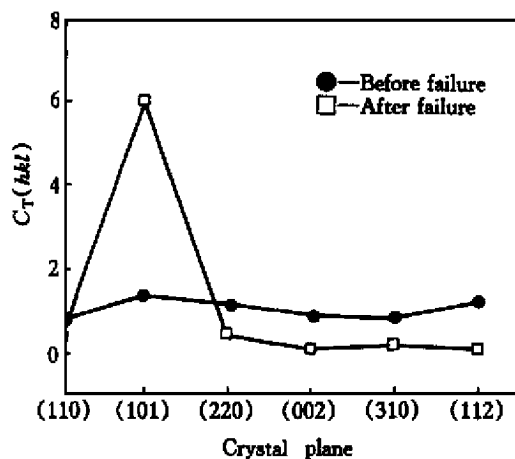


Fig. 5 Texture coefficient of rutile crystal in 100 %  $\text{IrO}_2$  deposit prepared at  $450^\circ\text{C}$

However, the experimental results for the Ir and Ta mixed oxide coatings are absolutely contrary to that of the pure  $\text{IrO}_2$  deposit. The results show that, the preferential orientation of (110) and (101) planes, which exists in the fresh samples, disappears in the mixed coatings after deactivation (see Fig. 6). The figure only displays the  $C_i$  variations for the mixed oxide coatings with the  $\text{IrO}_2$  content of 70 %. If only the volume factor is assumed to affect the location of Ta in the rutile lattice, Ta is probably preferentially located in the non-close-packed planes, such as (002) and (310) planes. The above result shows that by the solubilization of Ta, the stability of Ir on the non-close-packed planes is higher than that on the

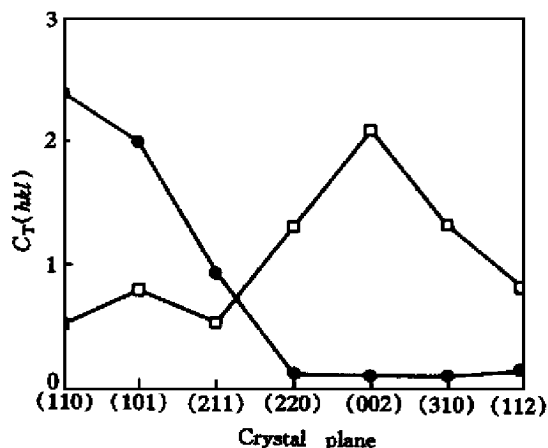


Fig. 6 Texture coefficient of rutile crystal in 70 %  $\text{IrO}_2 + 30\%$   $\text{Ta}_2\text{O}_5$  deposit prepared at  $450^\circ\text{C}$   
● — Before failure ; □ — After failure

close-packed ones in which Ta is absent. And the result also strongly supports the stability effect by addition inert of  $\text{Ta}_2\text{O}_5$  which was proposed by many workers<sup>[4,5,12,13]</sup>. It should be noted that with the  $\text{IrO}_2$  content less than 70 %, the preference of (110) and (101) orientation increased with decreasing content of  $\text{IrO}_2$ .

#### 4 CONCLUSIONS

1) There are two mechanisms for the degradation of  $\text{Ti}/(\text{IrO}_2 + \text{Ta}_2\text{O}_5)$  anodes in electrolysis: one is the dissolution of the active oxide  $\text{IrO}_2$ , the other is the anodic passivation of Ti base leading to detachment of deposit. The former mechanism is suitable for the anodes prepared at a low or intermediate temperature, and the latter is the main reason of the deactivation of the high temperature-prepared electrodes.

2) Over the whole composition range, as a result of the highest solubility between Ir and Ta binary oxide, the mixed coating with 70 %  $\text{IrO}_2 + 30\%$   $\text{Ta}_2\text{O}_5$  presents the highest stability.

3) In the pure  $\text{IrO}_2$  deposits, the close-packed plane (101) possess the highest corrosion resistance. Resulting from the preferential access of Ta to the non-close-packed planes of the rutile lattice in the mixed deposits, the stability of these planes increases, and close-packed planes such as (110) and (101) are preferentially attacked in electrolysis.

4) The preferential orientation of (110) and (101) in the oxide coatings with a low content of  $\text{IrO}_2$  is characterized to be one of the reasons for the low durability of the anodes corresponding to these compositions.

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