

# FAILURE ANALYSIS OF PEELING PROCESS FOR TITANIUM ANODES COATINGS<sup>①</sup>

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**ABSTRACT** The peeling failure is a common failure form occurring in titanium anode coatings, whereas the mechanism of its process has never been revealed. An analysis was made to study the data from accelerated life-time test (ALTT) and the feature of the surface morphology. The number of intersects between lines and cracks (NILC) and widths of cracks were measured. The result showed the failure process could be divided into three stages as exfoliating, separating and breaking ones.

**Key words** titanium anodes failure analysis coating peeling

## 1 INTRODUCTION

Titanium anodes, also called dimensionally stable anodes (DSA), are energy transforming materials. In 1968, Beer<sup>[1]</sup> invented such electrode materials by coating precious metal oxides to titanium support. The new materials were quickly applied to industries, which resulted in a revolution in electrochemical industry<sup>[2]</sup>. The early failure of a titanium anode will not only cause a waste of precious metals, but also influence industrial production, for an anode is a core component in electrochemical equipment. To reveal the failure process by failure analysis may have great help to prevent such mishaps and to design new titanium anode material with long life. The authors<sup>[3-5]</sup> firstly tried to introduce the failure analysis method which is mainly used to study mechanical components onto such electrochemical components. It was suggested that the failure forms for such materials might be classified as four: short circuit, loss of activity, coating peeling and corrosion of surface. Now the work of failure analysis for titanium anode materials is just at the beginning and has never been found in any report abroad. In

this paper, the authors focused on one of the most common form—coating peeling failure. The features of ALTT data and micro-morphology for the anodes in various stages were studied, the failure mechanisms at the three stages analyzed and the methods to modify its life-time suggested.

## 2 EXPERIMENTAL

The pure titanium plates TA<sub>2</sub> with 1 mm thickness were degreased in hot liquid with detergent. After washing with water, they were immersed and etched in a boiling acid solution concentrated with 2.3 mol/L HCl for 2 h. After washing and drying, they were brushed 18 layers with an isopropanol solution containing metal compounds of RuCl<sub>3</sub>, IrCl<sub>3</sub>, TiCl<sub>3</sub> and SnCl<sub>4</sub>. After brushing of each layer they were dried and kept at 300~550 °C for 10 min in air. After final coating, they were annealed at 450 °C for 2 h. So prepared titanium anode samples had rough bases and an oxide coating with the components of Ru31, Ir14, Ti45, Sn10 mol%.

The ALTT was performed in 2 mol/L H<sub>2</sub>SO<sub>4</sub> using glass cell, with titanium anode

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samples as studying electrodes and a platinum plate as cathode. The JWL-30 type constant-current power was used to provide anode current with c. d. = 4 A/cm<sup>2</sup>. The cell voltages were recorded at regular intervals.

The titanium anode samples electrolyzed for various times were studied by SEM of a JSM-35CF type apparatus. Numbers of the intersects between lines and cracks (NILC) and the widths of cracks<sup>6</sup> were determined, and the micro-morphology was observed.

### 3 RESULTS

#### 3.1 Results of the ALTT

The recorded cell voltages at various times in ALTT test are listed in Table 1. At the beginning of the electrolysis, the cell voltage rose slowly. This course used 17.5 h with the voltage rising rate of about 0.06 V/h, which made up about 73% of the whole test. So we can classify it as the first stage, or the voltage slowly rising stage. When electrolysis was continuing the voltage rising was accelerated. It rose 2 V from 17.5 to 23.5 h. The rising rate was about 0.3 V/h. We classified it as the second stage, or the voltage accelerately rising stage. When the test exceeded 23.5 h, it rose dramatically with the rising rate of about 20 V/h, which was referred to as the

**Table 1 The VRR, NILC and WC data in various stages**

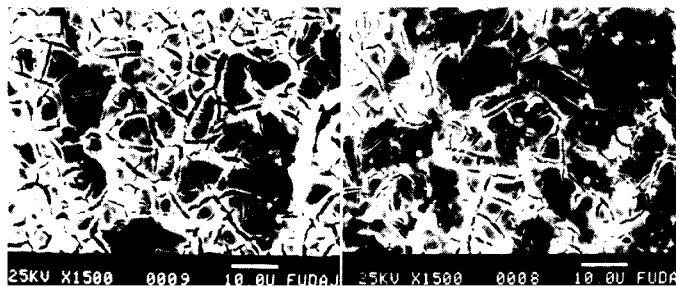
Stage	Electrolysis time /h	Voltage rising rate/V·h <sup>-1</sup>	NILC /mm <sup>-1</sup>	Width of cracks /μm
1	0~17.5	$6 \times 10^{-2}$	210~150	1.5~0.5
2	17.5~23.8	$3 \times 10^{-1}$	150~10	1.0~0.5
3	23.8~	$2 \times 10^1$	10~0	0.5~0

third stage, or the voltage dramatically rising stage.

#### 3.2 Results of the SEM

In the first stage, the surface morphology of titanium anode did not change very much. For the sample having electrolyzed for 2 h, the surface morphological change could not be found. Fig. 1a is the SEM photograph showing the typical surface of a titanium anode, for it has the characteristics of dry-mud surface. At a glance, we could see various cracks, large or small, deep or shallow, spreading all over the field. The NILC was about 210 mm<sup>-1</sup>, the width of cracks 0.5~1.5 μm. Not any damages could be seen in sight.

Having electrolyzed for 13 h, the overall morphology on surface did not change much (Fig. 1b). The NILC ≈ 195 mm<sup>-1</sup>, the width decreased to about 0.5~1.0 μm. Observed



**Fig. 1 The SEM photographs of anode samples having electrolyzed for 2 h(a) and 13 h(b)**

carefully, the decrease of NILC could be seen from the appearance of non-cracked area, whose predecessor might have been exfoliated in the process of electrolysis. According to the change of width, it could be known that the disappeared structures might have been the cracks whose widths were  $1.0 \sim 1.5 \mu\text{m}$ .

In the second stage, the morphology began to change. Fig. 2a is the SEM photograph for the sample electrolyzed for 19 h. Great change had taken place comparing with its original surface. The NILC decreased to approximately  $120 \text{ mm}^{-1}$ , the width was still  $0.5 \sim 1.0 \mu\text{m}$ . The surface could never maintain its flatness, the coating never complete. In some areas the ridges on titanium base could be seen, the coating materials were not in sight.

In some areas coating plateaus without cracks could be seen (arrowed). Almost all the valleys and hollownesses were filled with coating materials, on which the cracks were seen.

The uncovered areas on the ridges of titanium base enlarged as the electrolyzing continued. The coating materials in hollow areas also began to demolish. Fig. 3b is the SEM photograph for sample having electrolyzed for 23.5 h. The bumps and holes could be seen all over the surface. Almost all ridges were uncovered. There were a few sediments with or without cracks in hollow areas on titanium base. The NILC was about  $20 \text{ mm}^{-1}$ .

In the third stage, it could obviously be seen that the outlook of the surface was analogous to the one just taking out of the etching

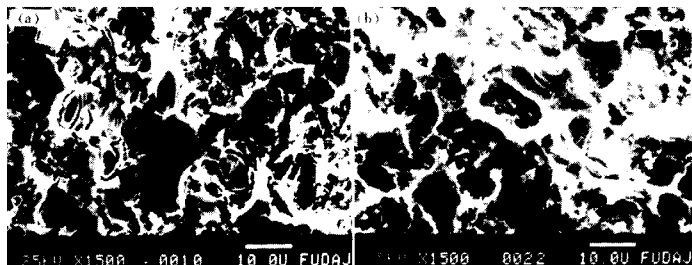


Fig. 2 The SEM photographs of anode samples having electrolyzed for 19 h(a) and 23.5 h(b)

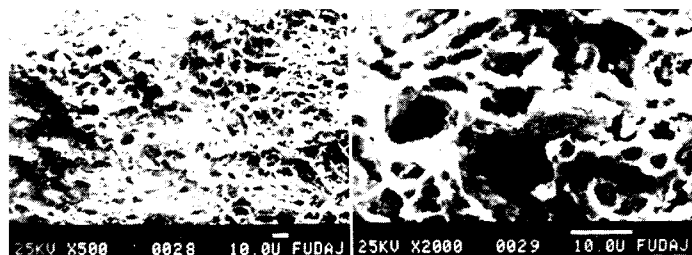


Fig. 3 The SEM photographs of anode samples having electrolyzed for 23.9 h, (a)  $400\times$  and (b)  $2000\times$

solution. Fig. 3a is the SEM photograph with magnification of 400 times for sample electrolyzed for 23.9 h. The bumps and holes, small and large, one by one spread throughout the surface, which is the typical morphology of etched surface. It seemed that the coating materials did not preserve. But when we magnified it to 2 000 times (Fig. 3b), it could be seen that the NILC  $\approx 10 \text{ mm}^{-1}$ , the width  $\approx 0.2 \mu\text{m}$ , and some sediments were still in hollownesses, although new continuous cracks had formed and encircled them. So the sediments would separate and lose at any time.

#### 4 DISCUSSION

The anode material transforming electrical power to chemical power should be immersed in corrosive medium. It may face the problems of electrochemical dissolution and wear by rushing gas. From the SEM analysis, the corrosion phenomenon had not been found in the whole electrolyzing process. For example, in careful observation of the sample having electrolyzed for 23.5 h, we could find that the edge of crack on the nearly separated sediment remained sharp (Fig. 3b). So it is suggested that the wear by rushing gas was the main reason to cause the anode failuring. To modify life-time of the anode, the binding strength of coating must be considered to increase wear resistivity against rushing gas.

The peeling process was carefully studied at the three stages in morphology (see Table 1). At first stage, the overall morphology did not change much. The looser structure area including the coatings with wider cracks tend to be pared and peeled, which could be referred to as exfoliate or selected peeling stage. At second stage, the coating began separating. The coatings on the ridges of titanium base incline to be rushed out by washing-gas. And the coatings on the bottom of the hollownesses may be eroded to form plateaus, which could be known as separating stage. At the third stage, the remaining coating seemed to be broken by rushing gas until the whole coating wore down and vanished into void.

Life-time of titanium anode depended on the first two stages, for they took up separately 73% and 26% of the whole service life. They must be emphasized if we want to improve the life-time of the anode. For different peeling behaviors of the two stages, different methods have to be adopted. To prolong the first stage, effective measure is to increase wear resistivity of coating surface. Firstly, wider cracks need to be controlled technologically. Secondly, a more viscous brushing solution may be used for the last brushing. As for the second stage, adherence between coatings and titanium base must be considered to retard the new crack nucleation and growth on the bottom of the coating.

#### 5 CONCLUSIONS

The various mechanism of peeling failure for the titanium anodes showed their different morphological features in the three stages. At the first, the exfoliation stage, the NILC and the crack width didn't change much, the cell voltage rose slowly. At the second, the separating stage, the NILC and the width dropped quickly as the voltage went up. At the third, the breaking stage, the voltage rose dramatically, the surface morphology was analogous to that of etched titanium. The first two were dominant stages which occupied almost all the service life of the anodes.

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