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A STUDY ON THE DURABILITY OF DIMENSIONALLY STABLE ELECTRODE IN HIGH-RATE ELECTROPLATING PROCESS CONDITION USING ACCELERATED LIFE TEST

In order to the long-term stability of DSE for electroplating process, the lifetime equations were calculated from the results of the accelerated life testing, and the lifetime of DSE was predicted. The nano-embossing pre-treatment led to 2.65 times in the lifetime of DSE. The degradation mechanism of DSE with a thick metal oxide layer for applied highly current density process condition was identified. The improvement of durability of DSE seems to be closely related to adhesion between titanium plate and mixed metal oxide layer.

Keywords: Durability, Prediction, Dimensionally stable electrode, Accelerated life test, Failure mechanism

1. Introduction

Dimensionally stable Electrode (DSE) is used various industry such as electrodeposited copper foil manufacturing process, electrowinning process, sea water treatment and sodium hypochlorite production. DSEs were manufactured mixed metal oxide composition such as iridium, ruthenium, platinum, palladium, tin and tantalum on titanium substrate [1,2]. The electroplating reactions are accompanied by the oxidation reaction of the anode and the reduction reaction of the cathode. The large amounts of oxygen evolution reaction at the anode for high-rate electroplating process condition is facilitated degradation on the surface coating of mixed metal oxide. The long lifetime of DSE is the most important for long-term stability of electroplating process. It was generally known that electroplating performance and long lifetime of the DSE could be determined by manufacturing process conditions such as component, composition, coating layer thickness, and heat treatment of the mixed metal oxide [3,4]. In addition, the study has been conducted that the durability of DSE can be greatly improved by using the process of surface pre-treatment on the titanium plate and then coating of and then metal oxide coating [5,6]. In general, the lifetime of DSE is from several months to several years, it is necessary to study DSE lifetime evaluation for a short-term through harsher process conditions than actual electrochemical conditions [7]. In order to improve the long lifetime of DSE for high-rate electroplating process, in the present study, mixed noble metal oxides with excellent electrochemical properties and durability were used and optimum surface pre-treatment of titanium plate and heat treatment. In order to improve the long lifetime of DSE for high-rate electroplating process, in the present study, mixed noble metal oxides with excellent electrochemical properties and durability were fabricated using optimum surface pre-treatment of titanium plate and heat treatment. The reactor for the accelerated life test of DSE was produced that the occurrence of oxidation/reduction reaction of the electrodes under the high current density process conditions were similar. The lifetime of the DSE was predicted under the actual high-speed plating process conditions through the accelerated life testing evaluation. The surface and cross-section morphologies of DSE were characterized by field emission scanning electron microscopy (FE-SEM) and focused ion beam (FIB).

2. Experimental

The high purity of titanium plate was surface treated by blasting, and then the surface oxides were removed in oxalic acid solution. The titanium plate substrate was treated by anodic oxidation treatment and remove oxidation treatment in order to

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enhancement of lifetime of DSA. The titanium anodizing process using a mixture of ammonium fluoride, D. I. water and ethylene glycol as electrolyte. And then titanium anodizing layer was removed in oxalic acid. The coating solution was dissolved in isopropyl alcohol with $IrCl_3 \cdot H_2O$ and $TaCl_5$. 70 wt.% IrO_2 and 30 wt.% Ta_2O_5 composition ratios were coated by brushing the coating solution on titanium plate, and then thermal decomposed at 823K for 1 hours. The brushing and thermal decomposition processes were repeated for thirty times. To evaluation the lifetimes of DSE were performed that accelerated life testing using the produced reactor. The immersed surface of anode and cathode plate was 0.75 cm^2, applied current density of 12 to 18 A/cm^2. The distance between the anode and cathode was maintained 15 mm, mixed solution of 1 M sulfuric acid and organic additive at temperature of 323K was circulated into the reactor using a magnetic pump with a capacity of 8 L per minute. The applied potential change between electrodes during the accelerated life test was measured, the failure time of the DSE was assumed when the voltage increased by 50% compared to the initial applied potential.

3. Results and discussion

The failure time of DSE was evaluated by accelerated life testing at various current densities in the produced reactor. The operating potential range of electroplating process is constant, the applied potential increase as the degradation of metal oxide coating layer of DSE. Figure 1 shows the behavior of the failure time of DSE decreases as the applied current density increases. The failure time of DSE increase significantly due to surface pre-treatment of titanium plate. In Figure 1, the failure time was converted using the logarithm to obtain the equation for the linear failure time of DSE. And then, the fitted linear can be used to estimate the lifetime of DSE under the electroplating process conditions. The lifetime of DSE can be formulated using equation (1) and (2), with respect to the applied current density.

$$y = 10^{-0.10465x} + 952379 \qquad (1)$$

$$y = 10^{-0.0964x} + 2524527 \qquad (2)$$

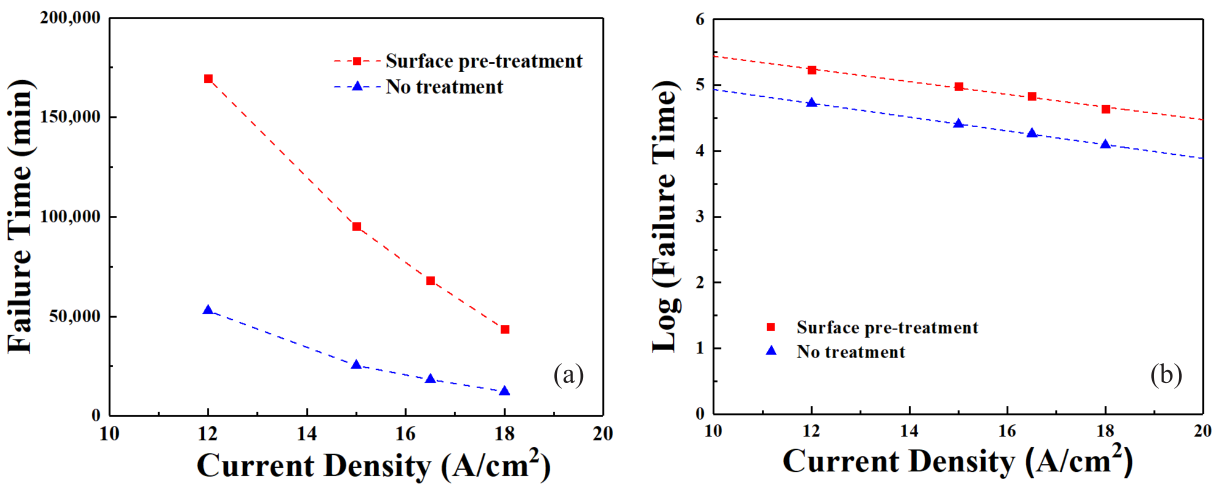

Fig. 1. Failure Time of DSE with and without the surface pre-treatment by accelerated life testing as function of applied current density; (a) failure time, (b) the fitted linear failure time

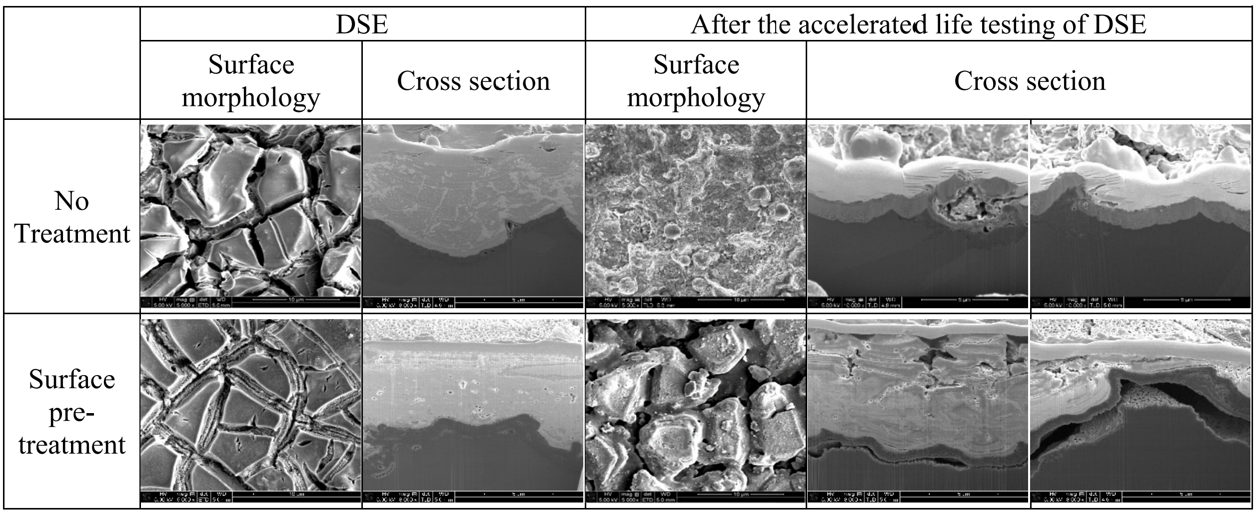

Fig. 2. The surface and cross-section morphologies of DSE before and after accelerated life testing

Equation (1) is the lifetime equation of DSE, and it is predicted that it can be used for about 15,873 hours under the 1 A/cm^2 current density process condition, which is an electrodeposited copper foil manufacturing generally used in the high-rate electroplating process. The lifetime of DSE made by metal oxide coating after surface pre-treatment of the titanium plate was predicted to be about 42,075 hours, which was greatly increased by Equation (2). After the accelerated life testing, the surface and cross-section morphologies of DSE were analyzed by FE-SEM and FIB, as shown in Fig. 2. The surface morphologies of the DSE, the mixed metal oxide layer was existed in the shape of mud crack generated by thermal decomposition at high temperature. The cross-section morphologies of the DSE, the mixed metal oxide coating layers with about 6.2 to 8.5 μm thickness was formed. The surfaces and cross-sections of the DSE after the accelerated life test were analyzed, the fabricated DSE without surface pre-treatment was not observed shape of mud cracks of metal oxide layer. However, the DSE with surface pre-treatment, the metal oxide layer having increased crack spacing was observed. It is reported that degradation mechanism of DSE is two type, the metal oxide was etched due to the long time of overpotential oxidation reaction. The other case, the DSE was degraded dissolution and anodic oxidation of titanium substrate which directly leads to mechanical loss of catalyst layer across the interface after the electrolyte penetrates through porous structure of thermally prepared oxide layer. In the results of accelerated life testing, the degradation mechanism of DSE with a thick metal oxide layer is as follows, as shown in Figure 3: i) the area of metal oxide layer gradually decreases due to the oxidation reaction by the high overpotential, ii) sulfuric acid penetrates through the wide mud crack, and the titanium oxide layer is formed by the oxidation reaction at the interface, iii) the thickness of the titanium oxide layer increases through a long time process, iv) cohesive failure occurs in titanium oxide layer. Figure 4 shows the surface morphologies on the titanium plate with and without surface pre-treatment by FE-SEM. The surface of the titanium plate without pre-treatment was observed a smooth and clean shape. But, the embossed shape of several to

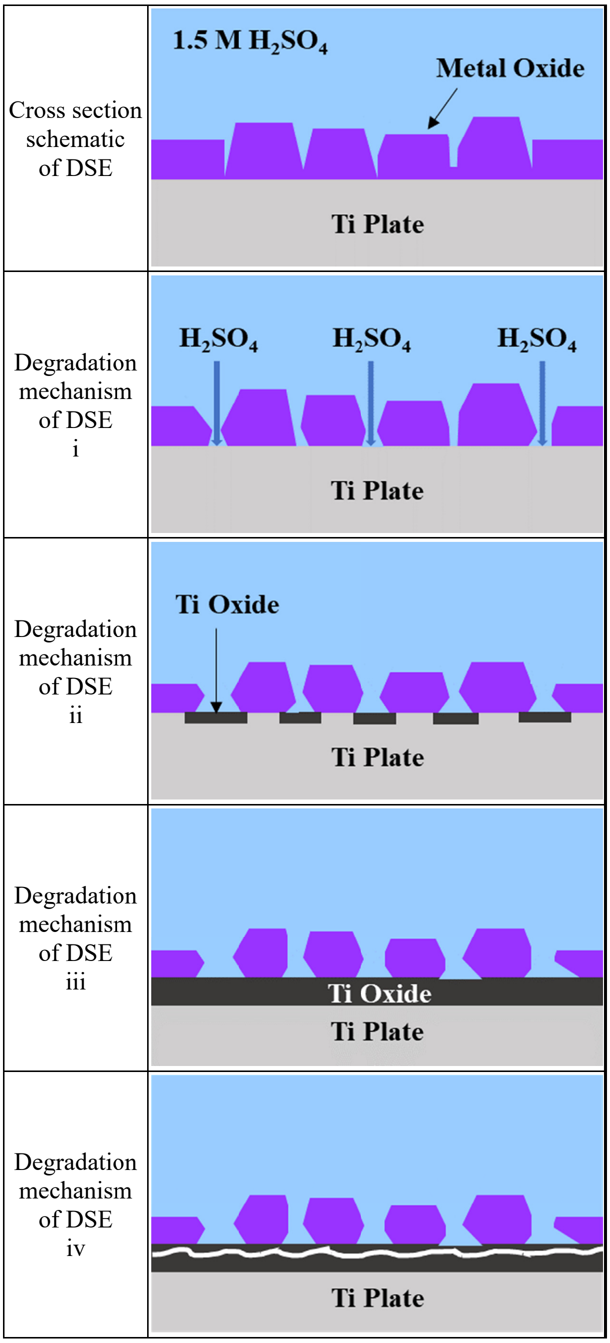

Fig. 3. The schematic diagram of degradation mechanism of DSE for high-rate electroplating process

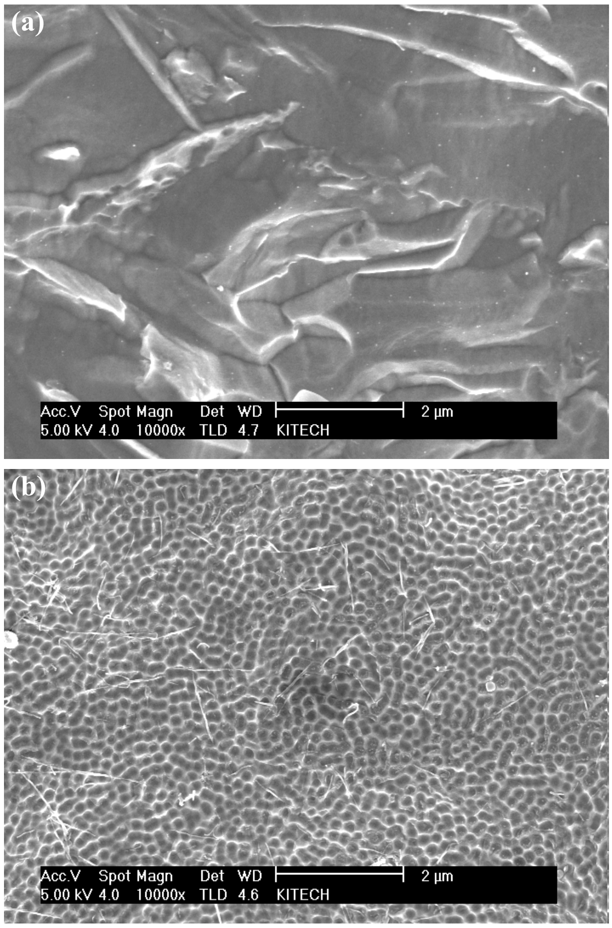

Fig. 4. FE-SEM images of surface morphologies on the titanium plate; (a) without treatment, (b) surface pre-treatment

tens of nanometers was observed on the surface of the titanium plate with pre-treatment. Surface pre-treatment of titanium pre-treatment leads to surface roughening of nano-embossing shape, the adhesion between the titanium plate and mixed metal oxide layer enhance due to the mechanical interlocking effect [8]. As a result, it seems that the durability of DSE is greatly improved while three effects occur. The crack area of the metal oxide layer is reduced, the generation of titanium oxide layer due to sulfuric acid penetration is reduced, and the cohesive failure of the titanium oxide layer is reduced.

4. Conclusions

The lifetime of the fabricated DSE was predicted according to the high-rate electroplating process conditions through the accelerated life test. After the test, the degradation mechanism of DSE was identified through the surface and cross-section morphologies analysis. The improvement of lifetime of DSE seems to be closely related to adhesion between titanium plate and metal oxide layer.

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