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Ordered Nano Particles in Amorphous IrO₂-Ta₂O₅ Coatings Detected by SEM with Low Accelerated Incident Electrons

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Surface morphology of IrO₂-Ta₂O₅ coatings produced by thermal decomposition was investigated by SEM with low accelerated incident electron beam. IrO₂-Ta₂O₅ coatings consisting of crystalline IrO₂ and amorphous Ta₂O₅ and of amorphous IrO₂ and Ta₂O₅ were examined, and a significant difference in surface morphology between them was found. The coating comprising crystalline IrO₂ showed a mud-cracked morphology with large segregated IrO₂ particles, and the flat area was porous with nano holes and cracks in addition to non-uniformly dispersed IrO₂ flakes of 20-60 nm. A smooth cracked surface with no segregated IrO₂ was observed for the amorphous coating, and ordered nano IrO₂ particles of 5-10 nm were further revealed.

Key Words : IrO₂-Ta₂O₅ Coatings, Ordered Nano Particles, Surface Morphology, Low Accelerated Electrons

1 Introduction

A mixed oxide coating consisting of iridium oxide and tantalum oxide is well known as oxygen evolution catalyst used in combination with a so-called valve metal substrate such as titanium or tantalum in industrial electrolysis, and we have reported oxygen evolution behaviors of the coating in acidic¹⁻³⁾ and alkaline⁴⁾ solutions and their applications in electrogalvanizing,^{5,6)} electroplating,^{7,8)} copper foil production,⁹⁾ and electrowinning.¹⁰⁾ Thermal decomposition of a precursor solution is used to form an IrO₂-Ta₂O₅ coating on a substrate, and one example of precursor solutions is prepared by dissolving H₂IrCl₆·6H₂O and TaCl₅ into 1-butanol containing HCl. The characteristics of IrO₂-Ta₂O₅ coatings depend on the composition and concentration of salts, solvent, and additives. Commercially available IrO₂-Ta₂O₅ coated Ti electrodes are produced by thermal decomposition of a precursor solution containing 70-80 mol% Ir and at a temperature of 450 °C or more, in which the coating consists of a mixture of crystalline IrO₂ and amorphous Ta₂O₅,⁶⁾ and the coating typically shows a heterogeneous mud-cracked surface, comprising IrO₂ aggregates, flat areas, and cracks.^{1,2,6,11-17)} The surface morphology is also affected by preparation conditions such as pretreatment of a substrate and painting method of a precursor solution.^{2,12-15)} For example, pretreatment of a titanium substrate was examined in some different ways, in which IrO₂ particles of 30-100 nm were observed on flat areas of the coating showing a low Tafel slope as a smooth titanium substrate was used.²⁾ Thermal decomposition temperature is further a crucial parameter for not only crystallographic and morphological structures but also catalytic properties of the obtained coatings. Our previous studies have demonstrated that low temperature decomposition at

380 °C or less results in amorphous IrO₂ in IrO₂-Ta₂O₅ coatings, and amorphous IrO₂ is also produced at low Ir mole ratio such as 50 mol% even when the decomposition temperature is higher than 400 °C.^{9,10)} It has been found in those studies that amorphous IrO₂-Ta₂O₅ coatings significantly influence on double layer charge and oxygen evolution in acidic aqueous solutions, which result in acceleration of oxygen evolution and suppression of unwanted side reactions such as anodic deposition of PbO₂ or MnOOH. However, little work on characterization of amorphous IrO₂-Ta₂O₅ coatings has been reported except by X-ray diffraction. This work focused on to surface morphology of such amorphous coatings and tried to explore the morphological feature with highly magnified SEM images obtained using in-lens detector and low acceleration voltage of incident electron beams.

2 Experimental

Two samples of IrO₂-Ta₂O₅ coatings were prepared on titanium substrates which had been degreased with acetone, etched in 10% oxalic acid solution at 90 °C for 60 min, washed with distilled water, and dried. One of the samples (sample A) used a precursor solution prepared by dissolving H₂IrCl₆·6H₂O and TaCl₅ into 1-butanol containing 6 vol% HCl, in which Ir:Ta ratio was 80:20 mol% and thermal decomposition was carried out at 470 °C for 20 min for one coating. The composition and thermal decomposition temperature are similar to those of commercially available IrO₂-Ta₂O₅/Ti electrodes. For the other sample (sample B), Ir mole ratio was 50 mol% and thermal decomposition temperature was set to be 380 °C. Decreasing Ir mole ratio or reducing thermal decomposition temperature each induces amorphization of IrO₂ so that we aimed in the preparation of sample B to promote

IrO_2 amorphization by both of them. Other preparation conditions are the same for two samples; total metal concentration of the precursor solution was 70 g dm^{-3} , and the coating and heating process was repeated five times. X-ray diffraction with Cu $K\alpha$ radiation (Bruker AXS Model D8 FOCUS) was performed to analyze crystallographic structure of the coatings. Surface morphology was observed using high-resolution SEM (ZEISS Model SUPRA^M 55VP) with two different modes: Low magnification images ($\times 10,000$ or less) were obtained using a normal SE detector with incident electron beam of 15 keV acceleration voltage, and high magnification images ($\times 70,000$ or more) using in-lens SE detector with 1 keV. Such a low acceleration voltage is advantageous to reduce penetration depth of electron beam; for example, the depth at 1 keV is 5 nm which is 1/8 of the depth at 15 keV.¹⁸⁾ A resolution at 1 keV can be achieved to 1.7 nm.

3 Results and Discussion

The XRD result of sample A presented a diffraction pattern of a titanium substrate and some diffraction peaks corresponding to crystalline IrO_2 as shown in Fig. 1A. Sample B also gave diffraction peaks of titanium, but two diffraction peaks of (110) and (101) of IrO_2 observed for sample A disappeared in Fig. 1B. Instead, a broad wave arose at $2\theta = 28\text{--}35^\circ$, which indicates that IrO_2 is amorphous in sample B. Ta_2O_5 prepared by thermal decomposition is amorphous as thermal decomposition temperature is lower than at least 600°C ^{19,20)}. Therefore, sample A consisted of crystalline IrO_2 and amorphous Ta_2O_5 , while sample B was composed of amorphous IrO_2 and Ta_2O_5 .

Figure 2 depicts SEM images of coating surface of two samples at low magnifications ($\times 1,500$ and $\times 10,000$). Sample A (left two photos of Fig. 2) showed a well-known feature of $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coatings; there are aggregated IrO_2 particles, flat areas, and cracks. Cracks are at least a few micro meters in length, and the morphology is heterogeneous and a so-called “mud-cracked” surface.

Fig. 1 XRD patterns of $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coatings formed on titanium substrates. Sample A (top): Ir = 80 mol%, 470°C . Sample B (bottom): Ir = 50 mol%, 380°C .

SEM images of sample B (right two photos of Fig. 2) reflected amorphous feature of the coating; *i.e.*, the surface seems to be smooth and no IrO_2 particle exists differently from sample A, although cracks are seen on samples B.

A significant difference between samples A and B was revealed from SEM images at high magnification, which were obtained using low accelerated electron beam at 1 keV. Figures 3a and 3c focus on flat area, and 3b shows magnified image of aggregated IrO_2 particles for sample A. The flat area is, in fact, not “flat” and is porous surface with nano holes and cracks of *ca.* 200 nm in maximum. This porous surface also comprises *ca.* 20–60 nm IrO_2 flakes, which are similar to those observed in our previous study.²⁾ The size of aggregated IrO_2 shown in Fig. 3b is 100 nm or more, and a three-dimensional architecture, upper cubic and lower triangle, of IrO_2 crystallites is clearly displayed. On the other hand, Figure 4 demonstrates that the surface of amorphous $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coating is really flat in nano scale, without no nano holes and cracks. Furthermore, highly ordered nano particles of IrO_2 , of which the size is 5–10 nm, can be seen. In our knowledge, the presence of such ordered nano IrO_2 has not been reported before for amorphous $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coatings and by SEM observation. This particular feature would be related to the fact that this binary oxide is an immiscible system and possibly to a difference in crystallization energy between two oxides.

As mentioned in Introduction, amorphous $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coatings are superior to crystalline $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coatings on oxygen evolution. This is because of higher active surface area of the amorphous coating, which has been proven by measurements of double layer charge and oxygen evolution current.^{9,10)} Here, this work supports those results by difference in surface morphology of two samples comprising amorphous or crystalline IrO_2 . One can easily understand that the increase in active surface area and oxygen evolution current by amorphization of IrO_2 results from generation of ordered nano IrO_2 as shown in Fig. 4. It is also presumed that such nano

Fig. 2 Surface morphologies of sample A (left two) and sample B (right two). Magnification: $\times 1,500$ (top two), $\times 10,000$ (bottom two). Acceleration voltage: 15 keV.

Fig. 3 Surface morphologies of sample A. Magnification: $\times 70,000$ (a and b), $\times 130,000$ (c). Acceleration voltage: 1 keV.

Fig. 4 Surface morphologies of sample B. Magnification: $\times 70,000$ (a), $\times 130,000$ (b), $\times 200,000$ (c). Acceleration voltage: 1 keV.

oxides are not preferable to be active points for nucleation and growth in anodic deposition of oxides, *e.g.*, PbO_2 deposition,⁹⁾ because high nucleation overpotential is required.

4 Conclusion

SEM observation with low accelerated electron beam gave valuable results on surface morphology of IrO_2 - Ta_2O_5 coatings prepared by thermal decomposition, and ordered nano IrO_2 particles were confirmed in the amorphous coatings. It should be noted that thermal decomposition can be applied for small to large sizes of and various shapes of substrates and one can control the crystallographic structure of mixed oxide and make nano oxide particles in an immiscible binary system only by changing thermal decomposition temperature. Further analysis of IrO_2 - Ta_2O_5 coatings prepared under various conditions of Ir:Ta ratio and thermal decomposition temperature is now under progress.

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