Ordered Nano Particles in Amorphous IrO$_2$-Ta$_2$O$_5$ Coatings Detected by SEM with Low Accelerated Incident Electrons

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Surface morphology of IrO$_2$-Ta$_2$O$_5$ coatings produced by thermal decomposition was investigated by SEM with low accelerated incident electron beam. IrO$_2$-Ta$_2$O$_5$ coatings consisting of crystalline IrO$_2$ and amorphous Ta$_2$O$_5$ and of amorphous IrO$_2$ and Ta$_2$O$_5$ were examined, and a significant difference in surface morphology between them was found. The coating comprising crystalline IrO$_2$ showed a mud-cracked morphology with large segregated IrO$_2$ particles, and the flat area was porous with nano holes and cracks in addition to non-uniformly dispersed IrO$_2$ flakes of 20-60 nm. A smooth cracked surface with no segregated IrO$_2$ was observed for the amorphous coating, and ordered nano IrO$_2$ particles of 5-10 nm were further revealed.

Key Words : IrO$_2$-Ta$_2$O$_5$ 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 acidic$^{[3-5]}$ and alkaline$^{[6]}$ solutions and their applications in electrogalvanizing,$^{[6]}$ electrocrystallization,$^{[7,8]}$ and copper foil production.$^{[9]}$ Thermal decomposition of a precursor solution is used to form an IrO$_2$-Ta$_2$O$_5$ coating on a substrate, and one example of precursor solutions is prepared by dissolving H$_2$IrCl$_6$·6H$_2$O and TaCl$_5$ into 1-butanol containing HCl. The characteristics of IrO$_2$-Ta$_2$O$_5$ coatings depend on the composition and concentration of salts, solvent, and additives. Commercially available IrO$_2$-Ta$_2$O$_5$ coated Ti electrodes are produced by thermal decomposition of a precursor solution containing 70-80 mol% Ir and at a temperature of 450 ℃ or more, in which the coating consists of a mixture of crystalline IrO$_2$ and amorphous Ta$_2$O$_5$,$^{[9]}$ and the coating typically shows a heterogeneous mud-cracked surface, comprising IrO$_2$ aggregates, flat areas, and cracks.$^{[10]}$ The surface morphology is also affected by preparation conditions such as pretreatment of a substrate and painting method of a precursor solution.$^{[11,12]}$ For example, pretreatment of a titanium substrate was examined in some different ways, in which IrO$_2$ 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.$^{[13]}$ 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 ℃ or less results in amorphous IrO$_2$ in IrO$_2$-Ta$_2$O$_5$ coatings, and amorphous IrO$_2$ is also produced at low Ir mole ratio such as 50 mol% even when the decomposition temperature is higher than 400 ℃.$^{[14-16]}$ It has been found in those studies that amorphous IrO$_2$-Ta$_2$O$_5$ 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 PbO$_2$ or MnOOH. However, little work on characterization of amorphous IrO$_2$-Ta$_2$O$_5$ 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 IrO$_2$-Ta$_2$O$_5$ coatings were prepared on titanium substrates which had been degreased with acetone, etched in 10% oxalic acid solution at 90 ℃ for 60 min, washed with distilled water, and dried. One of the samples (sample A) used a precursor solution prepared by dissolving H$_2$IrCl$_6$·6H$_2$O and TaCl$_5$ into 1-butanol containing 6 vol% HCl, in which Ir:Ta ratio was 80:20 mol% and thermal decomposition was carried out at 470 ℃ for 20 min for one coating. The composition and thermal decomposition temperature are similar to those of commercially available IrO$_2$-Ta$_2$O$_5$/Ti electrodes. For the other sample (sample B), Ir mole ratio was 50 mol% and thermal decomposition temperature was set to be 380 ℃. Decreasing Ir mole ratio or reducing thermal decomposition temperature each induces amorphization of IrO$_2$ 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 heating and curing process was repeated five times. X-ray diffraction with Cu Kα 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 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 $2\theta = 28$–35°, which indicates that IrO$_2$ is amorphous in sample B. Ta$_2$O$_5$ 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$_2$O$_5$, while sample B was composed of amorphous IrO$_2$ and Ta$_2$O$_5$.

Figure 2 depicts SEM images of coating surface of two samples at low magnifications (×1,500 and ×10,000). Sample A (left two photos of Fig. 2) showed a well-known feature of IrO$_2$-Ta$_2$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. 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 IrO$_2$-Ta$_2$O$_5$ coating is really flat in nano scale, without 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 IrO$_2$-Ta$_2$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 IrO$_2$-Ta$_2$O$_5$ coatings are superior to crystalline IrO$_2$-Ta$_2$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. 1 XRD patterns of IrO$_2$-Ta$_2$O$_5$ coatings formed on titanium substrates. Sample A (top): Ir = 80 mol%, 470°C. Sample B (bottom): Ir = 50 mol%, 380°C.](image1)

![Fig. 2 Surface morphologies of sample A (left two) and sample B (right two). Magnification: ×1,500 (top two), ×10,000 (bottom two). Acceleration voltage: 15 keV.](image2)
oxides are not preferable to be active points for nucleation and growth in anodic deposition of oxides, e.g., PbO₂ deposition, because high nucleation overpotential is required.

4 Conclusion

SEM observation with low accelerated electron beam gave valuable results on surface morphology of IrO₂-Ta₂O₅ coatings prepared by thermal decomposition, and ordered nano IrO₂ 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 IrO₂-Ta₂O₅ coatings prepared under various conditions of Ir:Ta ratio and thermal decomposition temperature is now under progress.

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