

PREPARATION OF HIGHLY CORROSION-RESISTANT (Pt,B₂O₃)/Ti ELECTRODE WITH NOVEL COATING LAYER MICROSTRUCTURE

Takashi Mitamura¹, Yuji Saeki², Yoichi Kamegaya³,
Hidehiko Kobayashi⁴ and Dong-Ying Ju⁵

¹*Advanced Science Research Laboratory, Saitama Institute of Technology,
1690, Fusaiji, Okabe 369-0293, Japan*

²*Graduate School of Engineering, Saitama Institute of Technology,
1690, Fusaiji, Okabe 369- 0293, Japan*

³*Ishifuku Metal Industry Co. Ltd., Aoyagi, Soka 340-0002, Japan*

⁴*Department of Applied Chemistry, Saitama University,
255, Shimo-ohkubo, Urawa 338-8570, Japan*

⁵*Department of Mechanical Engineering, Saitama Institute of Technology,
1690, Fusaiji, Okabe 369-0293, Japan*

SUMMARY: A (Pt, B₂O₃)/Ti electrode with a novel coating layer (derived from H₂PtCl₆.6H₂O and H₃BO₃) microstructure was prepared and evaluated. A coating solution of H₂PtCl₆.6H₂O and 530mass% H₃BO₃ powder dissolved in butanol was applied to a Ti substrate, and the (Pt, B₂O₃)/Ti electrode was prepared at 250.550. The novel coating layer microstructure, which consists of a network of fine Pt particles in an amorphous B₂O₃ matrix, was quite different from that of conventional (Pt, Ta₂O₅)/Ti electrodes. Furthermore, we found that the electrodes (Pt content greater than 0.4mg) prepared at 300. with 20mass% H₃BO₃ were remarkably stable and had excellent durability.

KEYWORDS: Durability, Boric acid, H₂PtCl₆.6H₂O, Pt coated Ti electrode, B₂O₃, Thermal decomposition

INTRODUCTION

Suppression of corrosion at the juncture between Ti substrate and coating layer improves the durability of Ti-substrate coated electrodes used in oxygen evolution. Corrosion of Ti substrate becomes particularly problematic under the relatively harsh conditions encountered

in H_2SO_4 solutions. The stability of the juncture between Ti substrate and coating layer is a particularly important factor in the durability of such electrodes. Amorphous SiO_2 (Mushiake, Mitsuda, Shida, Horiguchi, Yamashita and Matsusaka)[1], Ta_2O_5 (Kobayashi, Kamegaya, Noguchi and Mitamura)[2] and other ceramic oxides (Trasatti)[3] have previously been examined as materials for use in protecting the Ti substrate from corrosive environments.

Researchers have also examined the possibility of increasing endurance of electrodes by the introduction of Pt (for its conductivity) and an intermediate layer of amorphous Ta_2O_5 (for its high corrosion resistance) between the Ti substrate and the coating layer (Kamegaya, Sasaki, Oguri, Asaki and Mitamura)[4]. In this study, we explored the possibility of increasing the endurance of coated Ti electrodes through the use of amorphous B_2O_3 , which can selectively cover the grain boundary of Ti, at which there is high reactivity. Boric acid (H_3BO_3) was used to produce the B_2O_3 coating, and preparation conditions and durability of the (Pt, B_2O_3)/Ti electrodes were examined using the application-thermal decomposition method.

EXPERIMENTAL

The solution used to coat the Ti base body .10.10.0.5mm.consisted of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Pt concentration, 50g/l) and boric acid (H_3BO_3) dissolved in butanol at about 40., and the additive rate of H_3BO_3 was 5.30mass% (adjusted to control Pt concentration). Prior to use, Ti base bodies were etched in 4%HF solution, and then heated in (1+1) H_2SO_4 solution, washed with distilled water, and dried. The coating mixture was applied onto the Ti base body about 2 .l at a time. After drying at 70. for 30min, the substances were heated at 250.550. for 10min. By repeating this procedure, (Pt, B_2O_3)/Ti electrodes with a Pt content of 0.2.0.8mg were prepared.

The effective surface area of Pt in the coating layer of (Pt, B_2O_3)/Ti electrodes thus prepared was calculated from the electric quantity (C) of the hydrogen adsorption elimination wave on the CV figure, measured in 0.5M H_2SO_4 solution at 40. using a potentiostat. The lifetime of the electrode was calculated by applying a direct current of 1A, using the Pt plate as the counter electrode, in 1M H_2SO_4 solution at 40.. The end of life was defined as the time at which the cell voltage changed by a factor of 2 from the initial value. In addition, the microstructure of the (Pt, B_2O_3)/Ti electrode surface was studied by XRD (Rigaku Co., Rint 2000) and EPMA (JEOL Co., JXA8900R).

RESULTS AND DISCUSSION

(1) Thermal decomposition behavior of coating solution

The thermal decomposition behavior of coating solutions with 5 and 20mass% H_3BO_3 was investigated by TG-DTA. For comparison, TG-DTA values for $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ dissolved in

butanol and H_3BO_3 powder were also measured. In the case of the 20mass% H_3BO_3 coating solution, an endothermic peak equivalent to a weight loss equal to H_3BO_3 appeared near 170. In addition, exothermic peak equal to the $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ appeared, but the peak area decreased further than that of the 5mass% H_3BO_3 addition. The above results seem to indicate the reduction of the Pt of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ by the addition of H_3BO_3 . High-temperature XRD patterns of the product derived from a Ti base body and a coating solution with 5mass% H_3BO_3 , heating (in increments of 50.) from 250 to 650., are shown in Fig. 1. The diffraction peaks of Pt and B_2O_3 appeared at temperatures greater than 250 and 600., respectively.

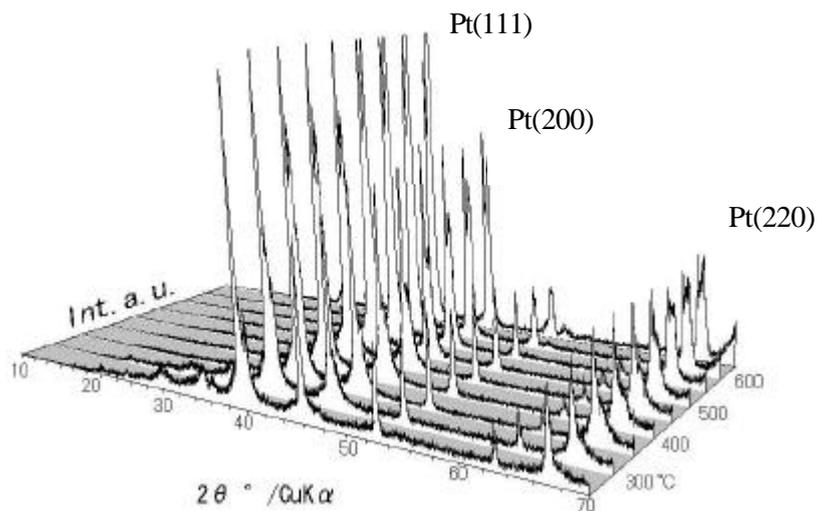


Fig.1 High-temperature XRD patterns of (Pt, B_2P_3)/Ti electrode.

These results indicate that the $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ decomposes to Pt at the relatively low temperature of 250., and that the H_3BO_3 acid becomes amorphous B_2O_3 at 300.550..

(2) Pt effective surface area of (Pt, B_2O_3)/Ti electrode

(Pt, B_2O_3)/Ti electrodes containing 0.2-0.8mg of Pt showed similar CV figures, and two clear peaks appeared in the adsorption elimination wave of the hydrogen. However, the reduction peak of O, in which only the first cycle appeared (generally near 0.5V), shifted by .025V, and the two peaks that were clearly observed in the adsorption elimination wave of the hydrogen did not appear. It seems that this is due to the electrolytic reduction of Cl. Subsequently, the relationship between effective surface area of Pt and thermal decomposition temperature of (Pt, B_2O_3)/Ti electrodes fabricated with 5mass% H_3BO_3 was examined. The surface area of electrodes containing 0.2-0.8mg Pt showed a maximum value of 495cm^2 at 250., and decreased with increasing calcination temperature. The results for the electrodes produced at 300. with 5.30mass% H_3BO_3 are shown in Fig. 2. The effective surface area of Pt increased with increasing Pt content.

The surface area of the electrode with 20mass% H_3BO_3 increased dramatically to a value of 604cm^2 at a Pt content of 0.8mg, while that of the electrode with 30mass% H_3BO_3 showed the

lowest values possibly because more of the Pt network was buried in B_2O_3 than was necessary.

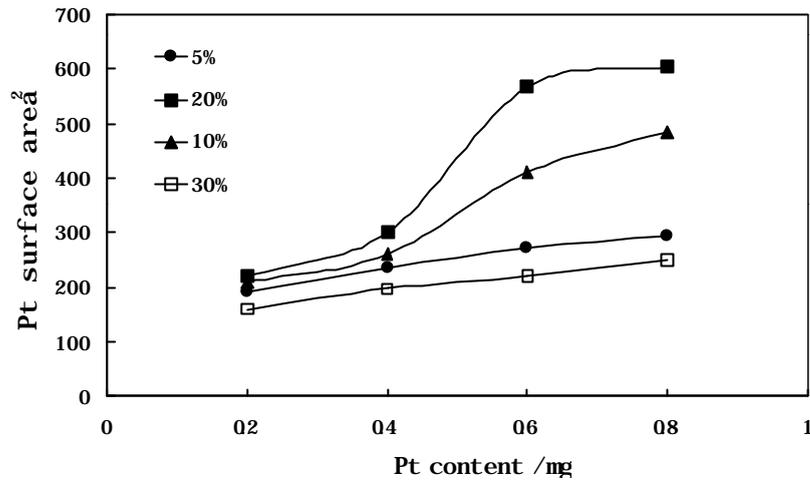


Fig.2 Effect of H_3BO_3 addition on the Pt surface area of $(Pt, B_2O_3)/Ti$ electrodes.

(3) Microstructure of $(Pt, B_2O_3)/Ti$ electrode

An SEM image of the surface of an electrode (Pt, 0.8mg) prepared at 300. using 20mass% H_3BO_3 is shown in Fig. 3. EPMA examination indicated that B (in the form of B_2O_3) and Pt were present in the grain and at the grain boundary of the Ti plate.

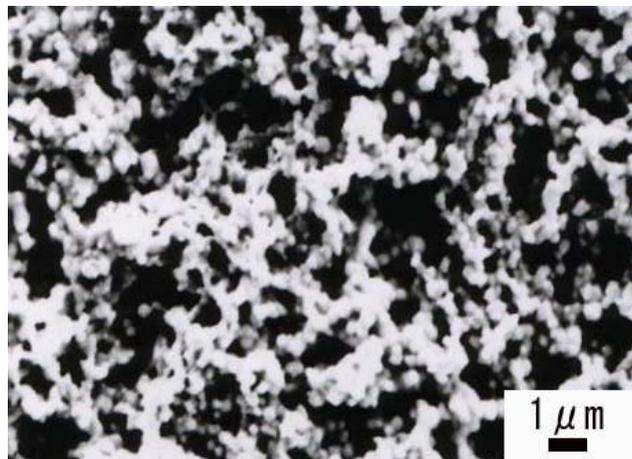


Fig.3 SEM micrograph of $(Pt, B_2O_3)/Ti$ electrode fabricated at 300 . using 20mass% H_3BO_3 (Pt:0.8mg).

Thus, it appears that this microstructure consists of a network of fine Pt particles in an amorphous B_2O_3 matrix. For comparison, an SEM image of a conventional $(Pt, Ta_2O_5)/Ti$ electrode is shown in Fig. 4. The coating is heterogeneous having a “cracked-mud” microstructure which differs remarkably from that of the $(Pt, B_2O_3)/Ti$ electrode.

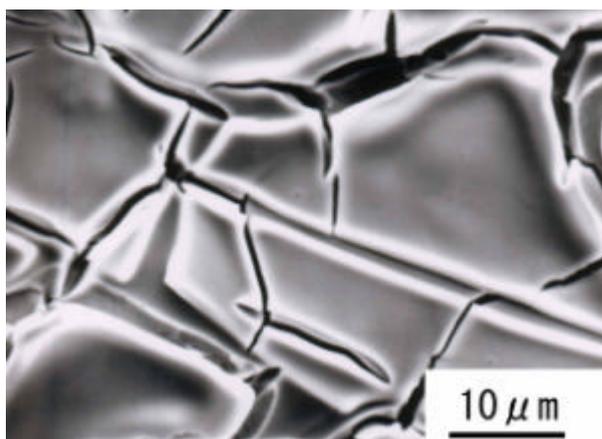


Fig.. SEM micrograph of (Pt,T₂O₅)/Ti electrode.

(4) Lifetime of (Pt, B₂O₃)/Ti electrode

The relationship between lifetime and Pt support content of (Pt, B₂O₃)/Ti electrodes produced at 300. is shown in Fig. 5. The durability of the electrode also improved in direct proportion to the Pt support content. In the case of the electrode (Pt, 0.8mg) with 20mass% H₃BO₃, the lifetime was about 2400h; i.e., 4 times that of the electrode with 5mass% H₃BO₃.

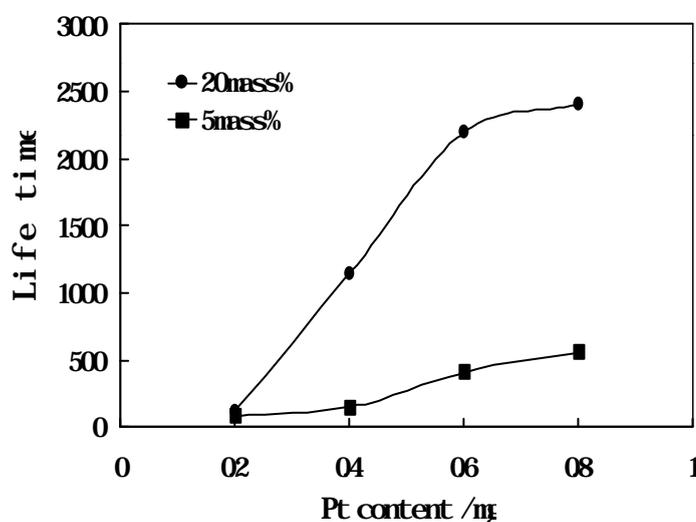


Fig.5 Effect of H₃BO₃ addition rate on the lifetime of (Pt,B₂O₃)/Ti electrodes.

The durability of (Pt, B₂O₃)/Ti electrodes was considerably greater (about 7-fold) than that of conventional (Pt, Ta₂O₅)/Ti electrodes, even at 5mass% H₃BO₃. After the lifetime test, plane analysis of Pt, B and Ti on the (Pt, B₂O₃)/Ti electrode surface was carried out by EPMA. The evidence indicates that the Pt in the crystal grains dissolves from the lattice into the electrolytic solution by elution during the lifetime test, but that the Pt and the B₂O₃ remain

near the grain boundary. The catalytic reaction of electrodes occurs preferentially in the crystal grain, and the grain boundary is most likely protected by B_2O_3 . Therefore, we can conclude that the coating layer of the (Pt, B_2O_3)/Ti electrode possesses a high degree of activity, and is highly durable.

CONCLUSION

A highly durable (Pt, B_2O_3)/Ti electrode was prepared at relatively low temperatures using a coating solution which consisted of $H_2PtCl_6 \cdot 6H_2O$ and H_3BO_3 dissolved in butanol. The results can be summarized as follows:

- (1) The microstructure of the coating layer of the (Pt, B_2O_3)/Ti electrodes was very different from that of conventional electrodes, such as (Pt, Ta_2O_5)/Ti electrodes, and consisted of a network of fine Pt particles in an amorphous B_2O_3 matrix.
- (2) The effective surface area of Pt of the (Pt, B_2O_3)/Ti electrode increased with increasing Pt content, and decreased as calcination temperature increased from 250 to 550.. It also increased as mass% of H_3BO_3 increased from 5 to 20, but it was lowest at 30mass% H_3BO_3 , possibly due to more of the Pt network being buried in B_2O_3 than was necessary.
- (3) The grain boundary of Ti in the (Pt, B_2O_3)/Ti electrode was most likely protected by amorphous B_2O_3 . Therefore, we can conclude that the coating layer of the (Pt, B_2O_3)/Ti electrode possesses high degree of activity, and is highly durable.

ACKNOWLEDGEMENT

The support provided by the High Technological Research Center of Saitama Institute of Technology in carrying out this work is gratefully acknowledged.

REFERENCES

1. Mushiake K., Mitsuda Y., Shida A., Horiguchi M., Yamashita S. and Matsusaka K., "Gradient of the Silica Content in IrO_2 - SiO_2 Catalyst Layers Stacked on a Titanium Substrate", *DENKI KAGAKU*, 1997. Vol.65, No.12
2. Kobayashi H., Kamegaya Y., Noguchi F. and Mitamura T., "Effect of Annealing Conditions on the Lifetime of Ta_2O_5 -Pt Coated Titanium Electrodes", *DENKI KAGAKU*, 1997. Vol.65, No.12
3. Trasatti, S., "Physical Electrochemistry of Ceramic Oxides", *Electrochim. Acta*, 1991. Vol. 36, No. 2
4. Kamegaya Y., Sasaki K., Oguri M., Asaki T. and Mitamura T., "A Newly Designed Titanium Anode for Oxygen Evolution at High Current Densities", *DENKI KAGAKU*, 1993. Vol.61, No.7