

# TiN coatings on copper and phosphor-bronze plates by the CVD process, and their oxidation and corrosion stabilities

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Copper and phosphor-bronze plates were coated with TiN layers by the chemical vapour deposition (CVD) process, and their oxidation and corrosion stabilities were examined in relation to the thickness of the TiN layer. TiN-coated copper plates were very stable to oxidation up to 700°C, and the weight increase of a specimen with a TiN layer thickness of 0.8 µm when exposed in air at 800°C was 1/8 of that of a bare specimen. The corrosion stabilities of copper and phosphor-bronze plates to concentrated HCl and 3.2 N HNO<sub>3</sub> solutions were improved outstandingly by TiN coatings with thicknesses of only 0.5 to 1.0 µm.

## 1. Introduction

Titanium nitride has very attractive characteristics such as high chemical and mechanical stabilities at elevated temperatures, high hardness, and also a fascinating golden lustre. Accordingly, titanium nitride has the most potential as a candidate for applications in protective coatings against severe corrosion, cavitation erosion and abrasion, and as a diffusion barrier in silicon device technology.

For example, Meletis and Carter [1] studied the corrosion resistivities of stainless steel (AISI 440C) coated with TiN layers against Ringer solution and NaCl solution, and found that the corrosion current densities were at least one order of magnitude less than those of the bare stainless steel. Matsumura *et al.* [2] reported that the cavitation erosion resistivities of stainless steel was outstandingly improved by coating TiN on the surface, and the weight decrease of a TiN-coated specimen (TiN thickness 10 µm) after 20 h of immersion was 1/30 of that of a chromium-coated specimen (chromium thickness 10 µm).

At the present time, titanium nitride coatings have been obtained by physical vapour deposition (PVD) methods such as ion plating [3, 4], reactive evaporation or sputtering [5-12] and ion implantation [13], by plasma chemical vapour deposition (CVD) [14-17], and by conventional thermal CVD [18-21].

We have reported on the corrosion and abrasion resistivities of TiN-coated stainless steel [22], and TiB<sub>2</sub> or TaB<sub>2</sub>-coated copper plates [23-26].

In this work, TiN layers were deposited on copper and phosphor-bronze plates, and their oxidation and corrosion stabilities were examined in relation to the thickness of the TiN layer.

## 2. Experimental procedures

The substrate (a pure copper or phosphor-bronze plate, 10 mm × 20 mm × 0.3 to 0.35 mm) was hung in the central part of a vertical reaction tube (quartz,

23 mm i.d. and 470 mm long) which was heated from the outside by a nichrome element. A gas mixture of titanium tetrachloride saturated into hydrogen, nitrogen, and argon was introduced into the lower gas inlet of the reaction tube. Representative gas flow rates used were as follows: total gas flow rate 2.0 ml sec<sup>-1</sup>, H<sub>2</sub> flow rate 0.55 ml sec<sup>-1</sup> and TiCl<sub>4</sub> flow rate 0.25 ml sec<sup>-1</sup>.

TiN-coated specimens were heated in an air atmosphere to an elevated temperature at a rate of increase of 20°C min<sup>-1</sup>, and the weight increase was measured. Specimens were also dipped in concentrated hydrochloric acid or 3.2 N nitric acid solution at a temperature of 60°C, and the weight decrease caused by corrosion was measured at intervals.

## 3. Results and discussion

### 3.1. Deposition parameters and morphology

The effects of the reaction (deposition) temperature on the thickness of the TiN layers deposited on the copper and phosphor-bronze plates are shown in Fig. 1. The lowest deposition temperatures of TiN layers on the copper plates as well as the phosphor-bronze plates were about 670°C, at which the characteristic colours of copper or phosphor-bronze metal disappeared completely to turn a golden colour, indicating the formation of TiN layers. This lowest deposition temperature of TiN layers is 30 to 150°C lower than that for other substrates. A similar lowering effect on the deposition temperature was also observed for the deposition of TiB<sub>2</sub>, TaB and TaB<sub>2</sub> layers on to a copper substrate [25, 26]. These lowering effects on the deposition temperature of the coating layer are probably attributable to a high catalytic activation of the surface of the copper or phosphor-bronze plate for the nucleation of crystallites.

The effect of the source gas flow ratio (N/Ti) on the deposition of TiN layers on to copper plates at a temperature of 900°C is shown in Fig. 2, in which the

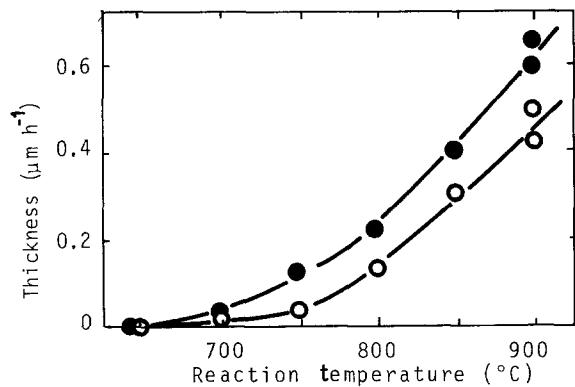


Figure 1 Effect of the reaction temperature on the deposition of TiN layers. Substrate (○) copper plate, (●) phosphor bronze plate. Reaction time 30 min, H<sub>2</sub> flow rate 2.0 ml sec<sup>-1</sup>, N<sub>2</sub> flow rate 0.55 ml sec<sup>-1</sup>, TiCl<sub>4</sub> flow rate 0.091 ml sec<sup>-1</sup>.

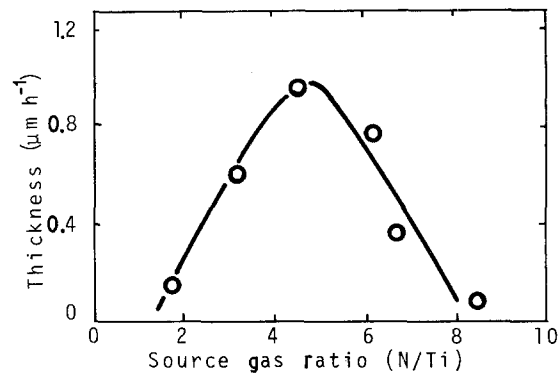


Figure 2 Effect of the source gas flow ratio (N/Ti) on the deposition of TiN layers. Substrate: copper plate, reaction temperature 900°C reaction time 30 min, H<sub>2</sub> flow rate 2.0 ml sec<sup>-1</sup>, sum of flow rates of N<sub>2</sub> and TiCl<sub>4</sub> 0.80 ml sec<sup>-1</sup>.

sum of the flow rates of N<sub>2</sub> and TiCl<sub>4</sub> was fixed at 0.80 ml sec<sup>-1</sup>. The greatest thickness of TiN layer was attained at ratios (N/Ti) of 4 to 6, and the thickness decreased steeply above or below these ratios

The thickness of the TiN layer increased linearly with increasing reaction time from the initial stage of deposition.

The surface appearances of TiN layers deposited on phosphor-bronze plates at various temperatures are shown in Fig. 3. The surfaces of TiN layers obtained below 900°C were considerably smooth and dense, and grain growth or apparent crystal facets were not observed (Figs 3a and b). However, wrinkles and cracks were observed sometimes here and there on the TiN layers obtained at 950°C (Fig. 3c), in which the thickness of the TiN layer was about 1.5 µm. Similar surface appearances to those of TiN-coated

phosphor-bronze plates were observed on copper plates.

Polished cross-sections of TiN-coated specimens are shown in Fig. 4. It can be seen that TiN layers deposited on the surface of the substrate encroached like saw-teeth into the substrate, which may be effective for good adhesion of the TiN layer. Thus, thin TiN layers (below 1 µm) were very adherent to copper or phosphor-bronze plates. However, thick TiN layers (above 1.5 µm) were apt to form cracks or to exfoliate, probably because of the large difference in the thermal expansion coefficients of TiN layers and substrates.

TiN layers obtained at temperatures below 800°C were amorphous and were not identified as TiN by X-ray diffraction, but could reasonably be considered to be TiN from their characteristic golden colour and the results of electron microprobe analysis (EPMA) by which titanium and nitrogen were found in the layers. Apparent peaks of TiN were observed for the deposits obtained at a temperature of 850°C.

### 3.2. Oxidation stability

The weight increase of a TiN-coated copper plate exposed in an air atmosphere at elevated temperatures is shown in Fig. 5, with that of the bare copper plate

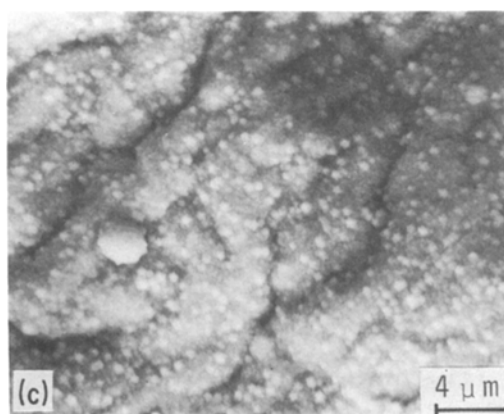
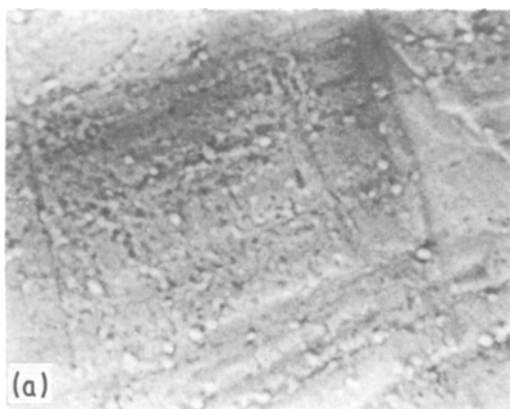


Figure 3 Surface appearances of TiN layers. Substrate: copper plate, reaction temperature (a) 750°C, (b) 900°C, (c) 950°C. Reaction time 30 min, H<sub>2</sub> flow rate 2.0 ml sec<sup>-1</sup>, N<sub>2</sub> flow rate 0.55 ml sec<sup>-1</sup>, TiCl<sub>4</sub> flow rate 0.25 ml sec<sup>-1</sup>.

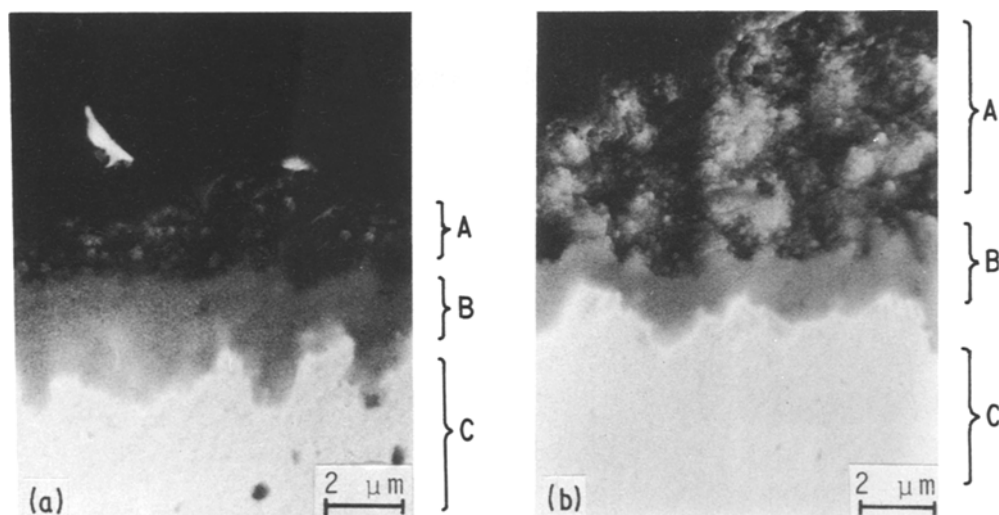


Figure 4 Cross-sections (polished obliquely) of the TiN coated plates. Substrate (a) copper plate, (b) phosphor-bronze plate. (A) Surface of TiN layer, (B) TiN layer, (C) substrate. Reaction temperature  $900^{\circ}\text{C}$ ,  $\text{H}_2$  flow rate  $2.0\text{ ml sec}^{-1}$ ,  $\text{N}_2$  flow rate  $0.55\text{ ml sec}^{-1}$ ,  $\text{TiCl}_4$  flow rate  $0.25\text{ ml sec}^{-1}$ .

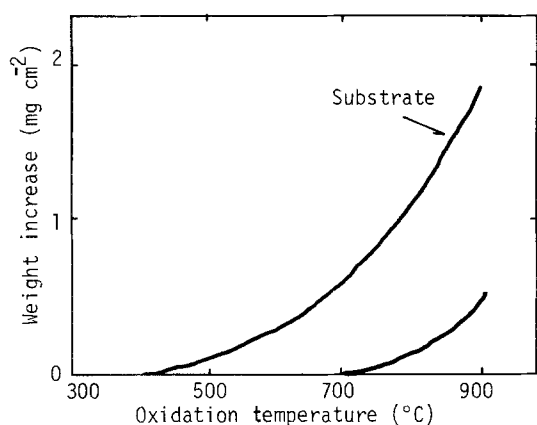


Figure 5 Weight increase of TiN-coated copper plates when exposed in air at elevated temperatures. Rate of increase of the oxidation temperature  $20^{\circ}\text{C min}^{-1}$ , thickness of TiN layer  $0.8\text{ }\mu\text{m}$ , reaction temperature  $850^{\circ}\text{C}$ ,  $\text{H}_2$  flow rate  $2.0\text{ ml sec}^{-1}$ ,  $\text{N}_2$  flow rate  $0.55\text{ ml sec}^{-1}$ ,  $\text{TiCl}_4$  flow rate  $0.25\text{ ml sec}^{-1}$ .

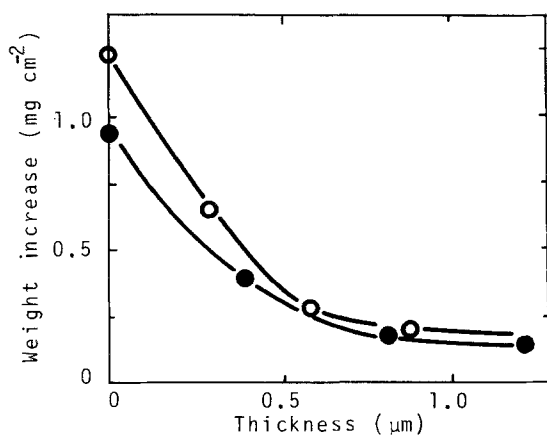


Figure 6 Effect of the thickness of the TiN layer on the weight increase of TiN-coated plates when exposed in air at temperatures up to  $800^{\circ}\text{C}$ . Substrate (○) copper plate, (●) phosphor-bronze plate. Rate of increase of the oxidation temperature  $20^{\circ}\text{C min}^{-1}$ , final oxidation temperature  $800^{\circ}\text{C}$ . Deposition conditions of TiN layers were the same as for Fig. 5.

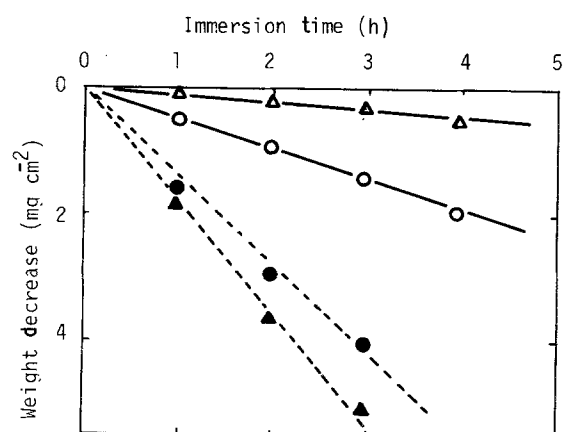


Figure 7 Weight decrease of TiN-coated plate when immersed in concentrated HCl solution at  $60^{\circ}\text{C}$ . Substrate (▲) bare copper plate, (●) bare phosphor-bronze plate, (○) TiN-coated phosphor-bronze plate (thickness of TiN layer  $0.4$  to  $1.1\text{ }\mu\text{m}$ ), (Δ) TiN-coated copper plate (thickness of TiN layer  $1.1\text{ }\mu\text{m}$ ). Deposition conditions of TiN layers were the same as for Fig. 5.

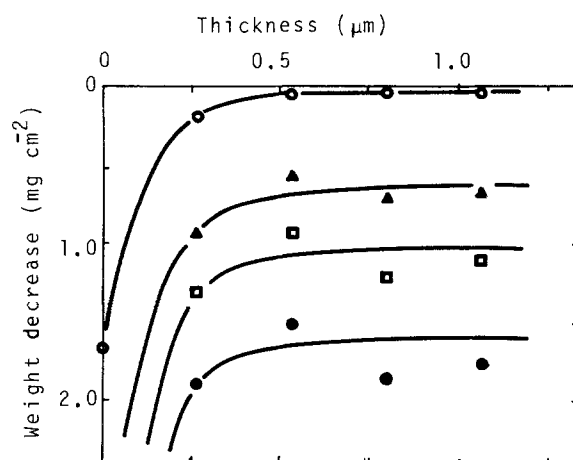


Figure 8 Effect of the thickness of the TiN layer on the weight decrease of TiN-coated phosphor-bronze plates when immersed in concentrated HCl solution at  $60^{\circ}\text{C}$ . Immersion time (○) 1 h, (Δ) 2 h, (□) 3 h, (●) 4 h. Deposition conditions of TiN layers were the same as for Fig. 5 except for the reaction temperature of  $750^{\circ}\text{C}$ .

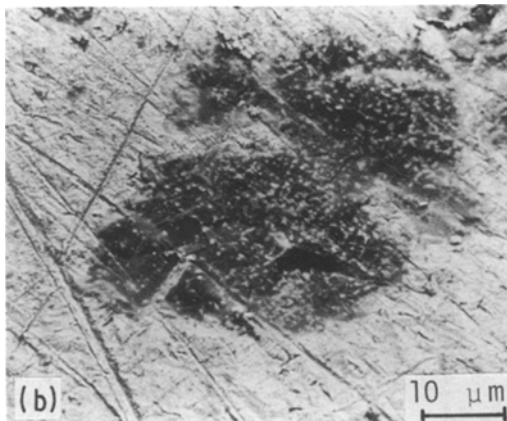
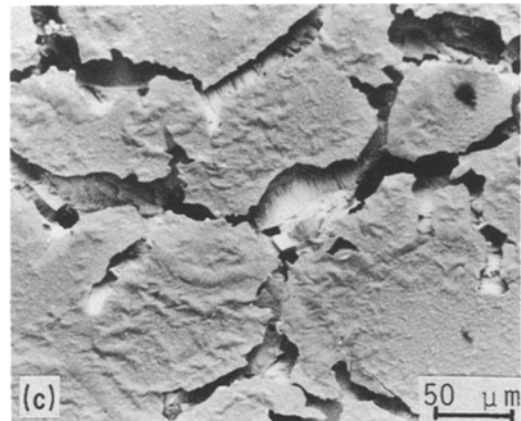
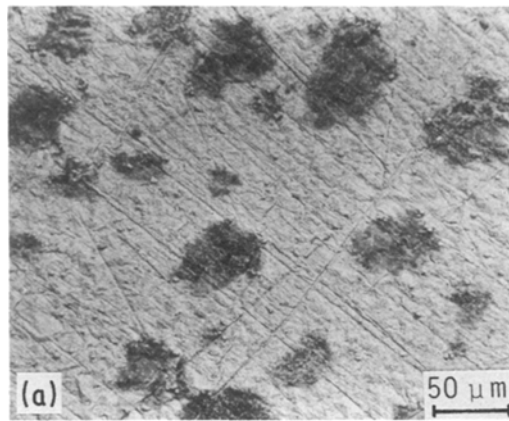


Figure 9 Surface appearances of TiN-coated phosphor bronze plates after immersion in concentrated HCl solution. Thickness of TiN layer (a, b) 0.2  $\mu\text{m}$ , (c) 1.5  $\mu\text{m}$ . Temperature of HCl 60° C, immersion time 3 h. Deposition conditions of TiN layers were the same as for Fig. 5 except for the reaction temperature of 900° C.

as a reference sample. The bare copper plate begins to be oxidized at temperatures above 400° C, and oxidized outstandingly above 700° C. On the other hand, a weight increase of the TiN-coated copper plate was not observed at all at a temperature of 700° C, and the weight increased gradually at temperatures above 700° C. The weight increase of a TiN-coated copper plate exposed in air at 800° C was 1/8 of that of the bare copper plate. A similar small weight increase as for the TiN-coated copper plate was observed for a TiN-coated phosphor-bronze plate.

The effect of the thickness of the TiN layer on the weight increase of TiN-coated plates exposed in air at 800° C is shown in Fig. 6. It can be seen that the weight increase of the TiN-coated plate was reduced outstandingly with increasing thickness of the TiN layer and attained a constant value above 0.5 to 1.0  $\mu\text{m}$  thickness. Thus the oxidation stability of copper and phosphor-bronze plates will be improved outstandingly by thin TiN coatings (< 1  $\mu\text{m}$ ) on their surfaces.

### 3.3. Corrosion stabilities

The weight decreases of TiN-coated copper and phosphor-bronze plates when immersed in concentrated HCl solution for a given time at 60° C are shown in Fig. 7, in which the thickness of the TiN layer was fixed at 1.1  $\mu\text{m}$  and the deposition temperature at 850° C. The weight of a TiN-coated plate decreased linearly with increasing immersion time, but the rate of decrease is considerably smaller than that of a bare plate: 1/30 for a copper plate and 1/3 for a phosphor-bronze plate.

The effect of the thickness of the TiN layer on the

weight decrease of a TiN-coated phosphor-bronze plate when immersed in concentrated HCl solution at 60° C is shown in Fig. 8, in relation to the immersion time. The weight decrease was reduced steeply with increasing thickness of the TiN layer and attained a constant value, depending on the immersion time, at a thickness above 0.5 to 1.0  $\mu\text{m}$  irrespective of the immersion time. The TiN layer itself is very stable to concentrated HCl solutions or HCl gas at high temperatures.

The surface appearances of the TiN-coated phosphor-bronze plates which were immersed in concentrated HCl solutions for 3 h are shown in Fig. 9, in which the thickness of TiN layer was 0.2  $\mu\text{m}$  (Figs 9a and b) or 1.5  $\mu\text{m}$  (Fig. 9c). Many tarnished regions were observed on the surface here and there (Fig. 9a), and the area of this region extended with increasing immersion time. Furthermore, exfoliation of a part of the TiN layer of these tarnished regions was also observed (Fig. 9b). It was also observed on a cross-section that a void or cavity was always formed beneath a tarnished region. It may be considered that concentrated HCl solutions diffuse into the boundary regions through pinholes or cracks present in the coated TiN layer, and then corrode the phosphor-bronze substrate. It is in general observed that the thicker the coated layer, the smaller the number of pinholes present in the coated layer, and that no pinholes are observed in coated layers with a thickness above 5 to 10  $\mu\text{m}$ . In the case of TiN-coated copper or phosphor-bronze plates, TiN layers with a thickness above 1.5  $\mu\text{m}$  are apt to form cracks or to exfoliate from the substrate (Fig. 9c). A large number of pinholes will be present in thin TiN layers with a thickness below 1  $\mu\text{m}$ . Thus, the weight decrease observed in this work may be attributable to the corrosion of the substrate through pinholes and/or cracks present in the TiN layers.

The effect of the thickness of the TiN layer on the weight decrease of a TiN-coated copper plate when immersed in 3.2N HNO<sub>3</sub> solution for a given time is shown in Fig. 10. The weight decrease was reduced

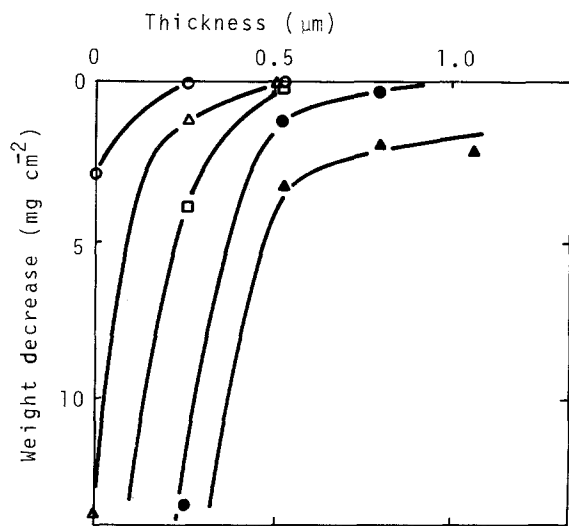


Figure 10 Effect of the thickness of the TiN layer on the weight decrease of TiN-coated copper plates when immersed in 3.2N HNO<sub>3</sub> solution. Temperature of HNO<sub>3</sub>, 20°C, immersion time (○) 30 min, (Δ) 60 min, (□) 90 min, (●) 150 min, (▲) 180 min. Deposition conditions of TiN layers were the same as for Fig. 5.

steeply with increasing thickness of the TiN layer, and reduced to zero at a thickness of 0.5 to 1.0 μm and an immersion time below 150 min. These results show that the corrosion stabilities of copper and phosphor-bronze plates to acid solutions will be improved outstandingly by coating thin TiN layers (<1 μm) on their surfaces.

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