

Photopotentials of Copper Coated with TiO₂ by Sol-Gel Method*

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The photoelectrochemical behavior of Cu coated with TiO₂ by sol-gel method was studied, aiming at the cathodic protection of Cu by the TiO₂ coating under illumination. It was found that the heat treatment in the coating process played a crucial role in determining the photo-effect of TiO₂ coating on the Cu substrate. Heat treatment at temperatures above 400°C was found to be essential to cause the potential of the TiO₂ coated Cu specimen to shift toward less noble direction under illumination. The optimum heat treatment temperature for cathodic protection was found to lie in the temperature range between 600°C and 700°C, in which the specimen exhibited the least noble photopotential. The increase in coating thickness more than 0.1μm seemed to have little influence on the photopotential in deaerated solutions. Under the appropriate heat treatment conditions, the results demonstrated an effective cathodic protection for Cu by the TiO₂ coating over the tested solution pH range from 4 to 12, because the photopotentials were in the immunity domain in the E-pH diagram of Cu.

Key words : TiO₂ coating, sol-gel method, heat treatment, copper, illumination, photo-effect, photopotential, cathodic protection.

1. Introduction

The photoelectrochemistry of TiO₂ has received much attention since Honda and Fujishima discovered its ability of water cleavage under illumination¹⁾. Although most of the research has deviated the early development toward solar energy conversion, the unique characteristics of TiO₂ as well as its high chemical stability, have made it a very important semiconductor in a wide range of research areas. The introduction of TiO₂ coating into corrosion science area lies in that the potential of photo-irradiated TiO₂ will change toward cathodic direction to approach its flat-band potential and that the photoelectrochemical reaction involved is not the decomposition

of the TiO₂ but the oxidation of H₂O by the photo-excited holes in valence band. These enable TiO₂ to protect some metallic materials from corrosion, with TiO₂ acting as a non-sacrificed anode. The concept of cathodic protection by TiO₂ coating under illumination was first realized by the recent work²⁾ in this laboratory, in which the photopotential of stainless steel was found to be driven into the passivity region by TiO₂ coating under illumination in the chloride solution.

The present paper provides experimental results on an attempt to the cathodic protection of Cu by TiO₂ coating under illumination. The Cu substrate was coated with a layer of TiO₂ by the sol-gel dip coating method. Basic steps involved in this coating process are TiO₂ sol solution preparation, gel coating formation, and the subsequent heat treatment of coating. Here, main attention has been directed toward the examination of photopotential under different heat treatment conditions.

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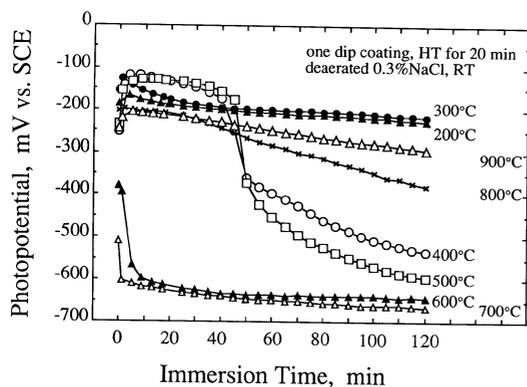


Fig.1 Effect of heat treatment temperature on the variation of photopotentials with immersion time for TiO_2 coated Cu in deaerated 0.3% NaCl solutions at room temperature. Heat treatment time was 20 minutes.

The results about the effects of coating thickness and solution pH are also presented in this paper.

2. Experimental

The specimens were cut from 99.99% pure Cu sheet (1 mm thick) to a size of 30×40 mm. The testing side of the specimen was polished to mirror finish with $0.05 \mu\text{m}$ Al_2O_3 , rinsed with acetone, and finally dried in the air.

The detailed procedure of the TiO_2 sol solution preparation can be found elsewhere³⁾. TiO_2 gel film was coated on Cu by dipping the specimen in the sol solution and pulling it up at a constant speed of 0.15 mm/s. After having been dried in the air for 10 min, the specimen was subjected to heat treatment under the atmosphere of nitrogen to avoid the oxidation of Cu. The repetition of this procedure brought about an increase in the thickness of TiO_2 coating by $0.1 \mu\text{m}$ for every one dip coating process^{4), 5)}. An uniform and adhesive TiO_2 coating on the Cu specimen was obtained under the above coating conditions.

The test solution was 0.3% NaCl prepared with analytical grade reagent and de-ionized water with an un-adjusted pH value of about 6.5. In one set of experiments, the solution pH was adjusted to a pH range from 4 to 12 by adding NaOH or HCl solutions. The photopotential measurement was conducted under the illumination of 500W high pressure Hg lamp. Before measurement, the solution was

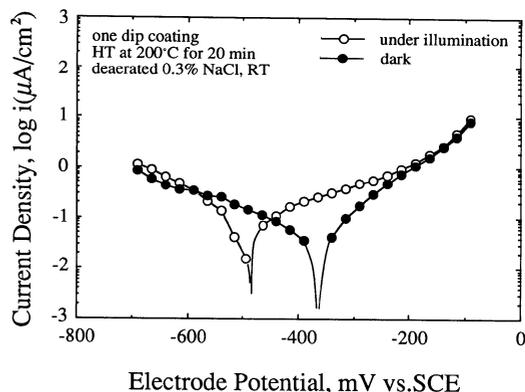


Fig.2 Polarization curves of TiO_2 -coated Cu in deaerated 0.3% NaCl solution at room temperature. Heat treatment condition : 200°C for 20 minutes.

deaerated with pure argon gas for 30 min. After two hours of photopotential measurement, polarization curves were recorded with a scanning rate of 25 mV/min. In some cases, the test solutions were not deaerated (referred to as aerated solution). All the measurements were conducted at room temperature. The electrode potentials were referred to the saturated calomel electrode (SCE).

3. Results and Discussion

3.1 Effect of heat treatment temperature

Fig. 1 shows the photopotential of TiO_2 -coated Cu heat-treated at different temperatures for 20 min. The heat treatment conditions can be divided into four temperature regions according to different photoelectrochemical behaviors.

3.1.1 200~300°C

The specimens treated in this temperature region exhibited a corrosion potential ranged from -140 to -170 mV under no illumination, which was more noble than that of Cu (-220 ~ -250 mV). Under the illumination of light, after a slight initial increase, the photopotential decreased gradually and finally reached a stable value corresponding to the dark corrosion potential of Cu. The polarization curves after two hours of illumination are shown in Fig. 2. It is evident that the difference in polarization behaviors between dark and illumination conditions was noted only within the potential region from -550 to -200 mV, in which a negative shift of corrosion potential

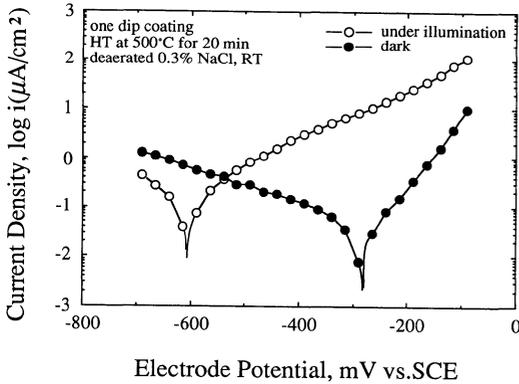


Fig.3 Polarization curves of TiO_2 -coated Cu in deaerated 0.3% NaCl solution at room temperature. Heat treatment condition : 500°C for 20 minutes.

and a slight increase in anodic current due to the illumination were observed, showing some evidence of photo-effect for the n-type semiconductor. In the subsequent measurement, however, the photopotential was still in the corrosion region of Cu. These results indicated that the TiO_2 coating treated in this temperature region has little photo-effect on Cu.

3.1.2 400~500°C

The dark corrosion potential was about $-180\sim-200$ mV. As shown in Fig. 1, a drastic change of photopotential was observed during the initial stage of illumination. First the potential of specimen sharply decreased to about -250 mV upon illumination. Within a few minutes, it jumped back toward noble direction and reached about -120 mV, more noble than its original dark corrosion potential. After a certain period of time, the photopotential dropped again and finally reached a stable state ($-500\sim-600$ mV) in the immunity region of Cu, a clear indication of the cathodic protection of Cu by TiO_2 coating due to its photo-effect. As this transition from p-type to n-type photo-effect occurred, it was found that the specimen surface started to be covered with a layer of black substance, which was dissolved during the subsequent anodic polarization. Compared with results in Fig. 2, the polarization curves in Fig. 3 demonstrate that significant anodic photocurrent was generated by TiO_2 coating, which enabled the coating to effectively protect the Cu substrate.

3.1.3 600~700°C

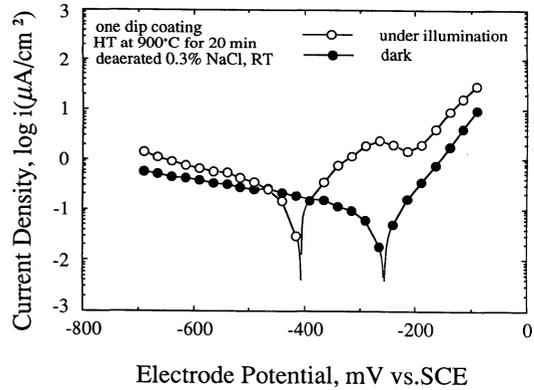


Fig.4 Polarization curves of TiO_2 -coated Cu in deaerated 0.3% NaCl solution at room temperature. Heat treatment condition : 900°C for 20 minutes.

Under these heat treatment conditions, the photopotential of specimen dropped directly into the immunity region of Cu upon illumination, showing strong photo-effect of the TiO_2 coating on the Cu substrate. The polarization curves were similar to that of Fig. 3, except that larger photocurrent and more negative photopotential were recorded.

3.1.4 800~900°C

The photopotential increased with temperature in this temperature region. The noble photopotential as well as its lower decreasing rate suggested that the photo-effect of the TiO_2 coating was degraded under such treatment conditions. The polarization curves given in Fig. 4 reveal that the photocurrent was also decreased, compared with the results in Fig. 3. Moreover, the occurrence of an anodic peak under illumination implied that the heat treatment in this temperature region caused some change in the TiO_2 coating.

It is seen that all the corrosion potentials in the polarization curves under both illumination and dark conditions are less noble than those measured under open-circuit conditions. This is because the polarization curves are recorded by the anodic scan from -700 mV and the scanning rate of 25 mV/min is probably too high for the electrochemical process to reach a stable state in the case of Cu substrate with TiO_2 coating.

Fig. 5 summarizes the results of the effect of heat treatment temperature on the photoelectrochemical behavior of TiO_2 -coated Cu. The

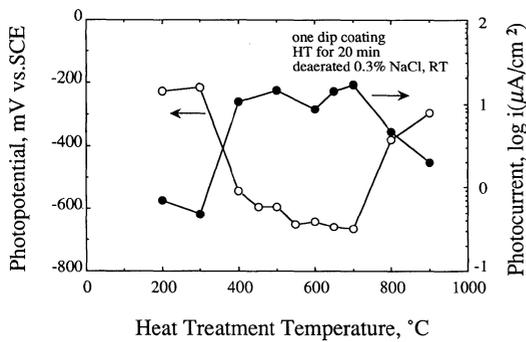


Fig. 5 Effect of heat treatment temperature on the photopotential after 2 hours of illumination and on the photocurrent at -240mV vs. SCE in deaerated 0.3% NaCl solutions at room temperature. Heat treatment time was 20 minutes.

anodic photocurrent at -240 mV was chosen from the polarization curves to evaluate the ability of cathodic protection by TiO_2 coating because this potential corresponded to the corrosion potential of Cu. From the viewpoint of cathodic protection, more negative photopotential or larger photocurrent is important. For sol-gel derived TiO_2 coating on Cu substrate, a temperature of 400°C seems to be a critical heat treatment temperature for the coating to impose photo-effect on the Cu substrate. Fig. 5 also demonstrates that the optimum heat treatment range is $600\sim 700^\circ\text{C}$, in which the least noble photopotential and the largest photocurrent are observed.

Fig. 6 shows the polarization curves of TiO_2 -coated Cu under dark condition. For comparison, the results for uncoated Cu as well as TiO_2 single crystal are also illustrated. The anodic polarization curves of TiO_2 coated specimens under dark conditions were almost the same as that of uncoated Cu, especially at higher heat treatment temperatures, indicating that the sol-gel derived TiO_2 coating can not retard the dissolution of Cu under anodic polarization due to its high porosity⁵⁾. As to the cathodic polarization curves, the cathodic currents of TiO_2 -coated Cu are less than that of bare Cu, but larger than that of TiO_2 crystal. For such a galvanic system as the Cu substrate with thin TiO_2 coating, the above results lead to the conclusion that the cathodic reactions most probably take place

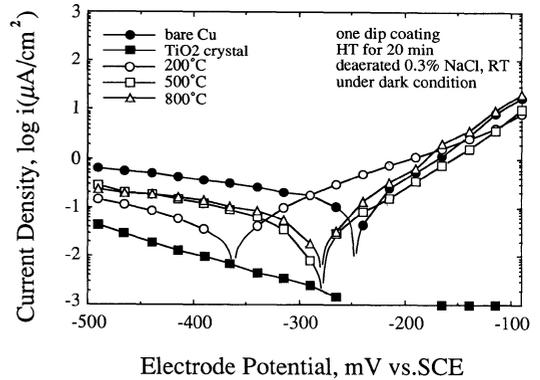


Fig. 6 Polarization curves of TiO_2 -coated Cu, bare Cu, and TiO_2 single crystal under dark condition in deaerated 0.3% NaCl solution at room temperature.

on the Cu substrate because of the high overpotential on the TiO_2 surface for cathodic processes⁶⁾.

3.2 Effect of cathodic treatment

It should be noted that when the heat treatment temperature was below 500°C , an obvious increase in photopotential was observed during the initial stage of illumination. Such a phenomenon might be connected with the existence of Cu oxide, because CuO or Cu_2O was p-type semiconductor and the potential of oxidized Cu would move toward anodic direction under illumination⁷⁾. The existence of Cu oxide was not unexpected since the TiO_2 coating contained a considerable quantity of water resulted from the hydrolysis of sol solution, which may cause the formation of Cu oxide during the gelation of the coating or in the subsequent heat treatment.

In order to eliminate the influence of Cu oxide, cathodic treatment at -600 mV was applied to the specimen before the measurement of photopotential. The results are shown in the Fig. 7. For the specimen treated at 500°C (almost same results were obtained for 400°C), Fig. 7a shows that the cathodic treatment decreases the p-type photo-effect and shortens the transition time for n-type photo-effect, which is simply because of the reduction of Cu oxide. If the specimen was given a thorough reduction (more than 1 hour at -600 mV), the p-type photo-effect totally disappeared and the photopotential behavior was just the same as the conditions of 600°C and 700°C . The results also show that the stable photopotential

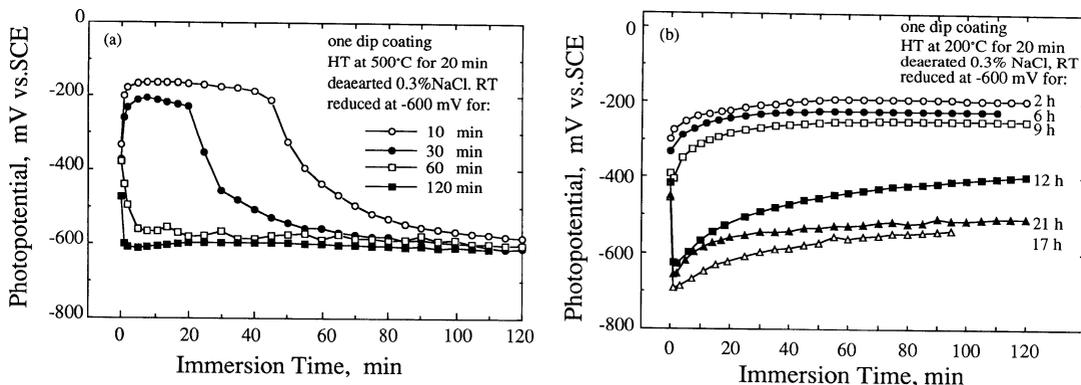


Fig. 7 Effect of cathodic reduction on the photopotentials of TiO₂-coated Cu. Specimens were reduced at -600mV vs. SCE for different time in deaerated 0.3% NaCl solution at room temperature. Heat treatment condition : 500°C (a), and 200°C (b) for 20 minutes.

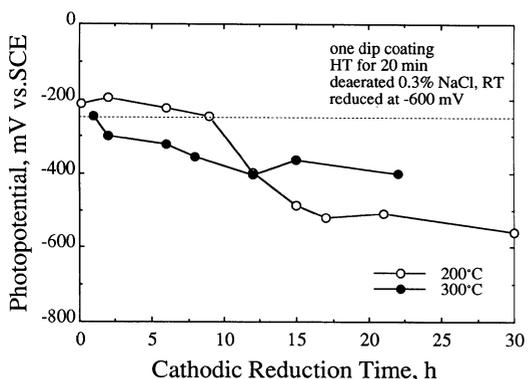


Fig. 8 Effect of cathodic reduction time on the photopotentials of TiO₂-coated Cu. Heat treatment conditions : 200°C and 300°C for 20 minutes. The specimens were reduced at -600mV vs. SCE in deaerated 0.3% NaCl solution at room temperature. The dotted line represents the E_{corr} of bare Cu.

remains nearly unchanged regardless of cathodic reduction. As to the nature of the photo-effect transition occurred during illumination, the above results implied that the photo-irradiated TiO₂ coating had the ability to reduce Cu oxide, which was confirmed by our XPS examinations⁸⁾.

As indicated in the previous sections, the TiO₂ coating seemed to have no photo-effect on the Cu substrate when the heat treatment temperature was below 300°C. However, it is noteworthy that cathodic reduction did result in a clear n-type photo-effect of the TiO₂ coating in this temperature region, as shown by the photopotential curves in Fig. 7b and the

summarized results in Fig. 8. Compared with the results in Fig. 7a, the differences between the two heat treatment conditions are obvious. First, the photopotential gradually increased to reach a stable state after an initial sharp decrease and no photo-effect transition was found. Furthermore, once the specimens showed n-type photo-effect, the photopotential decreased with cathodic reduction time (Fig. 8). Finally, the cathodic reduction time required for the appearance of n-type photo-effect was much longer than that required to eliminate the influence of Cu oxide for 400°C and 500°C (Fig. 9), especially in the case of 200°C, although the p-type photo-effect was stronger for 400°C and 500°C (Fig. 1).

3.3 Effect of heat treatment time

Fig. 10 shows the influence of heat treatment time on the photopotential of TiO₂-coated Cu. Temperatures of 400, 650, and 800°C were chosen because heat treatments at these temperatures led to three different photoelectrochemical behaviors. The results indicated that the photopotential increased with heat treatment time for all these temperatures, although at 650°C the influence seemed to be less prominent. At 400°C, a significant increase in photopotential as well as the time for the transition to n-type photo-effect was observed when the heat treatment time was longer than 20 min. In fact, no transition was observed during 2 hours of illumination for the specimen treated for 80 min at this temperature, and the photopotential remained more noble than the corrosion potential of

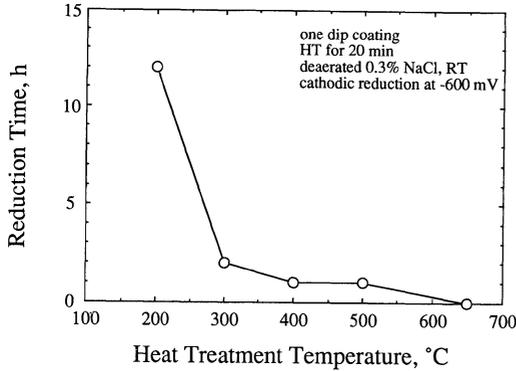


Fig. 9 Cathodic reduction time required to produce n-type photo-effect or to eliminate the effect of Cu oxide for different heat treatment temperatures.

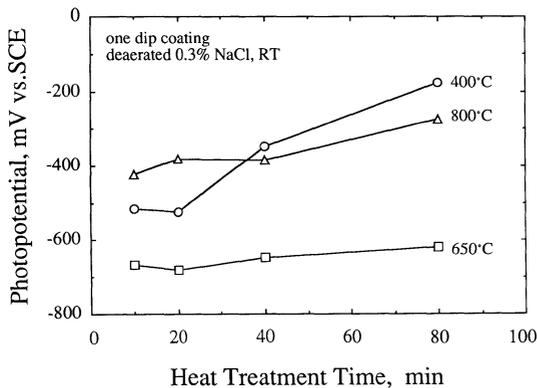


Fig. 10 Effect of heat treatment time at different temperatures on the photopotential of TiO_2 -coated Cu after 2 hours of illumination in deaerated 0.3% NaCl solution at room temperature.

bare Cu.

3.4 Effect of coating thickness

In the preparation of dip coating, thick TiO_2 coating can be obtained by repeating the process of gel coating formation and heat treatment, and the thickness is proportional to the dip numbers⁵⁾. Fig. 11 shows the photopotential vs immersion time plots of the specimens with different coating thicknesses. It was found that the specimens with thick coating exhibited a slow decrease of photopotential rather than the sharp drop upon illumination for one or two dip coatings, which can be related to the existence of Cu oxide due to the repeated heat treatment, as indicated by the initial increase of photopotential for thicker

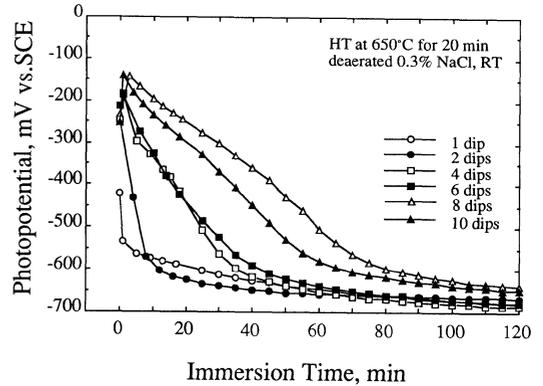


Fig. 11 Effect of the thickness of TiO_2 coating on the variation of photopotential with immersion time in deaerated 0.3% NaCl solution at room temperature. Heat treatment condition : 650°C for 20 minutes.

coating in Fig. 11. However, the specimens with different thickness of coating appeared to have nearly the same stable photopotential, as shown in Fig. 12. In this figure, the photopotentials measured in aerated solutions, together with the photocurrent at -240 mV in deaerated solutions for different coating thickness are also given. It was discovered that the photocurrent increased with the thickness up to five dips and then decreased with the further increase in thickness. A similar thickness dependence of photocurrent had been discussed with respect to the depletion layer and the change of resistance in the coating⁴⁾. In aerated solution, the photopotential, which was much higher than that in deaerated solution, seemed to decrease with the increase of coating thickness up to five dips.

The above results indicate a remarkable difference between the photopotentials in deaerated and aerated solutions. The explanation for this difference can be obtained if we compare the polarization curves in both solutions, as shown in Fig. 13. It was the large cathodic current that caused a notable positive shift of photopotential in aerated solutions. In the aerated neutral 0.3% NaCl solution, the reduction of dissolved oxygen is responsible for the large cathodic current. Obviously, the reduction of dissolved oxygen decreases the photo-effect of TiO_2 coating since the photo-induced reaction on TiO_2 surface is just the opposite process—the oxidation of OH^- into

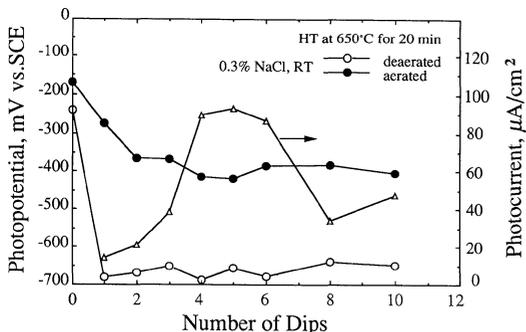


Fig.12 Effect of coating thickness on the photopotentials of TiO₂-coated Cu in both deaerated and aerated 0.3% NaCl solutions. The photocurrents were measured at -240 mV vs. SCE in deaerated solutions. Heat treatment condition : 650°C for 20 minutes. Test solutions were kept at room temperature.

oxygen. For the effect of coating thickness, Fig. 13 also reveals that the photopotential of the specimen is determined by both the anodic photocurrent generated by the TiO₂ coating and the cathodic current on Cu surface. In deaerated solutions, the photopotential could be very close to the flatband potential⁹⁾ of TiO₂ due to the lack of oxidizing species in the solution for cathodic reaction. Under these circumstances, the photopotential is determined only by the physical properties of the semiconductor, which leads to a thickness independent photopotential behavior, as indicated in Fig. 12. On the other hand, the existence of dissolved oxygen in solution ennobles the photopotential through a large enhancement of cathodic process. Evidently, an increase in anodic photocurrent should result in a negative shift of the photopotential in the presence of dissolved oxygen. In fact, the thickness dependencies of both the photopotential in aerated solution and the photocurrent manifest a satisfactory relationship for this argument.

3.5 Effect of solution pH

Fig. 14 shows the anodic polarization curves of the specimens under illumination in the solutions with different pH values. All the specimens were treated at 650°C for 20min. The photopotential after two hours of illumination decreased with the increase in pH.

The results of the influence of pH on the photopotential in both deaerated and aerated

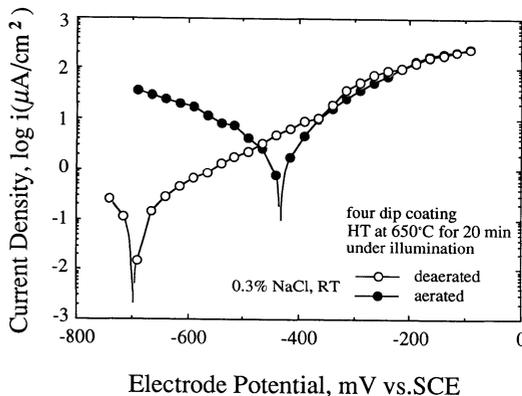


Fig.13 Polarization curves for four dips of TiO₂ coating on Cu in both deaerated and aerated 0.3% NaCl solutions at room temperature under illumination. Heat treatment condition : 650°C for 20 minutes.

solutions are summarized in Fig.15, which are plotted in the *E*-pH diagram of Cu. The photopotentials in deaerated solutions are almost the same as that of the hydrogen electrode, shown by the dotted line (a), while in aerated solutions, more noble photopotentials were observed. It is also shown that the photopotentials in both deaerated and aerated solutions decrease with the increase of pH at a rate of about 59 mV/pH, in good agreement with the well known pH dependence of the flatband potential of TiO₂¹⁰⁾. The above results clearly demonstrate the effective cathodic protection of Cu by TiO₂ coating within the tested pH range because all the photopotentials are located in the immunity domain of the *E*-pH diagram of Cu, even in the case of aerated solutions.

4. Conclusions

1. The photoelectrochemical behavior of TiO₂-coated Cu prepared by the current sol-gel method strongly depends on the heat treatment condition. Heat treatment above 400°C is critical for TiO₂ coating to exert photo-effect on Cu. The optimum heat treatment temperature range for cathodic protection of Cu is from 600°C to 700°C, in which Cu specimen with TiO₂ coating exhibits the least noble photopotential.

2. Copper oxide seemed to be formed in the coating process and had an obvious p-type photo-effect for the specimens treated below

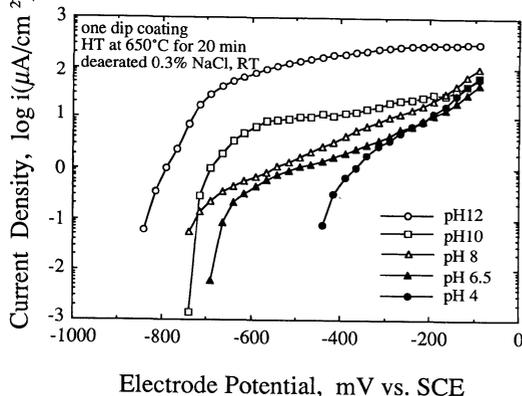


Fig.14 Effect of solution pH on the anodic polarization curves of TiO_2 -coated Cu under illumination in deaerated 0.3% NaCl solutions. Heat treatment condition : 650°C for 20 minutes.

600°C . Cathodic treatment at -600mV can eliminate the photo-effect of copper oxide, which even can make the TiO_2 coating exhibit photo-effect on the Cu substrate below the critical temperature.

3. The coating thickness has little influence on the photopotential in deaerated solution. In the presence of dissolved oxygen in solution, the photopotential, which is much higher than that in deaerated solution, decreased with thickness. However TiO_2 coating with more than five dips is of no practical significance because it can not lead to a further decrease of photopotential.

4. Given the proper heat treatment condition, the TiO_2 coating effectively protects Cu from corrosion in 0.3% NaCl solution over the pH range from 4 to 12 under illumination, because the photopotentials in both deaerated and aerated solutions are driven into the immunity domain in the E -pH diagram of Cu by the TiO_2 coating.

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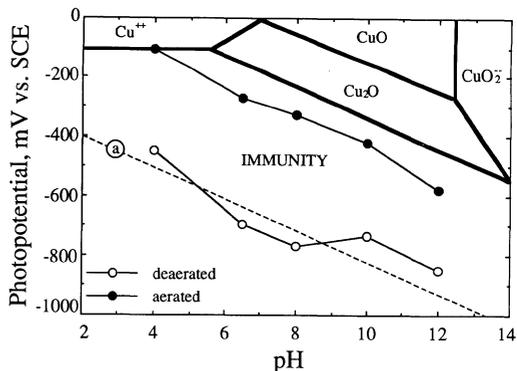


Fig.15 Photopotentials after two hours of illumination for TiO_2 -coated Cu plotted in the E -pH diagram of Cu at 25°C . Heat treatment condition for TiO_2 coating : 650°C for 20 minutes. Test solution: 0.3% NaCl at room temperature.

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