

Plasma Electrolysis for Anodization by Atmospheric Pressure Plasma in Deionized Water

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Abstract:

A plasma electrolysis was attempted for anodization of metal electrode in deionized water. The argon plasma generated at the gap between the high voltage electrode and the surface of water worked as a cathode, and the metal plate such as copper, zinc was assigned as an anode. The metal electrode was anodized after the plasma electrolysis of several hundreds of seconds, forming polyhedral structures. The change in properties of deionized water such as electrical conductivity and pH will be focused to discuss anodizing phenomena.

Keywords: Plasma electrolysis, Anodization, Deionized water

1. Introduction

Anodization is a technique to form oxide film in electrolytic cell. The formed oxide film provides not only enhanced chemical properties such as chemical- and corrosive resistance and physical properties such as hardness, but also various nanostructures. Electrolyte is essential to traditional anodization, because the electrical conductivity of pure water is not high enough to allow current flow required for anodization [1]. Moreover, a kind of electrolyte used in electrolytic cell has an influence on determining structure of oxide film. The addition of electrolyte, however, increases the content of impurity in the oxide film which decrease their performance in application field. In this study, the copper and zinc electrodes were anodized in the deionized water as a sole electrolyte. The atmospheric pressure plasma was assigned as a cathode. Herein, the plasma-water interaction was considered to induce the change in the properties of deionized water such as the electrical conductivity and pH which trigger phase change behaviour of metal. The anodizing phenomena of copper and zinc electrodes will be discussed with the change of deionized water according to the plasma electrolysis time.

2. Experimental

An electrolytic cell was composed of a high voltage power supply, a stainless steel pipe as a cathode, a copper plate as an anode and deionized water in a glass beaker. The copper plate was submerged in the deionized water and the stainless steel pipe was located 5 mm above the surface of water. Argon gas (500 mL/min) flew through the stainless steel electrode to sustain stable discharge.

3. Results and Discussion

Fig. 1 shows SEM images of the copper electrode according to the treatment time. It is found that the polyhedral structures were formed from 180 s and grew up as the electrolysis time increased until 300 s. However, the longer electrolysis time led to removal of these structure. It is confirmed that the density of polyhedral structure at 600

s is lower than that at 300 s. It was due to the dissolution of copper by the electrical breakdown. Actually, the color of solution became brown after 300 s, and became gradually browner as the anodization continued. The change of copper electrode including anodizing and dissolution was considered to be triggered by the change in electrical conductivity and pH of deionized water.

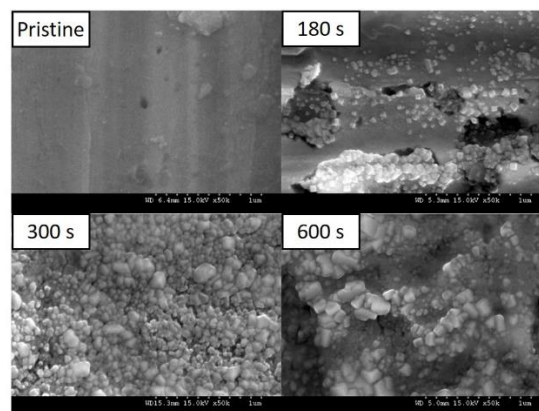


Fig. 1. SEM images of copper electrode anodized at 5 kV according to the plasma electrolysis time.

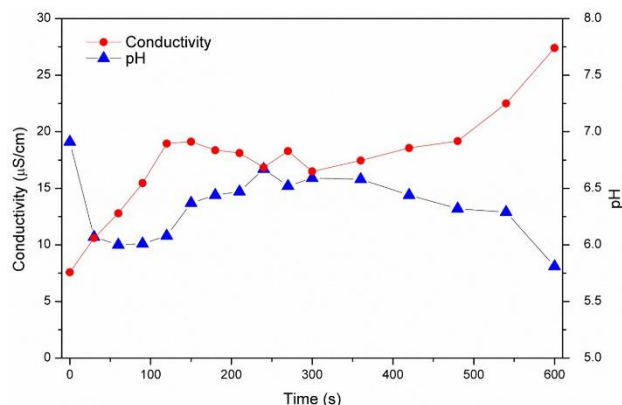


Fig. 2. Temporal changes in conductivity and pH of solution during the plasma electrolysis at 5 kV.

Fig. 2 shows the changes in pH and conductivity during the electrolysis of 600 s. The conductivity increased through the plasma electrolysis while the pH decreased from the initial value of 6.91 to 5.81. Both graphs, however, don't show linear trend throughout 600 s. Here, the consideration of the temporal change in the conductivity and pH provides the useful information to help the understanding of plasma electrolysis in this study. The initial pH drop until 60 s was due to dissolution of residual air and dissolved air through the plasma discharge. Other researches have reported that liquid discharge with nitrogen, oxygen or air generates reactive oxygen species (ROS) or reactive nitrogen species (RNS) which dissolve into water to decrease pH [2, 3]. However, only argon was introduced in the cell, so that ROS and RNS could not be continuously generated. When we conducted ionchromatography for the solution analysis, it was confirmed that the concentration of nitrate ion (NO_3^-) and nitrite ion (NO_2^-) increased until 30 s but was maintained without significant changes after 30 s.

Fig. 2 also shows an inversely proportional relationship between the pH and the conductivity, except between 30 s and 150 s. It suggests that the increase of conductivity was contributed by the generation of hydrogen ion. On the other hand, the rapid increase of conductivity between 30 s and 120 s was not due to the generation of hydrogen ion because the pH didn't change significantly. It means that the anodic or cathodic reactions could generate the ions which didn't affect pH only from the water in the plasma electrolytic cell. The increase of conductivity from 120 s to 150 s also supports this assumption.

From 150 s to 420 s, the conductivity and the pH did not significantly change. It is reasonable to assume that the reactions including plasma-liquid interaction, electrochemical reaction, generation of polyhedral structure, breakdown of polyhedral structures are in equilibrium.

The conductivity increased again after 420 s while the pH decreased. This phenomenon is considered due to the further breakdown of as-generated structures. It was actually observed that the solution became much browner after 420 s. The breakdown of oxide layer on the electrode are closely related to the applied voltage. In this study, the applied voltage also has changed as the conductivity of water has changed throughout the electrolysis. When the conductivity of deionized water increases, the voltage drop throughout the water decreases so that the applied voltage at the electrode increases. Thus, it is considered that the conductivity at 420 s led to the applied voltage corresponding to the breakdown voltage of copper oxide although it requires further investigation. This breakdown of oxide layer exposed the metallic surface of copper electrode so that the anodic reaction between copper-water became more active. Herein, this enhancement of anodic reaction which generates the hydrogen ion is considered to induce the decrease of pH after 420 s. As a result, it could be concluded that the water-plasma interaction could make the deionized water more electrically conductive so that the

copper electrode could be anodized without a support of extra electrolyte. However, the longer electrolysis led to the destruction of the anodized structures.

In the as-mentioned experiments, the unipolar pulsed voltage was applied to clarify the effect of anodic and cathodic reaction. The different result, however, was obtained when the bipolar pulsed voltage was applied. Fig. 3 shows the SEM images of the copper electrode treated by the bipolar pulsed plasma electrolysis of 300 s. The growth of cubic or polyhedral structures is observed as like applying the unipolar pulse. However, the size of those structures is much smaller compared to that observed from Fig. 1. The change in conductivity and pH also showed the different trend from that measured in the unipolar pulsed anodization. It is considered that it is due to alternate cathodic and anodic reaction at the metal electrode by bipolar pulse discharge. It should be further studied.

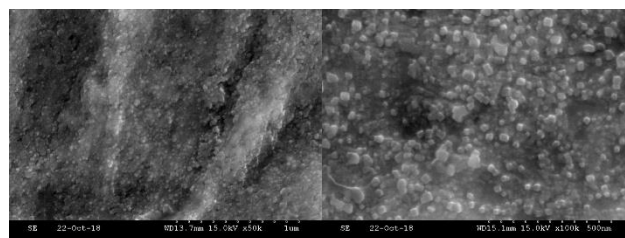


Fig. 3. SEM images of copper electrode anodized by bipolar plasma electrolysis at 5 kV for 300 s.

In addition, anodization of zinc was attempted in the same way. The SEM images of the zinc electrode anodized for 600 s are shown in Fig. 4. Likewise, the solution became turbid due to the breakdown of oxide layer. The conductivity and pH change with the zinc electrode also will be investigated to confirm the effect of types of electrode material in the plasma electrolysis technique.

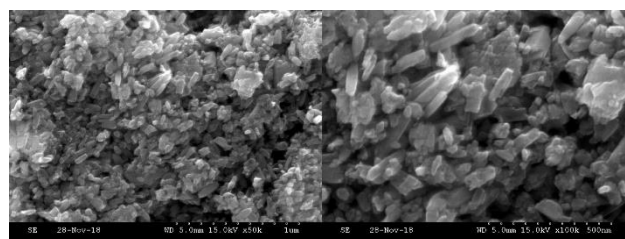


Fig. 4. SEM images of zinc electrode anodized for 600 s.

4. Conclusion

The effect of atmospheric pressure plasma on the anodization of metal electrode using the plasma electrolysis was investigated. The plasma electrolytic system employed a metal plate as an anode, an atmospheric pressure plasma as a cathode and a deionized water as an electrolyte. The results showed that the anodization was successfully conducted without any support of extra electrolyte. Also, the generation of polyhedral structures on the metal electrode by anodization was observed in both copper and zinc electrode. The anodizing phenomena were closely related to the change in the electrical conductivity

and the pH of the deionized water. The conductivity of deionized water increased through the plasma-water interaction so that it could trigger the anodization of metal electrode. However, the longer plasma electrolysis induced the dissolution of metal electrode due to the breakdown of as-generated oxide layer. In this study, it is concluded that the plasma electrolysis enables the anodization in water as an electrolyte.

5. References

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