Plasma Polymerization Coating of Tetraethoxysilane on Aluminum

Tatsuhiko Ihara*, Yu Iriyama**, Seishiro Ito*** and Mitsuo Kiboku*

Abstract

Tetraethoxysilane (TEOS) was polymerized by radio-frequency plasma and coated on aluminum for the purpose of corrosion protection. All plasma-coated films prevented aluminum from dissolving in alkaline solution remarkably. The corrosion resistance of the coated film was dependent on the plasma energy density (W/FM): The coated film polymerized at higher W/FM showed better corrosion protection in spite of the thinner coated layer. From the results of XPS analysis, it was considered that the component of the film is gradually approaching to SiO2 by increasing W/FM. The coated layer was thin and transparent enough to retain metallic appearance even after the immersion in alkaline solutions.

Key-words: Plasma Polymerization, Corrosion Protection, Aluminum foil, Tetraethoxysilane

1. Introduction

Plasma polymerization is known as a technique to form ultrathin films on most kinds of materials. Plasma polymers are usually said to be cross-linked, inert to most chemicals, and well-adherent to substrates. In utilizing those unique advantages, this technique has been applied to a variety of fields. Surface modification is its primary application, in which, for instance, because of their excellent bio and blood compatibilities, plasma polymers have been applied to the surfaces of contact lenses1 and artificial blood vessels2. Gas- (or liquid-) separation membranes are another application of plasma polymers, reported by many researchers3-5, in which thin plasma polymers are easily deposited uniformly on all kinds of porous substrates and have unique permeability characteristics. Plasma polymer films can also be a barrier against many kinds of invaders from outside, such as water, acids, bases, oxidizers, organic solvents, etc. as well as outflows from inside such as plasticizer in plastics6,7.

This technique is also applicable to metal surface for corrosion protection although a good adhesion between metal and plasma polymer can not always be achieved. One of the advantages of the use of plasma coating films is that a very thin layer of plasma coatings,
which is effective for the corrosion protection on metals, is expected to retain metallic appearance of the substrate when appropriate monomers are used or appropriate polymers are deposited.

In this study, tetraethoxysilane (TEOS), which is often used in sol–gel process to form transparent oxide glass or solid oxide, was used as a monomer, and the corrosion resistance and transparency of its plasma-coating layer on aluminum were examined.

2. Experimental

2.1 Materials

Aluminum sample used in this experiment was aluminum foil which is commercially available for cooking use. The aluminum-foil sample, cut to 1-cm square, was cleaned with acetone and vacuum-dried before use. As a monomer, 99.99 % TEOS, from Tokyo Kasei, was used after being degassed without further purification. For the quantitative analysis of dissolved aluminum, aluminum standard solution (1000 ppm for atomic absorption use) and xylenol orange (both from Wako Pure Chemical) were used. Another reagents used in this experiment were of reagent grade and used without further purification.

2.2 Procedure.

Plasma–polymerization coating was carried out with 10 sheets of the aluminum sample in a batch for 10 min in the radio-frequency (13.56 MHz) plasma–polymerization apparatus shown in Fig. 1. The flow rate of the monomer was controlled by a metering valve. The round-bottomed rotatable Pyrex reactor (1000 -mL capacity) was kept rotating at about 12 rpm during the polymerization for uniform coating. The plasma-coating conditions are summarized in Table 1. Measurement of the deposition rate was done as follows: A crystal sensor wrapped by aluminum foil (3 cm × 3.5 cm) with hole at a center (hole size r = 0.4 cm; same size as crystal sensor holder), was placed in the reactor without aluminum sample. The deposition rate was calculated as μg/cm² min from the difference of reading of Thickness Monitor (JEOL, Model JTM–200R).

After the plasma coating, the aluminum samples were dipped into 3 mL of NaOH solutions of pH 10 and 11 for 24 h. The alkaline resistance (corrosion resistance) of the samples was examined by the measurements of dissolved amounts of aluminum and

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Power (W)</th>
<th>Flow Rate (cm³(STP)/min)</th>
<th>W/FM (GJ/kg)</th>
<th>Dep.Rate (μg/cm²·min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>Uncoated</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>13</td>
<td>0.132</td>
<td>0.63</td>
<td>0.33</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>0.083</td>
<td>0.81</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>37</td>
<td>0.250</td>
<td>0.94</td>
<td>0.17</td>
</tr>
<tr>
<td>4</td>
<td>27</td>
<td>0.116</td>
<td>1.49</td>
<td>0.11</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>0.053</td>
<td>1.58</td>
<td>0.08</td>
</tr>
<tr>
<td>6</td>
<td>27</td>
<td>0.050</td>
<td>3.44</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*a*coating time was fixed to 10 min.

Fig. 1 Scheme of plasma coating apparatus.
color change. The dissolved amounts of aluminum in the alkaline solution after dipping were determined by visible absorption spectroscopy at 530 nm after the reaction with xylenol orange, a metal indicator. The color change of the aluminum surface was measured by a color analyzer (Tokyo Denshoku, Model TC-1800).

The chemical composition of the surface after TEOS coating by plasma was analyzed by X-ray photoelectron spectroscopy (XPS, Kratos 800XPS).

### 3. Results and Discussion

**Figure 2** represents the relationship between deposition rate and W/FM for the plasma polymerization of TEOS. W/FM is a composite parameter for plasma polymerization, in which plasma power (W) is divided by the mass flow of a monomer (FM), that indicates input energy density per unit mass of a monomer. In this figure, the deposition rate is shown at the W/FM of 0.6 GJ/kg or more because powdery polymer formed at below 0.5 GJ/kg as reported previously\(^8\). In this figure, the deposition rate decreases monotonously with increasing W/FM. In general, however, the deposition rate increases with increasing W/FM in the energy-deficient region, where input energy is not adequate; while it decreases with W/FM in the monomer-deficient region, where excess energy is applied\(^9\). Therefore, the range above 0.6 GJ/kg in this experiment must be the monomer-deficient region, and the maximum of the deposition rate should be found somewhere below 0.5 GJ/kg.

The detailed plasma–polymerization condition and the resulting deposition rate are shown in Table 1. The experimental numbers in this table correspond to the numbers in **Fig. 3**. Since the deposition rate naturally varies depending on the experimental condition and the polymerization time is fixed at 10 min, the resulting total thickness for each experiment is not identical. Estimated thickness of these deposited films with 10 min deposition time is varied from 30 to 330 nm with decreasing W/FM when the density of the plasma polymer is assumed to be 1.0 g/cm\(^3\).

After the corrosion test, in which aluminum samples were dipped into alkaline solutions (pH 10 or 11) for 24 h, the amounts of dissolved aluminum were measured. **Fig. 3** shows the amounts of dissolved aluminum from aluminum in alkaline solutions of pH 10 and 11. Evidently, the dissolved amounts for all plasma-coated samples were remarkably decreased. The dissolved amounts in pH 10 for
all plasma-coated samples were around 5 \( \mu \text{g} \), which was about one third of that of uncoated one. The dissolved amounts were not dependent on W/FM or film thickness. In pH 11, the dissolved amounts, which were much higher than those in pH 10, also dropped to less than one half of uncoated one, and a clear dependence on W/FM was found: It decreased with increasing W/FM although film thickness became thinner. The coated film (as thin as 30 nm) is probably thick enough for the corrosion protection. Therefore, the corrosion resistance was not affected by the film thickness in this range but might have been affected by the nature of the coated films. In other words, the plasma-coated film at higher W/FM had better corrosion resistance in spite of thinner film thickness\(^{10,11} \). At higher W/FM, in general, tighter network is said to be formed and the adhesivity is often improved. In this experiment, sample no.6, coated at the highest W/FM showed the best corrosion protection.

The appearance of the aluminum sample is an important factor when it is used where characteristic of metallic appearance is required. Also, the appearance can be a factor for the judgment of the degree of corrosion. In appearance change after plasma coating, sample no.6 is expected to be least affected because of the thinnest coating thickness. It is also expected to be least affected after dipping in the alkaline solution from the results above (Fig.3). The appearance of all plasma-coated samples by human eye was not affected at all and their metallic appearance was retained. And the color and metallic appearance of dipped sample no.6 looked unaltered. The dipped uncoated sample, however, lost its metallic appearance and became brown, which indicated apparent corrosion. For a more quantitative analysis of the appearance, surface reflectance was measured in the visible region by a color analyzer. Fig. 4 shows the reflectance curves in the visible region for uncoated sample and sample no.6 before and after the dipping in pH 11 for 24 h. After the plasma coating (before the immersion), the appearance of sample no.6 was fairly transparent and its reflectance curve was almost the same as that of uncoated one. The appearance of the other plasma-coated samples also looked like uncoated one and their reflectance curves did not change after the coating, that indicates that the deposited plasma polymer hardly affected the appearance. After the dipping, however, the reflectance of uncoated sample was lowered significantly throughout the visible region. On the contrary, that of no.6 was little affected in alkaline solution of pH 11 and retained the original reflectance.

From the results above, the corrosion resistance of the plasma-coated films was found to be dependent on W/FM: Sample no.6, coated
at the highest W/FM, showed the best corrosion resistance. Therefore, the composition of the plasma-coated film should have been varied depending on the W/FM applied in the polymerization. It can be assumed that a higher W/FM tends to eliminate organic fragments to form more SiO₂-like (inorganic) films, which could be effective as a barrier against alkaline solution because of better adhesion on metals. Accordingly, we analyzed the coated films on aluminum by XPS. Fig. 5 shows C₁s XPS spectra of plasma-coated films of sample nos. 2 and 6, which had been polymerized at W/FM of 0.81 and 3.44 GJ/kg, respectively.

![Fig. 5 XPS spectra of C₁s in TEOS plasma-coated films of sample nos. 2 and 6, which had been polymerized at W/FM of 0.81 and 3.44 GJ/kg, respectively.](image)

Table 2 Surface atomic percent for sample nos. 2 and 6 obtained by XPS analysis

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>C</th>
<th>O</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>81.1</td>
<td>4.2</td>
<td>14.7</td>
</tr>
<tr>
<td>6</td>
<td>56.9</td>
<td>28.7</td>
<td>14.4</td>
</tr>
</tbody>
</table>

decrease of the oxygen-related peak means the decrease of the number of carbon atoms bonded to oxygen. Comparing the surface atomic percent of each element (C, O, and Si) for the two samples, 24.2 % decrease in C and 24.5 % increase in O are recognized while Si is almost the same, as shown in Table 2. Expectedly, a clear component difference between the two samples prepared at different energy density can be detected by XPS. In addition, the chemical composition of those samples after the dipping in alkali did not change at all. From the results above, it seems that the component of the film is gradually approaching to SiO₂ by increasing W/FM, although a lot of carbon is still existing despite high W/FM, 3.44 GJ/kg, had been applied. However, the films with very tight cross-linking may have been obtained at higher W/FM, which can suppress the penetration of even small molecules including hydroxide ion. Since XPS cannot detect hydrogen, the degree of cross-linking has not be estimated.

A fairly effective corrosion protection was achieved by the plasma polymerization of TEOS on aluminum. However, more inorganic film could improve the efficiency in view of adherence and tightness. In order to obtain more SiO₂-like film in the plasma polymerization of TEOS, some other chemicals such as oxygen or water may need to remove organic fragment during the plasma polymerization of TEOS.

4. Conclusions

For the purpose of corrosion protection of metals, plasma polymerization coating of
TEOS was examined on aluminum foil. From the results of corrosion test against alkaline solutions of pH 10 and 11, the plasma-coated film at higher W/FM showed better corrosion resistance in spite of thinner film thickness. After the dipping into alkaline solution of pH 11, the reflection curve of plasma coated-sample was little affected while the reflectance of uncoated sample was lowered significantly throughout the visible region. It was found that the film prepared at different energy density differed in their component by XPS measurement. It seems that the component of the film is gradually approaching to SiO2 by increasing W/FM.

Acknowledgements

This work was supported by the Japan Private School Promotion Foundation and the Environmental Science Research Institute of Kinki University.

References