Metal Surface Treatment for Enhancement of Hydrophilic Property Using Atmospheric-Pressure Dielectric Barrier Discharge

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Abstract: The metal treatment for hydrophilic surface is carried out using atmospheric-pressure DBD. After the plasma treatment, an enhanced wettability of the metal surface is resulted with formation of abundant hydrophilic functional elements, such as oxides of iron and chromium. In the Ar-O₂ discharge, the treated surfaces are more wettable than those in the He-O₂ plasma, due to its high electron temperature and higher power density.

Keywords: Dielectric barrier discharge, surface treatment, hydrophilic metal surface.

1. Introduction

Hydrophilic metal surfaces are of increasing interest to enhance adhesion, biocompatibility, and heat transfer properties of metal used in various industrial fields [1, 2]. Such peculiar surfaces have been made by surface treatment methods usually using low-pressure plasma sources, such as rf (radio-frequency) glow plasmas and dc reactive plasmas [3, 4]. The low-pressure plasma treatment requires expensive vacuum equipment and components which escalate the capital cost and yield the limited area of treated surface.

On the other hands, the atmospheric-pressure plasmas do not require the complex and costly vacuum facilities. Moreover, some processes using them have shown acceptable characteristics of treatment results comparable to the low-pressure plasma processing. Because of these advantages, various atmospheric-pressure plasma sources have been suggested as the substitute for the low-pressure ones [1, 5, 6].

Recently, the atmospheric-pressure dielectric barrier discharge (DBD) is widely used as a non-equilibrium plasma source for surface treatment. The DBD exhibits various discharge features according to the reactor type and operating condition. Its selective characteristics can be adopted to a variety of treatments for the substrates of diverse shapes and materials.

In this work, enhancing the hydrophilicity of metal surface is investigated by the atmospheric-pressure DBD process. The stainless steel plates are treated in the He-O₂ and Ar-O₂ plasmas, respectively, generated by the DBD. The generated plasmas are characterized by the electrical measurements for power density, electron density, and temperature. The hydrophilicity of the treated surface is evaluated using the contact angle measurement and the X-ray photoelectron spectroscopy (XPS) analysis.

2. Experiment

2.1 Plasma generation

Fig.1 shows a schematic diagram of a surface treatment system using atmospheric-pressure DBD. The discharge reactor consists of two electrode plates (Al, 72 × 68 mm²) covered with two 1-mm-thickness dielectric sheets (Al₂O₃, εᵣ=8.0), respectively, which are separated by a 3-mm discharge gap. A sinusoidal power of 20 kHz is applied to the electrodes by varying its amplitude from 4 to 7 kV. The plasma forming gas of He or Ar is injected into the discharge gap at a flow rate of 10 slpm containing uniformly mixed O₂ additive of 0 ~ 1 % volumetric concentration. The DBD reactor is operated at atmospheric pressure and placed in a ventilation system.

The generated plasma is characterized by the electrical measurement with an estimation model [7]. In this measurement, the electric signals, such as applied voltage, discharge current, and accumulated charges, are measured with time variation. Using an equivalent circuit model, the discharge voltage and bulk electric field are obtained. And the average electron temperature and density are estimated from the discharge current and the Einstein’s relation with calculated electric fields. From the resultant discharge voltage and current, the power density deposited in the DBD plasma is also calculated.

2.2 Materials

The AISI 304 stainless steel (SS304) sheet of 0.1 mm-thickness is used as a substrate for hydrophilic plasma treatment. Before the treatment, the substrate surfaces are cleaned by ethanol for the removal of contaminants, and then rinsed with de-ionized water using an ultrasonic cleaning method. The prepared substrates are treated by directly exposing to the DBD plasma inside the discharge gap for 5 minutes.

2.3 Contact angle analysis

For the characterization of hydrophilic treated surface, a contact angle analysis is carried out using the sessile drop method with 1 µl of de-ionized water. 7 points measurements are performed at randomly selected positions on each substrate. The average value of contact angle on 7 points is regarded as the contact angle of each treated substrate sample.
2.4 XPS (X-ray photoelectron spectroscopy) analysis

The surface chemical compositions of the substrate are examined by X-ray photoelectron spectroscopy (XPS, Model: Sigma Probe, Thermo-VG, UK) with monochromatic Al Kα (1486.7 eV) X-ray source. XPS spectra are obtained at C 1s, O 1s, Fe 2p, and Cr 2p with the resolution of 0.1 eV.

3. Results

3.1 Plasma characteristics

The measured plasma parameters, such as plasma power density ($P_p$), electron density ($n_e$), and temperature ($T_e$), are presented in Fig.2 depending on the variations of operating conditions. As the volumetric concentration of O₂ additive increases, the plasma power density generally increases, while the electron density and temperature slowly decrease. Such tendencies of the plasma characteristics originated from more O₂ addition can be explained by the fact that the O₂ additive elevates the breakdown voltage of each discharge gas and reduce the electron generation in the DBD due to quenching the meta-stable species, like He* or Ar* [7].

At the high applied voltage, the higher power density is preserved as seen in Fig.2(b), and the electron density becomes larger with a higher electron temperature as the applied voltage rises. Since the elevated applied voltage strengthen the electric field intensity in the discharge region, the electron temperature is raised along with more production of electrons. Because of these variations, the discharge voltage and current also increase to lead the plasma power density to elevate.

Comparing the discharge characteristics between the He-O₂ and Ar-O₂ plasmas, the Ar-O₂ plasma shows higher values of power density (0.11 ~ 0.25 W/cm³) and electron temperature (6.86 ~ 7.61 eV) than the He-O₂ plasma (0.07 ~ 0.19 W/cm³ for power density, 3.29 ~ 3.86 eV for electron temperature). On the contrary, the electron density of the Ar-O₂ plasma reveals lower value than that of the He-O₂ plasma ($3.1 \times 10^8 \sim 6.7 \times 10^9$ cm⁻³ for Ar-O₂ plasma and $6.1 \times 10^8 \sim 1.2 \times 10^9$ cm⁻³ for He-O₂ plasma).

3.2 Contact angle measurement for hydrophilic properties

Fig.3 shows the images of water drops on the stainless steel substrate surface for an untreated reference and a plasma treatment. After the surface treatment by the Ar-O₂ plasma including 1-% O₂ additive at 7 kV, the wettability of surface turns out to be considerably enhanced as appeared in the contact angle change from 81° to 5°. In Fig. 4, the variations of contact angle are plotted according to O₂ mixing content (%) and applied voltage (kV).

As the concentration of O₂ additive increases in a range of below 0.5 %, the contact angle is rising, i.e., the hydrophilicity is getting worse. This result may be closely related to the characteristics of the Ar-O₂ plasma, of which electron temperature and density decrease with increasing the O₂ additive concentration as seen in Fig. 2(a). But, at the 1-% concentration of O₂ additive, the contact angle shows a bit lower value and the hydrophilicity is slightly better than the 0.5-% concentration. This result should be separately analyzed from the case of lower O₂ additive concentration.
The contact angle has a tendency of decreasing with increment of the applied voltage. This implies that the hydrophilicity of the stainless steel surface is more enhanced at the high applied voltage, and this feature can be explained by the previous results, described in the section 3.1, that higher power density of the DBD plasma is preserved with elevated temperature as the applied voltage increases.

As represented in Figs. 3 and 4, in all the process conditions, the stainless steel surfaces treated by the Ar-O₂ plasma have lower contact angles (higher wettabilities) than the ones by the He-O₂ plasma. This phenomenon of the plasma treatment is attributed to the characteristics of the Ar-O₂ plasma which dissipates larger power density and preserves lower density of electrons with higher temperature compared with those of the He-O₂ plasma.

3.3 Surface chemical composition analysis by XPS

Figs. 5 and 6 depict the XPS analysis spectra of Fe 2p and Cr 2p, respectively. These spectra are corrected by the subtraction of background ones using the Shirley method, and then deconvoluted to the peaks of each chemical component concerning the spin doublet separation of 2p spectrum.

As represented in Fig. 5 and Table 1, the hydrophilic surfaces, which are treated by the He-O₂ and Ar-O₂ plasmas, contain larger amounts of iron oxides (e.g., Fe₂O₃ - 15.24, 15.06 at.% and FeOOH - 7.61, 7.89 at.%), respectively, compared to those of the untreated substrate (Fe₂O₃ - 8.09 at.% and FeOOH - 1.72 at.%). Moreover, the shake-up satellite peaks of oxides which are remarkably appeared in Fig. 5 (b) and (c) confirm the formation of iron oxides in the treated hydrophilic surface. On the other hand, the composition of Fe-Fe is reduced from 0.85 to 0.52 and 0.69 at.% after the He-O₂ and Ar-O₂ plasma treatment, respectively. Therefore, from the measured results of the contact angle in conjunction with those of the chemical composition analysis, it can be inferred that the iron oxides of Fe₂O₃ and FeOOH play the role as the hydrophilic functional elements.

From the results of Cr 2p spectra analysis described in Fig. 6, the oxides of chromium, such as Cr₂O₃ and CrO₃, are abundant in the treated hydrophilic surface compared to the untreated reference. As listed in Table 1, the composition of Cr₂O₃ is slightly reduced in the treated hydrophilic surface. However, the relative composition ratio of Cr₂O₃ compared to Cr-Cr is increased from 4.55 to 10.25 and 14.60 after the He-O₂ and Ar-O₂ plasma treatment, respectively. The compositions of Cr₂O₃ in the plasma treated surface (1.65 and 1.86 at.% by the He-O₂ and Ar-O₂ plasmas, respectively) are also larger than that in the reference surface (1.28 at.%). From these results, it can be deduced that the chromium oxides of Cr₂O₃ and CrO₃ also perform as the hydrophilic functional elements.

Table 1. Chemical compositions and their relative ratios of the oxides of iron and chromium formed in the untreated and treated surfaces of stainless steel.

<table>
<thead>
<tr>
<th></th>
<th>Untreated reference</th>
<th>He-O₂ plasma treatment</th>
<th>Ar-O₂ plasma treatment</th>
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<tr>
<td>Fe-Fe</td>
<td>0.85 at.%</td>
<td>0.52</td>
<td>0.69</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.09</td>
<td>15.25</td>
<td>15.06</td>
</tr>
<tr>
<td>FeOOH</td>
<td>1.72</td>
<td>7.61</td>
<td>7.89</td>
</tr>
<tr>
<td>Cr-Cr</td>
<td>0.64</td>
<td>0.28</td>
<td>0.15</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>2.91</td>
<td>2.87</td>
<td>2.19</td>
</tr>
<tr>
<td>CrO₃</td>
<td>1.28</td>
<td>1.65</td>
<td>1.86</td>
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Relative composition ratios compared to Fe-Fe peak

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<thead>
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<th>Ar-O₂ plasma treatment</th>
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<tr>
<td>Fe₂O₃</td>
<td>9.52</td>
<td>29.31</td>
<td>21.83</td>
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<tr>
<td>FeOOH</td>
<td>2.02</td>
<td>14.63</td>
<td>11.43</td>
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Relative composition ratios compared to Cr-Cr peak

<table>
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<th>Ar-O₂ plasma treatment</th>
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<tbody>
<tr>
<td>Cr₂O₃</td>
<td>4.55</td>
<td>10.25</td>
<td>14.60</td>
</tr>
<tr>
<td>CrO₃</td>
<td>2.00</td>
<td>5.89</td>
<td>12.40</td>
</tr>
</tbody>
</table>
Comparing the figures (b) with (c) in Figs. 5 and 6, the difference in oxide compositions between the He-O₂ and Ar-O₂ plasma treatment is relatively minute in the Fe 2p spectrum, but this difference is remarkable in the Cr 2p spectrum. In the treated surface by the Ar-O₂ plasma, the CrO₃ peak is relatively swollen, and the relative composition ratio of CrO₃ compared to Cr-Cr peak is larger than that in the He-O₂ plasma treated one. This means that the Ar-O₂ plasma is advantageous to form CrO₃. And this result can be related with the measured results in Sec. 3.2 that the Ar-O₂ plasma treatment is promising to make the improved wettable surface with smaller contact angle.

4. Conclusion

The plasma treatment by the atmospheric-pressure DBD enhances the hydrophilicity of the metal surface that is modified to have abundant oxides of iron and chromium, such as Fe₂O₃, FeOOH, Cr₂O₃, and CrO₃ containing hydrophilic functional groups.

Comparing the plasma characteristics between the He-O₂ and Ar-O₂ DBD, the latter shows higher power density with elevated electron temperature than the former. Consequently, the Ar-O₂ plasma treatment produces more wettable surfaces than the He-O₂ plasma treatment. It is, therefore, expected that the Ar-O₂ plasma has more advantageous to enhancing the hydrophilic property of metal surface.

Acknowledgement

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References