Corrosion Resistance of Co-Cr-Mo Alloy Treated by Electrolytic In-process Dressing (ELID) Grinding / Thermal Oxidation Hybrid Process*

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Abstract
In order to improve the corrosion resistance of Co-Cr-Mo alloy, a hybrid process combining ELID (Electrolytic in-process dressing) grinding with thermal oxidation (TO) was performed and then the treated surfaces were observed and analyzed using a scanning electron microscope (SEM), a glow discharge optical emission spectrometer (GD-OES) and an X-ray photoelectron spectrooscope (XPS). In order to evaluate corrosion resistance, potentiodynamic polarization measurement and metallic ion elution tests were carried out. The color of the treated surfaces changed and the levels of oxygen content increased significantly due to the thermal oxidation treatment. In particular, specimens treated with ELID/TO hybrid processing showed the thicker oxide layers than those of the P/TO hybrid processed ones. In addition, the amount of cobalt on the surface diminished by ELID/TO hybrid processing. Specimens treated with the ELID/TO hybrid processing showed a lower amount of cobalt ion elution among all specimens. These results suggest that it is possible to apply a ELID/TO hybrid process as a surface finishing method for metal implants and improve their corrosion resistance by applying an ELID/TO hybrid process.

Key words: Biomaterial, Co-Cr-Mo alloy, ELID grinding, thermal oxidation, surface modification, corrosion resistance

1. Introduction
Biomaterials used in the human body are susceptible to corrosion, wear and biochemical reactions. Therefore, titanium alloys, austenitic stainless steel and Co-Cr-Mo alloys are commonly used as metallic biomaterials. In particular, forged high carbon Co-Cr-Mo alloys have superior wear resistance compared to the other alloys. For this reason, Co-Cr-Mo alloys are applied to the sliding parts of artificial hip joints.

Artificial hip joints are usually composed of four parts: a cup, liner, ball and stem. Currently polyethylene liners and Co-Cr-Mo alloy balls are usually used as sliding parts. However, because of the poor wear resistance of polyethylene, this combination generates a
lot of abrasive powder which causes inflammation of the tissues around the artificial hip joint in use [1]. In order to reduce the generation of abrasive powder, there has been interest in metal on metal artificial hip joints whose sliding parts are composed of Co-Cr-Mo alloys only. Recent progress in manufacturing methods has enabled metal on metal artificial hip joints reducing abrasive powder dramatically. With longer term use, however, metal on metal artificial hip joints also generate abrasive powder and release metallic ions [2-4].

Recently, we reported that electrolytic in-process dressing (ELID) grinding can improve corrosion and wear resistance due to the formation of an oxide layer during the grinding process [5-7]. However, the thickness of the oxide layer which is formed following the grinding of the sliding parts is insufficient for the practical application for the artificial hip joint.

Therefore, we focused on an ELID/TO hybrid process combined with ELID grinding and thermal oxidation. Thermal oxidation can form thick and dense oxide layers on the treated surface. Our previous work using stainless steel specimens showed that the ELID/TO hybrid process improved the surface roughness and wear resistance of the treated surfaces due to the existence of thick oxide layers [8]. There is a possibility that this hybrid process improves the corrosion resistance of Co-Cr-Mo alloys, however, this report didn’t mention about corrosion resistance. Thus, the aim of this study is to improve corrosion resistance of Co-Cr-Mo alloys and inhibit the release of metallic ion using the ELID/TO hybrid process.

2. Experimental Procedure

The material used in this study was a Co-Cr-Mo alloy, the chemical composition of which is shown in Table 1. Discs of this alloy, 12.8 mm in diameter and 4 mm in thickness, were machined from rods. Eight types of specimens were prepared. The EO400, EO500 and EO600 series were the specimens treated with ELID grinding followed by thermal oxidation with an elevated temperature of 400, 500 and 600 °C, respectively. The PO400, PO500 and PO600 series were the specimens polished before the thermal oxidation. The E series was finished with ELID grinding, and the P series was completed only with polishing. The conditions of ELID grinding and thermal oxidation are shown in Table 2 and Fig. 1.

In order to evaluate processing properties, surface observation was carried out by the use of a scanning electron microscope (SEM). Cobalt and oxygen distribution as a function of the depth from the surface was estimated by glow discharge optical emission spectroscopy (GD-OES) analysis. X-ray photoelectron spectroscopy (XPS) analysis was carried out to investigate the chemical-bonding state. In order to investigate the corrosion properties of the specimens, potentiodynamic polarization measurements and metallic ion elution tests were conducted.

| Table 1 Chemical composition of Co-Cr-Mo alloy (mass %) |
| Co  | Cr  | Mo  | Mn  | Si  | Fe  | C  | N  |
| 61.77 | 29.6 | 6.5 | 0.7 | 0.7 | 0.3 | 0.23 | 0.17 |

<table>
<thead>
<tr>
<th>Table 2 Condition of ELID grinding</th>
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<tbody>
<tr>
<td><strong>Grinding wheel</strong></td>
</tr>
<tr>
<td>Cast iron bonded diamond wheel #365,#1200</td>
</tr>
<tr>
<td>Copper and resin bonded diamond wheel #4000, #8000</td>
</tr>
<tr>
<td><strong>Electrolyze condition</strong></td>
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<tr>
<td>Voltage : 90V</td>
</tr>
<tr>
<td>Electrolytic current : 5A</td>
</tr>
<tr>
<td><strong>Grinding condition</strong></td>
</tr>
<tr>
<td>Grinding wheel rotating speed: 132rpm</td>
</tr>
<tr>
<td>Work piece rotating speed: 137rpm</td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1 Characterization of specimen surface treated by ELID/TO hybrid process

Figure 2 shows the macroscopic observation of each specimen. The color of the surface of each specimen was changed from yellow to blue by the increase of treatment temperature. This was because the refractive index of light altered according to the thickness of the oxide layer formed. This implies that the EO series have thicker oxide layers than the PO series. Figure 3 shows the typical features of the surface of the EO and PO series observed by SEM. In this figure, the EO series showed some scratch marks. Such scratch marks indicate that ELID grinding was performed appropriately. Moreover, some particles existed over the whole surface area when the treatment temperature was elevated. In the process of oxide film formation, the oxide particles are generated on the surface. Therefore, the particles which exist in the EO and PO series are assumed to be oxide particles.
In order to investigate the element distribution, GD-OES analysis was carried out. Figure 4 shows depth profiling of the oxygen, chromium and cobalt content in each series. In Fig. 4 (a), oxygen content increased significantly by means of the thermal oxidation process and the EO series specimen had a thicker oxide layer than that of the PO series. In addition, the EO and PO series showed different decreasing behavior in oxygen content below the oxide layer. In the EO series, oxygen decreased gradually. In the PO series, however, the decrease was rapid. This was because the amount of oxygen was different between P and E series. In the E series, the oxygen diffused deeper than the P series due to generation of oxide film by means of ELID grinding. The decreasing behavior of oxygen was the same at all treatment temperatures. From Fig. 4 (b) and (c), chromium and cobalt existed in the surface of PO series. In the EO series, however, only chromium existed in the treated surface. In addition, cobalt free area existed in the surface. The cobalt free area was generated when the heating temperature was 500°C or more.
In order to obtain in-depth consideration, XPS analysis was carried out. Figure 5 (a) shows the chemical-bonding state of chromium at the surface of the specimen and (b) shows that of cobalt. In this analysis, depth-wise atomic conditions were investigated by using argon ion sputtering. In the P and E series, the peak of Cr$_2$O$_3$ disappeared following 40 and 60 seconds argon ion sputtering, respectively. On the other hand, there was still a Cr$_2$O$_3$ peak after 60 seconds sputtering on the PO and EO series which was treated by thermal oxidation. These results agree with GD-OES analysis. In particular, the peak of the EO series was more prominent than that of the PO series. The EO series showed no visible peak of cobalt oxide (Co(OH)$_2$). Therefore, the oxide observed in EO series consisted almost entirely of chromium oxide. It was reported that the case of cobalt chromium alloy, the surface composition is cobalt oxide as a priority when the oxidation reaction proceeds [9]. Therefore, in ordinary circumstance, cobalt oxide peaks should be presented on the surface of the EO series, however, in Fig. 5 (b), no peak of cobalt oxide was observed. The difference is thought to be related to the amount of cobalt on the surface after pretreatment.
Compared with the P and E series, the peak level of cobalt at after 2 seconds sputtering was different. From the value of ionization tendency, it is known that chromium can oxidize more easily than cobalt. Therefore, at the thermal oxidation, chromium oxide generates faster than cobalt oxide. In the EO series, the amount of cobalt was so small that chromium oxide could form before cobalt oxidization. As a result, the amount of cobalt element was suppressed on the surface.

3.2 Evaluation of corrosion resistance of ELID/TO hybrid process treated Co-Cr-Mo alloy

In order to investigate the corrosion response of the specimen, potentiodynamic polarization measurements were carried out. Figure 6 shows the results. In this figure, the E and EO series which are treated by ELID grinding showed the wider passive state than that of the P and PO series. In addition, the EO series showed the lowest electrical current density of the passive state in all series. Regarding to the E and EO series, the E series showed wider region of passive state than the EO series, although the EO series have a thicker oxide layer than the E series. This was because rough surface of the EO series decreased corrosion resistance [10].

Figure 7 shows the results of the cobalt ion elution test. The amount of cobalt ions in the solution was measured using a portable total reflection X-ray fluorescence spectrometer. The E series showed lower cobalt ion elution than P series. This was due to oxide layer which was made by ELID grinding. From the elemental analysis, cobalt oxide was presented in the surface of the PO series. Cobalt oxide is more stable than cobalt. Therefore, it was expected that the PO series showed the lower cobalt ion elution than the E series, however, the amount of cobalt ion were same level. This was thought to be due to increasing surface area. The EO series showed the lowest cobalt ion elution of all the series.
This was because of a decrease in the amount of cobalt due to the application of the ELID/TO hybrid process. As the EO series have a low peak of cobalt we proposed that the usage of the EO series will be longer.

4. Conclusion

In this study, hybrid process combined with ELID grinding and thermal oxidation was performed to improve corrosion resistance of Co-Cr-Mo alloy. This treatment created a thick and dense oxide layer and a low peak of cobalt area was generated when heated at a temperature of greater than 500 ℃. The corrosion resistance of Co-Cr-Mo alloy with the hybrid process was better than that of the specimens with other treatments. Moreover, specimens treated by hybrid process showed the lowest cobalt ion elution due to presence of a cobalt-free layer. These results suggest that it is possible to apply the hybrid process to improve the corrosion resistance for metal implants.

References


