Effect of Sigma Phase in Co-29Cr-6Mo Alloy on Corrosion Behavior in Saline Solution

Shingo Kurosu¹*, Naoyuki Nomura² and Akihiko Chiba²

¹Department of Material Science, Graduate School of Engineering, Iwate University, Morioka 020-8551, Japan
²Department of Welfare Engineering, Faculty of Engineering, Iwate University, Morioka 020-8551, Japan

Effect of the sigma (σ) phase in Co-Cr-Mo alloy on corrosion behavior in saline solution has been investigated. The area fraction of the σ phase contained in Co-29Cr-6Mo alloy varies depending on the aging time at 1023 K. The σ phase is mainly observed at grain boundaries. The area fraction of the σ phase increases with increasing aging time and reaches 0.6% after aging at 1023 K for 21.6 ks.

The Co-29Cr-6Mo alloys aged at 1023 K for various aging times were immersed in saline solution at 310 K for 1 week and metal ions released from the alloys were examined by inductively coupled plasma atomic emission spectrometer (ICP-AES). The quantity of a released Co ion does not depend on the aging time and shows almost the same value regardless of the different area fraction of the σ phase, while that of released Cr, Mo and Ni ions increases with increasing area fraction of the σ phase. Results of polarization test in saline solution at 310 K revealed that passive current density and breakdown potential of Co-29Cr-6Mo alloys aged at 1023 K for various aging times exhibit almost the same values, although the alloys have different area fraction of the σ phase. These results suggest that a small amount of the σ phase (<0.6%) hardly affect the formation and breakdown of passive film in the Co-29Cr-6Mo alloy aged at 1023 K. [doi:10.2320/matertrans.47.1961]

(Received May 8, 2006; Accepted July 11, 2006; Published August 15, 2006)

Keywords: cobalt-chromium-molybdenum alloy, biomaterial, metal ion release, corrosion, sigma phase (σ), isothermal aging treatment

1. Introduction

The Co-Cr-Mo alloys have been widely used for surgical prostheses such as hip and knee joint replacements due to their high mechanical properties, corrosion resistance and wear resistance. In as-cast condition, the alloys consist of the γ phase (F.C.C.) and the ε phase (H.C.P.) formed by martensitic transformation from γ to ε during cooling. As far as the Co-Cr-Mo alloys are concerned, properties of the alloys significantly depend on the ratio of these phases. Elongation of Co-29Cr-6Mo alloy increases with increasing the γ phase fraction.1,2) On the other hand, the quantity of released metal ion tends to decrease with increasing the ε phase.3) In addition, wear resistance of Co-Cr-Mo alloys consisting of the ε phase are excellent under metal-on-metal condition.4) From the above properties, it can be summarized that the alloy consisting of the γ phase is favorable for plastic forming and the alloy consisting of the ε phase is promising for the application used in corrosion or wear circumstance. Although the effect of heat treatment and carbon addition on the stability of γ phase have been reported so far,5) the stability of the ε phase has not been investigated in detail yet.

Figure 1 shows the ternary phase diagrams of Co-Cr-Mo alloy system6) at (a) 1473 K and (b) 1200 K. The solid circles in the Fig. 1 show the composition of ASTM-F75 (Co-27–30Cr-5–7Mo(at mass%)). At the composition, the ε phase and the σ phase coexist at 1200 K, although only the γ phase is stable at 1473 K. The σ phase in Co-Cr-Mo alloys has the same crystal structure (P42/mnm) as that appeared in Fe-Cr alloy system. In the ferritic stainless steels (Fe-29Cr-4Mo), the σ phase precipitates in the grain boundaries during isothermal aging treatment at 1123 K in the early stage, and the volume fraction of the σ phase reached 20% after aging at 1123 K for 36 ks.7) In the 25Cr duplex stainless steel alloys, Agelini et al.8) reported that the volume fraction of the σ phase reached 2.5 and 5 vol% after aging at 923 K for 3.6 ks and 14.4 ks, respectively. Furthermore, Aguilar et al.9) reported the volume fraction of the σ phase reaches approximately 5 vol% even if after aging at 1123 K for 0.3 ks. Corrosion resistance of these stainless steels decreased with the presence of the σ phase because of the galvanic corrosion and pitting corrosion.5–9) Therefore, the σ phase is supposed to affect the corrosion resistance of Co-Cr-Mo alloys as well.

The objective of this study is to investigate microstructure of Co-29Cr-6Mo after isothermal aging at the ε phase region.

---

*Graduate Student, Iwate University
and the effect of the $\sigma$ phase in Co-29Cr-6Mo alloy on corrosion behavior in saline.

2. Experimental Procedure

2.1 Alloys

The vacuum induction melting technique was employed to prepare Co-29Cr-6Mo-1Ni (mass%) alloy. The chemical composition of the investigated Co-Cr-Mo alloy was listed in Table 1. The Co-Cr-Mo casting alloys for surgical implants are allowed to contain less than 1 mass% Ni according to ASTM standard (ASTM F75). In the present study, 1 mass% Ni was intentionally added to the alloys to investigate Ni ion released from the alloy. Each specimen was cut out by using electrical wire cutting machine. The heat treatment was carried out to stabilize the $\sigma$ phase. The solution heat treatment was carried out at 1523 K for 7.2 ks for homogenization. After cooling from 1523 to 1023 K at a rate of 0.166 K/s, isothermal aging treatments were conducted at 1023 K for 0, 1.8, 3.6, 7.2, 14.4 and 21.6 ks, followed by water quenching.

2.2 Metallography

Microstructures of aged specimens were observed with an optical microscope (OM) and a scanning electron microscope (SEM). Phase identification was performed with X-ray diffractometer (XRD) using monochromated Cu Kα radiation over $40^\circ \leq \theta \leq 55^\circ$. The surface was polished by alumina powder with a diameter of 0.05 μm for a mirror finish and then electropolished at 6 V and room temperature in solution of 10% H$_2$SO$_4$-90% CH$_3$OH. The area fraction of the $\sigma$ phase was analyzed by using image analysis from backscattered electron image (BEI).

2.3 Static immersion test

The static immersion test was performed in accordance with the JIS T304. The specimens were immersed in saline solution (0.9 mass% NaCl solution) at 310 K for 1 week. The released metal ions in saline were examined with inductively coupled plasma atomic emission spectrometer (ICP-AES). The quantity of released metal ion, $W_i$ were calculated as follows:

$$W_i = L (IC_i - IB_i)/S$$

where $L$ is amount of solution (ml), $IC_i$ the metal concentration in each test solution (g/cm$^3$), $IB_i$ the average of metal concentration in blank test (g/cm$^3$), $S$ the surface area of specimens (cm$^2$).

The size of specimens was $40 \times 15 \times 1 \text{ mm}^3$ and amount of solution was 30 ml. Prior to the immersion test, the specimens were polished with waterproof emery papers up to 1000 grit under running distilled water, and then rinsed with distilled water and acetone for 0.3 ks in an ultrasonic cleaning bath.

2.4 Polarization test

The polarization test at 310 K in saline solution was performed at a scan rate of 0.33 mV/s to determine the passive current densities and breakdown potentials. The specimen was polished with waterproof emery papers up to 600 grits under running distilled water and then rinsed with distilled water and acetone for 0.3 ks in an ultrasonic cleaning bath. Prior to and throughout the polarization test, Ar gas was bubbled in the solution to remove dissolved oxygen. The specimens were immersed in the solution for 1.8 ks to stabilize open-circuit potential and then potential was swept up to $-1000 \text{ mV}$ as cathodic treatment. The polarization curve was measured from $-1000$ to $1000 \text{ mV}$ at least three times with each specimen. A saturated calomel electrode (SCE) and a Pt plate were used as a reference electrode and a counter electrode, respectively.

3. Results and Discussion

3.1 Effect of isothermal aging treatments on metallography

Figure 2 shows the X-ray diffraction patterns of the Co-29Cr-6Mo-1Ni alloy aged at 1023 K for (a) 0 ks, (b) 1.8 ks, (c) 3.6 ks, (d) 7.2 ks, (e) 14.4 ks and (f) 21.6 ks. The $\gamma$ and $\epsilon$ phases coexist in the specimens of (a) to (d). The peak from the $\gamma$ phase is hardly detected in that of (d). On the other hand, only peaks from the $\epsilon$ phase are detected in those of (e) and (f), suggesting that the complete transformation from $\gamma$ to $\epsilon$ for the Co-29Cr-6Mo-1Ni alloy requires the prolonged isothermal aging treatments at 1023 K for more than 7.2 ks.

Figure 3 shows the optical micrographs of the Co-29Cr-6Mo alloy aged at 1023 K for (a) 0 ks, (b) 1.8 ks, (c) 3.6 ks, (d) 7.2 ks, (e) 14.4 ks and (f) 21.6 ks. The jagged grain boundaries are observed in all the aged alloys and there are no striations formed by martensitic transformation from the $\gamma$ phase to the $\epsilon$ phase. When the solution heat treatment was carried out over 1443 K, followed by water quenching, the striations are clearly observed.

Therefore, the microstruc-

<table>
<thead>
<tr>
<th>[mass%]</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>C</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal.</td>
<td>28.68</td>
<td>6.01</td>
<td>1.06</td>
<td>&lt;0.005</td>
<td>40</td>
<td>129</td>
<td></td>
</tr>
</tbody>
</table>
ture observed in Fig. 3 may be formed by massive transformation\textsuperscript{10} during cooling from 1523 K to 1023 K.

The average grain sizes of the aged alloys at 1023 K for 0, 1.8, 3.6, 7.2, 14.4 and 21.6 ks are 285, 250, 211, 259, 220 and 256 μm, respectively. The aged alloys exhibit almost the same size, although the isothermal aging treatments were conducted for different aging times.

3.2 Effect of isothermal aging treatments on the precipitation of the σ phase

Figure 4 shows the backscattered electron image (BEI) of Co-29Cr-6Mo-1Ni alloys aged at 1023 K for (a) 0 ks, (b) 1.8 ks, (c) 3.6 ks, (d) 7.2 ks, (e) 14.4 ks and (f) 21.6 ks. Obviously, the σ phase precipitates in grain boundaries. The particle size of the σ phase is less than 1 μm.

Figure 5 shows the area fraction of the σ phase in the aged alloys with different aging times. The area fraction increases with increasing aging time, and reaches 0.6% after aging at 1023 K for 21.6 ks. The precipitation of the σ phase is also observed at 0 ks, indicating that the σ phase have started to precipitate during cooling from 1523 to 1023 K.

3.3 Effect of the amounts of the σ phase on corrosion behavior

Figure 6 shows the effect of the amount of the σ phase on metal ion release; (a) Co ion, (b) Cr, Mo and Ni ions. The quantities of released Cr, Mo and Ni ions increase with increasing the amount of the σ phase. It should be noted that the quantity of released Cr and Mo ions shows lower value compared to that of released Ni ion although Cr and Mo content of the alloy is higher than Ni content. These suggest that Cr and Mo ions are more difficult to be released from the alloy than Ni ion, because Cr and Mo contribute the formation of passive film, while Ni does not contribute.\textsuperscript{11}

Precipitation of the σ phase causes the depletion of Cr and Mo around the σ phase because the σ phase contains richer Cr and Mo than matrix.\textsuperscript{7,12} On the other hand, Co and Ni would concentrate at the region reversely.\textsuperscript{9} Therefore corrosion preferentially occurs around the σ phase.

The quantity of released Co ion shows no difference among the aged alloys although the value is much higher than that of Cr, Mo and Ni, as shown in Fig. 6(a). The major factors affecting corrosion are constituent phases (including secondary phase) and grain size from the view point of microstuctural features. In the present study, the aged alloys mostly consists the ε phase, and possess almost the same grain size regardless of various aging times. The major difference among them is the area fraction of the σ phase. This indicates that released Co ion is not affected by the precipitation of σ phase at least as small as 0.6% in the area fraction.

Figure 7 shows the effect of the amounts of the σ phase on
the passive current densities \((i_p)\) and the breakdown potentials \((E_b)\). The passive current density was determined at a potential of 200 mV where the polarization curve shows plateau. The breakdown potential was determined at the intersection of the extrapolated passive and transpassive current densities. The passive current densities and breakdown potentials of the aged alloys exhibit almost the same values, although the alloys have different area fraction of the \(\sigma\) phase. It was reported that passive current density increased and breakdown potential of stainless steels shifted to less noble significantly by precipitation of the \(\sigma\) phase.\(^7\)–\(^9\) This is also attributed to the depletion of Cr and Mo in the matrix by precipitation of the \(\sigma\) phase.\(^7\)–\(^9\) Since the fraction of the \(\sigma\) phase is quite less (<0.6%), the difference of break down potentials and passive current densities among the aged alloys may be quite small and hard to be detected through the test. Thus the small amount of the \(\sigma\) phase (<0.6%) hardly affects the formation and breakdown of passive film in the \(\varepsilon\)-treated Co-29Cr-6Mo alloy.

4. Conclusions

The effect of \(\sigma\) phase on corrosion behavior of Co-29Cr-6Mo alloy was investigated. The obtained results are summarized as follows:

1. The specimens are completely transformed to the \(\varepsilon\) phase by isothermal aging treatments at 1023 K for more than 7.2 ks.
2. The \(\sigma\) phase precipitates in grain boundaries during isothermal aging treatments at 1023 K. The area fraction of the \(\sigma\) phase increases with increasing aging time, and reaches 0.6% after aging at 1023 K for 21.6 ks.
3. The quantity of released Co ion is almost the same regardless of different amount of precipitated the \(\sigma\) phase, while the quantity of released Cr, Mo and Ni ions increases with increasing the \(\sigma\) phase.
4. The small amount of the \(\sigma\) phase (<0.6%) hardly affects the formation and breakdown of passive film in the \(\varepsilon\)-treated Co-29Cr-6Mo alloy.

Acknowledgements

The authors would like to thank to Dr. Katsunori Yamaguchi at Department of Materials Science and Engineering, Faculty of engineering, Iwate University for the measurement with ICP-AES and technical supports. This research was supported by a Cooperation of Innovative Technology and Advanced Research in Evolutional Area from Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES