Mass Loss and Ion Elution of Biomedical Co–Cr–Mo Alloys during Pin-on-Disk Wear Tests

Kyosuke Ueda¹*, Kaori Nakaie¹, Shigenobu Namba², Takashi Yoneda³, Keita Ishimizu⁴ and Takayuki Narushima¹

¹Department of Materials Processing, Tohoku University, Sendai 980-8579, Japan
²Materials Research Laboratory, Kobe Steel, Ltd., Kobe 651-2271, Japan
³Yoneda Advanced Casting Co., Ltd., Takaoka 933-0951, Japan
⁴Kyocera Medical Co., Ltd., Osaka 532-0003, Japan

Pin-on-disk wear tests using biomedical Co–Cr–Mo alloy pins and alumina disks were conducted in Kokubo and 1% lactic acid solutions. The mass loss and elution of metallic ions were measured and the surface of the pin was observed after the wear test. Mass loss of the alloy pins in 1% lactic acid solution was 10 times higher than the mass loss in Kokubo solution. In Kokubo solution, the as-cast pins exhibited higher mass loss and higher total amount of eluted ions than solution-treated pins. The Cr and Mn ion content in Kokubo solution was lower than expected, based on the chemical composition of the alloy. The incorporation of Cr and Mn ions into the calcium phosphate detected on the wear track of disks is the possible reason for the small amount of these ions in Kokubo solution. [doi:10.2320/matertrans.ME201316]

(Received March 19, 2013; Accepted May 16, 2013; Published June 21, 2013)

Keywords: cobalt–chromium–molybdenum alloy, precipitate, pin-on-disk wear test, Kokubo solution, lactic acid solution, ion elution

1. Introduction

Cobalt (Co)–chromium (Cr)–molybdenum (Mo) alloys are frequently used as implants in dental and medical fields because of their excellent mechanical properties and high corrosion and wear resistance. The American Society for Testing of Materials (ASTM) F75 standard permits the addition of carbon and nitrogen to Co–Cr–Mo alloys at 0.35 and 0.25 mass%, respectively.¹¹ Carbon and nitrogen content is related to suppression of σ-phase, stabilization of the metallic face-centered-cubic (fcc) Co-based phase (γ-phase), and strengthening of the material by the formation of carbides and nitrides. This alloy has been used in the stem, ball and cup components of artificial hip joints in both metal-on-ultrahigh molecular weight polyethylene (UHMWPE) and metal-on-metal type implants, as well as in the sliding components of artificial knee joints.

The main concern in using these metal-based hip replacements is the formation of wear debris²) and ion elution,³) which seem to be closely related to the microstructure and precipitates of the Co–Cr–Mo alloy implants.

It is well known that the phase, morphology, size and distribution of the precipitates affect the properties of Co–Cr–Mo alloys.⁴-¹¹ In our previous study, we found that carbon, nitrogen, silicon (Si) and manganese (Mn) content in the acceptable range given by ASTM F75 standard, along with heat treatment, could be used to control the phase of precipitates.¹²-¹⁹

In metal-on-metal wear tests of Co–Cr–Mo alloys, many studies have been reported on the effects of precipitates on wear behavior. Chiba et al. reported that the marked abrasive wear was caused by precipitates,¹⁰) while other studies showed that precipitates improved wear properties.⁵,²¹) The combination of Co–Cr–Mo alloy and alumina (Al₂O₃), which is of the metal-on-ceramic type, is a potential candidate for artificial joints because of its low wear rate.²²) As in the case of metal-on-metal type joints, the wear behavior of metal-on-ceramic type is speculated to be affected by the precipitates in the metal, Co–Cr–Mo alloys. There are very few reports on the wear behavior in metal-ceramic combinations.²²,²³)

Although Yan et al.²³) conducted pin-on-plate wear tests using wrought Co–Cr–Mo alloy pins and Al₂O₃ plates and studied the corrosion behavior of the alloy pins during the tests, they did not discuss the effects of the microstructure and precipitates in the Co–Cr–Mo alloys on the mass loss and ion elution.

It has been reported that small amounts of Ni ions tend to elute from Co–Cr–Mo alloys in spite of their low Ni content.²⁴) Clarifying the elution of nickel (Ni) ions during wear tests is an important step towards characterizing the further suitability of Co–Cr–Mo alloys for medical implants, due to the toxicity of Ni ions in the human body.²⁵)

In the present study, pin-on-disk wear tests using Co–Cr–Mo alloy pins and Al₂O₃ disks were conducted using Kokubo and 1% lactic acid solutions as lubricants. The mass losses in the pins and ion elution into the lubricants were evaluated. The objective is to clarify the effect of microstructure on the wear properties and ion elution of biomedical Co–Cr–Mo alloys.

2. Experimental Procedures

2.1 Specimens

Four types of Co–Cr–Mo alloy ingots (7 mm in diameter and 50 mm in length) with different Si, Mn, nitrogen and Ni content were fabricated using an induction melting furnace with a copper (Cu) mold. Table 1 shows the composition of the alloys. The carbon content remained constant at 0.25 mass%. To investigate the effect of Ni content on Ni ion elution, an alloy with a higher Ni content than that of the ASTM F75 standard was also used. In the present study, alloy notations were as follows: 0Si0Mn0.3N, 1Si1Mn0.3N,

*Corresponding author, E-mail: ueda@material.tohoku.ac.jp
1Si1Mn0N and 1Si1Mn3Ni0N depending on the contents of added elements. Solution treatment (ST) was conducted at 1508 K for 86.4 ks for complete precipitate dissolution. The precipitates in the alloys were observed using optical microscopy (OM, BX60M, Olympus, Tokyo, Japan) and scanning electron microscopy (SEM, XL30FEG, Philips, Hillsboro, OR) after electrolytic etching in a 10% sulfuric acid in ethanol solution. The precipitates were electrolytically extracted from the alloy in a 10% sulfuric acid solution and precipitate phases were identified using X-ray diffraction (XRD, D8 ADVANCE, Bruker AXS K.K., Karlsruhe, Germany).

2.2 Pin-on-disk wear test

Pin-on-disk wear tests were conducted referring to Japan Industrial Standards (JIS) T0303 and using Co–Cr–Mo alloy pins and Al2O3 disks. A wear machine designed by our group can conduct the wear test in lubricant with constant temperature and collect the lubricant after the test is completed.26) The Co–Cr–Mo alloy pins were 5 mm in diameter and 40 mm in length and the contact surface of the pins was worked to a spherical radius (SR) of 100 mm to avoid stress concentration at the edge of the pins. The Al2O3 disks (99.9%, CRA3846-0, KYOCERA, Kyoto, Japan) were 50 mm in diameter and 5 mm thick. Both the contact surfaces of pins and disks were mirror-polished (Ra < 0.05 µm) and ultrasonically cleaned in ethanol, followed by ultrapure water for 300 s each. 20 mL each of Kokubo solution27) (pH = 7.4) and 1% lactic acid solution (pH = 2.3) were used as lubricants maintained at 310 K. The disks rotated 25 mm·s⁻¹ (15.91 rpm) at a sliding diameter of 30 mm. The rotation or sliding speed was set at the same value of a hip joint simulator previously reported.21) Pin load was set to 1.0 kgf, corresponding to 166 MPa of contact stress as calculated by Hertzian contact theory.28) To investigate the effects of wear and stress on metallic ion elution in the lubricant, a static immersion test was carried out. The Co–Cr–Mo alloy plates (7 mm in diameter and 2 mm in thickness), polished with emery papers up to # 1500, were immersed in either 10 mL of Kokubo solution or 1% lactic acid solution at 310 K. These solutions with specimens were kept in a shaking bath at a speed of 0.27 s⁻¹.

After the wear test, the pins were ultrasonically cleaned in ethanol and ultrapure water, and then weighed to evaluate mass loss. The pin surface was observed with SEM. The chemical composition of the disk surface was measured with energy dispersive X-ray spectrometry (EDX). After wear and static immersion tests, the lubricant was filtered with a membrane filter (polycarbonate, 0.2 µm pore size). The metal ion concentrations in the filtrate were quantitatively determined using inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7500cx, Agilent, Tokyo, Japan).

3. Results

3.1 Precipitates in pins

Figure 1 shows a representative microstructure of the as-cast and ST 1Si1Mn0.3N alloys. A dendritic matrix with interdendritic and grain boundary precipitates were observed in the as-cast alloy. No precipitates were observed in any of the ST alloys. The spherical features observed in the image (Fig. 1(b)) are the pores formed during heat treatment.13) Figure 2 shows the XRD patterns of the precipitates electrolytically extracted from the as-cast alloys.

\[ \text{X-phase precipitates (M}_2\text{T}_3\text{X-type precipitate with } \beta\text{-Mn structure, where M and T are metallic elements and X is carbon or nitrogen)} \]

The area percents of the precipitates were calculated using at least three OM images (500©). The area percent of each precipitate was calculated using the ratio of the intensity of the strongest peak to the sum of the intensities of the strongest peaks of the precipitates in the XRD patterns. The area percents of the precipitates are shown in Fig. 3. Morphologies of precipitates are shown in Fig. 4.
morphology of the $\pi$-phase precipitates was starlike-dense with typical sizes of 2 to 5 µm. M$_2$X-type precipitates coexisted with $\gamma$-phase in the lamellar cellular colony. As well, M$_{23}X_6$-type precipitates and $\gamma$-phase exhibited starlike with patterns of stripes.

3.2 Mass loss and surface morphology of pins

The mass loss of the pins after wear tests in Kokubo and 1% lactic acid solutions is shown in Fig. 5. The mass loss of the as-cast pins in Kokubo solution was higher than that of the ST pins, while the mass losses of both the as-cast and ST pins were comparable in a 1% lactic acid solution. The mass losses in the 1% lactic acid solution were approximately 10 times higher than those in the Kokubo solution.

The surface morphologies of the as-cast and ST 1Si1Mn0.3N alloy pins after wear tests in Kokubo and 1% lactic acid solutions are shown in Fig. 6. The wear direction is top to bottom in the figures. Continuous wear grooves were observed in Figs. 6(b), 6(c) and 6(d). On the other hand, in Fig. 6(a), discontinuous deep wear grooves were detected in the as-cast pin after a wear test in Kokubo solution. Figure 7 depicts the microstructure around precipitates in the as-cast pins after wear tests. In Figs. 7(a), 7(b) and 7(c) of as-cast pins after wear tests in Kokubo solution, cavities were observed next to precipitates, and discontinuous grooves originated from these cavities. This observation suggests that the discontinuous grooves were formed by wear debris detached from cavities. On the other hand, for wear tests conducted in 1% lactic acid solution, such cavities were not observed.

3.3 Total elution of metallic ions

Figure 8 shows the total amount of eluted metallic ions (Co, Cr, Mo, Si, Mn and Ni) from pins after wear and static immersion tests. The total amounts of eluted ions after wear tests were 3 to 4 orders of magnitude higher than the amounts after static immersion tests. These results indicate that wear accelerated ion elution, possibly because the passivation film on the pin was destroyed during wear, and bare metallic surfaces were exposed to lubricants. The total amount of eluted ions from as-cast pins was higher than that for ST pins in Kokubo solution.

---

**Fig. 2** XRD patterns of precipitates electrolytically extracted from the as-cast alloys.

**Fig. 3** Area percent of precipitates in the as-cast alloys.

**Fig. 4** SEM images of (a) $\pi$-phase, (b) M$_{23}X_6$-type and (c) M$_2$X-type precipitates.
4. Discussion

4.1 Formation of cavities and discontinuous grooves

The formation of cavities and discontinuous deep grooves is likely to cause a higher mass loss and a higher total elution of ions in Kokubo solution for the as-cast pins than for the ST pins. Wear debris of both precipitates and metallic matrix were found in Kokubo solution after wear tests of as-cast pins. A part of precipitate first detached from the metallic matrix, forming cavities during wear tests, and then caused deep discontinuous grooves (Fig. 6(a)) through the three-body abrasion. The higher hardness,\(^{29}\) i.e., slower wear rate, and higher Young’s modulus of precipitates as compared to the metallic matrix led their detachment during wear tests in Kokubo solution. The formation of the cavity and discontinuous groove did not depend on the phase of precipitates, which suggests that the difference of hardness and Young’s modulus between precipitates and metallic matrix are dominant in cavity and discontinuous groove formation.

![Fig. 5 Mass loss of pins after wear tests in (a) Kokubo solution and (b) 1% lactic acid solution.](image)

![Fig. 6 SEM images of the surfaces of (a), (b) as-cast and (c), (d) ST pins of 1Si1Mn0.3N alloy after wear tests in (a), (c) Kokubo and (b), (d) 1% lactic acid solution.](image)
In the 1% lactic acid solution, the detachment of precipitates was not significant because both precipitates and metallic matrix worn out relatively uniformly due to the fact that 1% lactic acid is more corrosive than Kokubo solution. The mass loss of the pins in a 1% lactic acid solution was much higher than the loss when using Kokubo solution, while the mass of the total amount of eluted ions from the pins after wear tests in 1% lactic acid solution was approximately same as the mass loss of the pins.

Chiba et al. reported that Co–Cr–Mo alloys with $\epsilon$-phase obtained from strain-induced martensitic transformation exhibited excellent wear resistance because of the increased hardness. In the Co–Cr–Mo alloys, nitrogen addition stabilizes the $\gamma$-phase. On the other hand, in the present study, XRD and SEM analysis revealed that the formation of the $\epsilon$-phase by strain-induced martensitic transformation during wear tests was not significant, even in the alloys without nitrogen addition. Therefore, there was no significant difference in mass loss between the as-cast alloys with and without nitrogen addition.

### 4.2 Elution of each metallic ion

The amount of eluted ions for each metallic element is shown in Fig. 9. Small amounts of Ni ion were detected after wear tests on 0Si0Mn0.3N, 1Si1Mn0.3N and 1Si1Mn0N alloy pins, caused by Ni impurities in these alloys. Decreasing Ni content in these alloys will be necessary to decrease Ni ion elution and improve the safety of Co–Cr–Mo alloys.

The mass ratios of Co/Cr and Co/Mn for eluted ions from the 1Si1Mn3Ni0N alloy pin into Kokubo solution were 53.1 and 225.0, which were much higher than the same mass ratios in the alloy content, 2.1 and 49.3, respectively. This means that the Cr and Mn ion content in Kokubo solution is lower than expected, based on the chemical composition of the alloy. EDX spectra of the surface of the disk on and out of the wear track are shown in Fig. 10. Calcium and phosphorus signals were detected on the wear track, which indicates the formation of calcium phosphate. These species would precipitate because of the decreasing solubility of calcium phosphates at the contact points between pin and disk, where

![SEM images of the surface of the as-cast pins with precipitates of (a), (d) $\pi$-phase, (b), (e) $M_2X_r$-type and (c), (f) $M_2X$-type after wear test in (a), (b), (c) Kokubo solution and (d), (e), (f) 1% lactic acid solution.](image-url)
the temperature of the solution locally increased. The calcium phosphate on the disk after the wear test using the 1Si1Mn3Ni0N alloy pin was dissolved using a 0.5% nitric acid solution and the composition of the calcium phosphate precipitates were analyzed using ICP-MS. The calcium phosphate included Co, Cr, Si, Mn and Ni with a mass ratio of 61.2 : 36.2 : 0.5 : 1.5 : 0.6. These results indicated that the Cr and Mn ions were preferentially incorporated into calcium phosphate, resulting in the low concentration of these ions in the Kokubo solution.

In previous study, the formation of calcium phosphate on the wear track after wear tests of Co–Cr–Mo alloys in Hanks’ solution was reported. It has also been reported that Cr and Mn ions were incorporated into the Ca site of calcium phosphates. Results obtained in this study agreed with these previous studies.

5. Conclusion

Pin-on-disk wear tests using biomedical Co–Cr–Mo alloy pins and Al2O3 disks were conducted in Kokubo and 1% lactic acid solutions and the effects of alloy microstructure on mass loss and metallic ion elution were investigated. Following results were obtained.

1. The mass loss of Co–Cr–Mo pins in a 1% lactic acid solution was 10 times higher than that in a Kokubo solution. In Kokubo solution, as-cast pins exhibited a higher mass loss and a higher total amount of eluted ions than ST pins.

2. Discontinuous deep wear grooves were observed on the as-cast pins after wear tests in the Kokubo solution. The discontinuous grooves started from cavities next to the precipitates. On the other hand, for wear tests conducted in the 1% lactic acid solution, neither cavities nor discontinuous grooves were observed.

3. The total amount of metallic ions eluted during wear tests was higher than the amount eluted during static immersion tests. In the Kokubo solution, the total amount of metallic ions eluted from the as-cast pins was higher than the amount eluted from the ST pins.

4. The Cr and Mn ion content in Kokubo solution after wear tests was lower than expected, based on the chemical composition of the alloy. The incorporation of Cr and Mn ions into the calcium phosphate detected on the wear track of disks is the possible reason for the small amount of these ions in Kokubo solution.

5. A small amount of Ni ion elution was detected from wear tests conducted using the alloy pins where Ni was not intentionally added. This is likely from Ni impurities in metals used for these alloys.

Fig. 8 Total amounts of eluted metallic ions (Co, Cr, Mo, Si, Mn, Ni) after (a), (c) wear and (b), (d) static immersion tests in (a), (b) Kokubo solution and (c), (d) 1% lactic acid solution.
Acknowledgments

The authors would like to thank Dr. K. Kobayashi of Tohoku University for analyses of precipitates and wear debris.

REFERENCES

11) E. Bettini, T. Eriksson, M. Boström, C. Leygraf and J. Pan:

Fig. 9 Amount of eluted Co, Cr, Mo, Si, Mn and Ni ions after wear test in (a) Kokubo solution and (b) 1% lactic acid solution.

Fig. 10 EDX spectra of the surface of the disk on and out of the wear track after wear test in Kokubo solution.