Effects of Heat Treatment and Hot Forging on Microstructure and Mechanical Properties of Co-Cr-Mo Alloy for Surgical Implants

Yoshimitsu Okazaki

Institute of Mechanical Systems Engineering, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8564, Japan

The effects of heat treatment and hot forging on the microstructure and mechanical properties of Co-Cr-Mo alloy for implant applications were examined. In an alloy annealed at 1200 °C for 1 h, M23C6 carbides precipitated along the grain boundary in the γ phase matrix containing a small amount of ε phase. The 0.2% proof strength (σ02PS), ultimate tensile strength (σUTS), total elongation (T. E.), and reduction of area (R. A.) of annealed alloy were 553 ± 2 MPa, 928 ± 41 MPa, 21 ± 2%, and 15 ± 1%, respectively. The σ02PS and σUTS of the Co-Cr-Mo alloy hot-forged at a starting temperature of 1100 °C increased linearly with an increase in reduction in area, whereas T. E. gradually decreased with an increase in the reduction. The σ02PS, σUTS, T. E., and R. A. of 57% hot-forged alloy were 715 ± 86 MPa, 1109 ± 61 MPa, 8 ± 1%, and 10 ± 1%, respectively. In the 57% hot-forged Co-Cr-Mo alloy, a large amount of M23C6 carbide and a small amount of M6C carbide were observed in the γ phase matrix containing the ε phase. In the light of these results, it appears that hot forging with a starting temperature of approximately 1100 °C provided excellent mechanical properties to the alloys. [doi:10.2320/matertrans.MRA2007274]

(Received November 7, 2007; Accepted January 29, 2008; Published March 25, 2008)

Keywords: microstructure, mechanical property, cobalt alloy, heat treatment, hot forging

1. Introduction

Co-Cr-Mo alloys are increasingly being used as metallic materials for orthopedic implants. For example, a Co-Cr-Mo casting alloy has been used in the femur component of artificial knee joints. A wrought Co-Cr-Mo alloy has been used in artificial components such as hip heads, hip stems, metal-on-metal hip joint bearings, and knee stems. Recently, it has been reported that fretting corrosion is caused by micromotion between bone cement and cemented artificial hip stems made of Ti alloys, which have a much lower elasticity than Co-Cr-Mo alloys.1) Co-Cr-Mo alloys are thus increasingly replacing by Ti alloys as a material for cemented artificial hip stems. In particular, wrought Co-Cr-Mo alloys, which show excellent elasticity and high mechanical strength, have received considerable attention as a material for cemented artificial hip joint stems and metal-on-metal bearing parts for artificial hip joints.2–9) The chemical requirements and mechanical properties of Co-Cr-Mo casting alloy and wrought Co-Cr-Mo alloy for application in medical devices and surgical implants are respectively specified by the ISO 5832-4 and ISO 5832-12 standards.

In order for Japanese companies to stay competitive with the large influx of foreign products, cost reduction of manufacturing orthopedic implants has become more important every year; thus, the development of a hot forging process for Co-Cr-Mo alloy has been required. It is therefore necessary to examine the effects of heat treatment and hot forging on the microstructure and mechanical properties of Co-Cr-Mo alloy. However, there appear to be few in-depth research studies that adequately examine such effects. In this study, to obtain basic data to develop a new forging process, we examined how annealing and hot forging affect the microstructure and mechanical properties of Co-Cr-Mo alloy. Microstructure changes were analyzed by optical microscopy, X-ray diffraction analysis and transmission electron microscopy, and tensile tests were carried out at room temperature to examine the aforementioned effects on the mechanical properties of Co-Cr-Mo alloy.

2. Experimental Materials and Methods

2.1 Alloy specimens and heat treatment

Figure 1 shows annealing and hot-forging processes for Co-Cr-Mo alloy. Co-Cr-Mo alloy, which meets the specifications of the ISO 5832-12 standard for implants, were prepared by vacuum-induction melting. Co-Cr-Mo alloy ingot was first homogenized at 1250 °C for 5 h. The portion of the homogenized ingot was maintained at 1200 °C for 1 h and then hot-forged into rod specimens of 30 mm diameter. The rod specimens were reheated at 1200 °C for 1 h and then air-cooled (annealed). Another portion of the homogenized alloy was hot-forged into rod specimens of 42 mm diameter after being maintained at 1200 °C for 1 h. Part of them were maintained at 1100 °C for 1 h and then hot-forged to the reduction in area of 40%, 42%, 47%, 49%, and 57%, respectively. To examine the effect of heating temperature on microstructure, one of the rod specimens was maintained at 1000 °C for 1 h and hot-forged to a 50% reduction in area at a starting temperature of 1000 °C. Through these processes, annealed and hot-forged Co-Cr-Mo alloys were prepared for microstructural observation and mechanical tests. The chemical composition of the Co-Cr-Mo alloy is shown in Table 1.

2.2 Microscopic observation and X-ray diffraction analysis

The microstructures of the annealed and hot-forged Co-Cr-Mo alloys were evaluated by an optical microscopy, transmission electron microscopy (TEM), and X-ray diffraction analysis. The specimens used for microscopic observation were cut from the sample alloys and covered with epoxy
resin. Then, the specimen surfaces were polished with waterproof emery paper from 120 to 2400 grit under running water. The sample surfaces were finished by buff-cleaning using a high-quality SiO$_2$ (OP-S) suspension and etched with aqua regia before the observation. A Nikon upright microscope was used for microscopic observation. TEM was performed using disc specimens of 3 mm diameter. The 3-mm-diameter disc specimens were prepared by electrolytic polishing with 95% methanol + 5% perchloric acid solution. Microstructures were analyzed using a transmission electron microscope (Hitachi, Ltd., H-800, at 200 kV) equipped with an EDX system (Horiba, Ltd., EMAX-2200). Precipitates were also analyzed by electron beam diffraction analysis and EDX. The surfaces of the sample used for X-ray diffraction measurement were finished by buff cleaning. RINT1500, manufactured by Rigaku Corp., was used for X-ray diffraction analysis. The diffraction patterns were obtained using an X-ray source of Cu K$_\alpha$ at a tube voltage of 40 kV, a tube current of 0.02 A, and a scanning rate ($\theta$) of 1$^\circ$/min. The lattice constants of the precipitates were also accurately measured. The silicon powder (NIST, 640C), for use in XRD analysis, was thinly spread onto the buff-cleaned sample surface so that it was as flat as possible, according to the testing manual. The scanning rate ($\theta$) and sampling step were set to 1$^\circ$/min and 0.01$^\circ$, respectively. To ensure the accurate calculation of lattice constants, the tested peak values were corrected by comparison with the standard Si peak values.

2.3 Tensile tests

To investigate the effect of annealing and hot forging on the mechanical properties of the alloys, tensile tests were also carried out at room temperature. The tests were performed in accordance with Japanese Industrial Standard (JIS) H 4600. Each specimen of 8 mm diameter and 40 mm gauge length were pulled at a crosshead speed of 1 mm/min until the 0.2% proof strength was reached. The crosshead speed was then changed to 2.5 mm/min until the specimen fractured. The mean values of 0.2% proof strength ($\sigma_{0.2\%PS}$), ultimate tensile strength ($\sigma_{UTS}$), total elongation (T. E.), and reduction in area (R. A.), and the standard deviation were calculated using three tested specimens.

3. Experimental Results and Discussion

3.1 Microstructure and mechanical properties of annealed Co-Cr-Mo alloy

Figures 2(a) and 2(b) show 100× and 400× optical micrographs of the Co-Cr-Mo alloy that was annealed at 1200°C for 1 h and then air-cooled. For a comparison, micrographs of the Co-Cr-Mo alloy maintained at 1100°C for 1 h and hot-forged up to a 57% reduction in area are shown in
Figs. 2(c) and 2(d). Many precipitates were observed at the grain boundary of the annealed Co-Cr-Mo alloy. This might be caused by the relatively high carbon content. The optical microstructure of the hot-forged Co-Cr-Mo alloy showed a much finer structure than the annealed Co-Cr-Mo alloy. Figures 3 and 4 show TEM images of the annealed Co-Cr-Mo alloy. As shown in Fig. 3(b), the diffraction pattern of the twin boundary at the position indicated by the arrow in Fig. 3(a) showed an fcc structure. As clearly shown in Fig. 3(c), many inclusions precipitated along the grain boundary, while they were hardly observed in the grain. Figure 4 shows a TEM image of the inclusion that precipitated along the grain boundaries. The inclusion was confirmed to be $M_23C_6$ carbide on the basis of the diffraction pattern for this inclusion indicated by the arrow in Fig. 4(a). In the EDX pattern of the $M_23C_6$ carbide, shown in Fig. 4(c), the counts of Cr and Co were markedly high, and the Mo count was relatively high. The $M_23C_6$ carbide was considered to be mainly composed of Cr, Co and a small amount of Mo. As shown in Fig. 5, many peaks of only $M_23C_6$ carbide ($a = 1.0687 \pm 0.0002 \text{ nm}$) were seen in the X-ray diffraction pattern of the Co-Cr-Mo alloy along with the $\gamma$ (fcc, $a = 0.3590 \pm 0.0001 \text{ nm}$) phase matrix and a small amount.
of the \( \varepsilon \) (hcp, \( a = 0.2556 \pm 0.0004 \, \text{nm}, \ c = 0.4120 \pm 0.0004 \, \text{nm} \)) phase. From these results, it was evident that almost all the precipitates observed at the grain boundary in the annealed Co-Cr-Mo alloy, which showed a relatively high carbon content, were \( \text{M}_{23}\text{C}_6 \) carbide particles. In a Co-29Cr-6Mo-0.18C alloy, \( \text{M}_{23}\text{C}_6 \) precipitate has been reported.\(^3\) Also, in this Co-29Cr-6Mo-0.18C alloy, the volume fraction of the \( \gamma \) phase increases slightly with an increase in C content (0.02, 0.09, and 0.18 mass%).\(^3\)

The mechanical properties of the annealed Co-Cr-Mo alloy are shown in Table 2. The \( \sigma_{0.2\%PS} \), \( \sigma_{\text{UTS}} \), T. E., and R. A. of the annealed Co-Cr-Mo alloy were 553 ± 2 MPa, 928 ± 41 MPa, 21 ± 2%, and 15 ± 1%, respectively. These values were close to those of the annealed alloy (\( \sigma_{0.2\%PS} \geq 500 \), \( \sigma_{\text{UTS}} \geq 750 \), T. E. \( \geq 16\% \)) specified in the ISO 5832-11 standard report for implantable alloys. It was considered that further improvement of these mechanical properties could be achieved.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \sigma_{0.2%PS} ) (MPa)</th>
<th>( \sigma_{\text{UTS}} ) (MPa)</th>
<th>T. E. (%)</th>
<th>R. A. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed</td>
<td>553 ± 2</td>
<td>928 ± 41</td>
<td>21 ± 2</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>Hot-forged</td>
<td>715 ± 86</td>
<td>1109 ± 61</td>
<td>8 ± 1</td>
<td>10 ± 1</td>
</tr>
</tbody>
</table>

Table 2 Mechanical properties of Co-Cr-Mo alloys annealed at 1200°C for 1 h and 57% hot-forged at starting temperature of 1100°C.

![Fig. 6](image-url) Effects of hot forging (starting temperature of 1100°C) on 0.2% proof strength (\( \sigma_{0.2\%PS} \)), ultimate tensile strength (\( \sigma_{\text{UTS}} \)), and total elongation of Co-Cr-Mo alloy.

![Fig. 7](image-url) TEM images of Co-Cr-Mo alloy hot-forged at starting temperature of 1100°C (reduction in area: 57%). (c) Diffraction pattern of matrix indicated by arrow in (b).
could be achieved by decreasing the amount of M\(_2\)C\(_6\) carbide at the grain boundary, and distributing the M\(_2\)C\(_6\) carbide finely into the intragranular region. It has been reported that the \(\sigma_{0.2\%\text{PS}}\), \(\sigma_{UTS}\), and T. E. of a Co-29Cr-6Mo-0.18C alloy are approximately 320 and 1100 MPa, respectively.\(^3\)

The \(\sigma_{0.2\%\text{PS}}\), \(\sigma_{UTS}\), and T. E. of a Co-28.5Cr-6Mo-0.2C alloy annealed at 1220°C for 1 h have been reported as follows: 462–482 MPa, 719–854 MPa, and 13–21%, respectively.\(^4\)

Adding 0.17% N to this Co-28.5Cr-6Mo-0.2C alloy markedly increases its \(\sigma_{0.2\%\text{PS}}\) (up to approximately 1080 MPa) and \(\sigma_{UTS}\) (up to approximately 1470 MPa).\(^4\)

### 3.2 Effects of hot forging on microstructure and mechanical properties

To obtain basic data to develop a hot forging process for Co-Cr-Mo alloys, the effects of hot forging on the microstructure and mechanical properties of the Co-Cr-Mo alloy were examined. The rod specimens of the Co-Cr-Mo alloy were hot-forged up to a 57% reduction in area, starting at 1100°C. Figure 6 shows the effects of hot forging on \(\sigma_{0.2\%\text{PS}}\), \(\sigma_{UTS}\) and T. E. \(\sigma_{0.2\%\text{PS}}\) and \(\sigma_{UTS}\) increased linearly with an increase in reduction in area, whereas T. E. gradually decreased with an increase in the reduction in area. \(\sigma_{0.2\%\text{PS}}\) and \(\sigma_{UTS}\) increased up to approximately 700 and 1000 MPa at a reduction of approximately 50%, respectively, at a total elongation of approximately 12%. At a 50% reduction, \(\sigma_{0.2\%\text{PS}}\), \(\sigma_{UTS}\), and T. E. satisfied the required values for a hot-worked alloy (\(\sigma_{0.2\%\text{PS}} \geq 700\), \(\sigma_{UTS} \geq 1000\), and T. E. \(\geq 12\)) specified by the ISO 5832-11 standard. The mechanical properties of the alloy hot-forged at a starting temperature of 1100°C are shown in Table 2. The \(\sigma_{0.2\%\text{PS}}\), \(\sigma_{UTS}\), T. E., and R. A. of the 57% hot-forged alloy were 715 ± 86 MPa, 1109 ± 61 MPa, 8 ± 1%, and 10 ± 1%, respectively. Figure 7 shows TEM images of the Co-Cr-Mo alloy 57% hot-forged at a starting temperature of 1100°C. Many dislocations were seen in the grain and grain boundary. The diffraction pattern of the matrix indicated by the arrow in Fig. 7(b) was the fcc structure, as shown in Fig. 7(c). Figure 8 shows X-ray diffraction pattern of the 57% hot-forged Co-Cr-Mo alloy. High peaks of the M\(_{23}\)C\(_6\) carbide (\(a = 1.0693 \pm 0.0002\) nm) and low peaks of the M\(_6\)C carbide were observed along with the \(\gamma\) (fcc, \(a = 0.3582 \pm 0.0001\) nm) phase matrix containing a small amount of \(\varepsilon\).
(hcp, \(a = 0.2544 \pm 0.0003\) nm, \(c = 0.4113 \pm 0.0003\) nm) phase. TEM images of the \(M_6C\) carbide are shown in Fig. 9. \(M_6C\) carbide particles precipitated in the grain containing a dislocation network produced by hot forging. In the EDX pattern of the \(M_6C\) carbide, the counts of Co, Mo, and Cr were high. The Mo count in the \(M_6C\) carbide was higher than that in the \(M_{23}C_6\) carbide. As shown in Fig. 10, the \(M_6C\) carbide tended to increase in concentration in the grain of the Co-Cr-Mo alloy 50% hot-forged at a starting temperature of 1000°C. Presumably, the hardness improving factors by hot forging are, stored-strain energy, grain refining, and the inhibition of dislocation glide which was produced by carbide precipitation during hot forging. No precipitates of the intermetallic sigma (\(\sigma\)) phase, which is a brittle phase, were observed in any of the forging processes because the Cr content in this Co-Cr-Mo alloy was 28%. Lowering the ratio of (Cr + Mo) to Co can prevent the formation of this brittle phase. 4)

4. Conclusions

We examined the effects of heat treatment and hot forging on the microstructure and mechanical properties of Co-Cr-Mo alloy. In the Co-Cr-Mo alloy annealed at 1200°C for 1 h, which contained a relatively high carbon content, \(M_{23}C_6\) carbide (\(a = 1.0687\) nm) precipitated along the grain boundary in the \(\gamma\) (fcc, \(a = 0.3590\) nm) phase matrix containing a small amount of \(\varepsilon\) (hcp, \(a = 0.2556\) nm, \(c = 0.4120\) nm) phase. In the EDX pattern of the \(M_{23}C_6\) carbide, the counts of Cr and Co were markedly high, while the Mo count was relatively high. The 0.2% proof strength (\(\sigma_{0.2\%PS}\)), ultimate tensile strength (\(\sigma_{UTS}\)), total elongation (T. E.), and reduction in area (R. A.) were 553 ± 2 MPa, 928 ± 41 MPa, 21 ± 2%, and 15 ± 1%, respectively. The microstructure of the hot-forged Co-Cr-Mo alloy showed a much finer structure than that of the annealed microstructure. \(\sigma_{0.2\%PS}\) and \(\sigma_{UTS}\) increased linearly with an increase in reduction in area. On the other hand, T. E. gradually decreased with an increase in the reduction. The \(\sigma_{0.2\%PS}\), \(\sigma_{UTS}\), T. E., and R. A. of the 57% hot-forged alloy were 715 ± 86 MPa, 1109 ± 61 MPa, 8 ± 1%, and 10 ± 1%, respectively. In the hot-forged alloy, a large amount of \(M_{23}C_6\) carbide and a small amount of \(M_6C\) carbide were observed in the \(\gamma\) phase matrix containing the \(\varepsilon\) phase. The \(M_6C\) carbide precipitated in the grain containing a large number of dislocations produced by hot forging. In the EDX pattern of the \(M_6C\) carbide, the counts of Co, Mo, and Cr were high. No precipitates of \(\sigma\) phase were observed in any of the forging processes. These results suggest that excellent mechanical properties were obtained by hot forging at a starting temperature of approximately 1100°C.

REFERENCES

4) G. Berry, J. D. Bolton, J. B. Brown and S. McQuaide: Cobalt-Base
Effects of Heat Treatment and Hot Forging on Microstructure and Mechanical Properties of Co-Cr-Mo Alloy for Surgical Implants


