Effect of Heat Treatment on Microstructure and Mechanical Properties of Ni- and C-Free Co–Cr–Mo Alloys for Medical Applications

Sang-Hak Lee¹, Eiji Takahashi¹, Naoyuki Nomura² and Akihiko Chiba²

¹Center for Regional Collaboration in Research and Education, Iwate University, Morioka 020-8551, Japan
²Department of Welfare Engineering, Faculty of Engineering, Iwate University, Morioka 020-8551, Japan

The effect of pre-heat treatments, followed by a hot forging process, on the microstructure and strength of Co–Cr–Mo alloys was investigated. Four pre-heat treatments were conducted at 1170, 1200, 1230 and 1260°C for three different time conditions: 2, 6 and 15 h and then water cooled to room temperature. Tensile tests and XRD analyses were carried out on both as-cast alloy and heat-treated alloys. The volume fraction of retained γ phase increases with increasing the heat treatment temperature, suggesting that the γ → ε martensitic transformation is suppressed by a higher temperature heat treatment. Tensile strength slightly decreases with increasing the heat treatment temperature and the heat treatment time, whereas the ductility slightly increases. The σ phase completely dissolves into matrix when the alloy is heat-treated at 1260°C for longer than 6 h.

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1. Introduction

The Co–Cr–Mo alloy has been used for surgical prostheses due to its high corrosion resistance and wear resistance.¹ However, in the as-cast condition, cast defects such as microporosity and cored matrix structure significantly decrease the alloy ductility. Several solutions to this problem have been proposed to improve the ductility and strength of this alloy. The heat-treatment and the mechanical properties of hot-forged Co–Cr–Mo alloys also have been studied.² More recently, wrought Co–Cr–Ni–Mo alloy has been used as implant materials for a good match of excellent strength and workability. Nickel is generally added to a Co–Cr–Mo alloy to increase ductility and to stabilize an fcc Co matrix. However, the added nickel originates allergic reaction to people having sensitivity to metal. Thus, a Ni-free Co–Cr–Mo alloy is needed to eliminate the Ni allergic problem. By the way, carbon is known to act as carbide formation and solid-solution hardening element in the austenitic stainless steel. In addition, carbon is an austenite-forming element in the austenitic stainless steel.³ It can be thought that carbon has similar functions for Co–Cr–Mo alloy in the aspect of the physical properties.⁴ Carbides formed at the grain boundary can cause stress concentration along the grain boundary, resulting in an origin of alloy fracture. This stress concentration can induce stress corrosion cracking between the carbide and matrix. These phases cause a significant drop of both strength and ductility. Moreover, they decrease the workability at elevated temperatures. Thus, there is a need for a study about nickel and carbon-free Co–Cr–Mo alloy in great detail. In the present study, the pre-heat treatment, followed by a hot forging process, is investigated to understand the change of microstructure and mechanical properties of the Co–Cr–Mo alloy as a function of heat treatment temperature and heat treatment time.

2. Experimental

The vacuum induction melting technique was adopted to prepare the alloys employed in the present study to minimize the oxidation of the alloying elements such as Cr and Mo. The metal mold was used for casting and alloy ingot with a 5 kg in weight was cooled in the furnace. The chemical composition of the alloy was as follows: Cr 28.54, Mo 5.43, Ni 0.18, C 0.008, Si 0.08 and balance Co (all in mass%). The heat treatment was carried out in an electrical resistance tube furnace in a high purity argon atmosphere. The heat treatment consisted of four heat treatment temperatures at 1170, 1200, 1230 and 1260°C under three different time conditions: 2, 6 and 15 h, followed by water quenching. These heat treatment temperatures and times were decided by a phase diagram in consideration of fcc ↔ hcp phase transformation temperature of Co–Cr–Mo alloy. Specimens for metallography were mechanically polished and etched in a sulfuric acid. Crystal structures of alloys were analyzed using X-ray diffraction for 2θ = 40–80°. Tensile tests were performed at an initial strain rate of 5.4 × 10⁻⁴ s⁻¹ using an Instron type testing machine. The gauge size of the tensile specimens was 16 mm × 3 mm × 1.3 mm. The alloys were tested under the as-cast and heat-treated conditions.

3. Results and Discussion

3.1 Effect of heat treatment on microstructures

Figure 1 shows the microstructure of the as-cast Co–Cr–Mo alloy. The microstructure consists of cobalt-rich matrix with dendritic structure and a relatively large volume fraction of interdendritic precipitates. During the solidifying stage, some amount of the metastable γ phase retained at the room temperature when Co–Cr–Mo alloy solidified through the fcc phase field. The resultant phase of cobalt-rich matrix consists of residual γ phase and ε phase coupled with intragranular striations. The interdendritic precipitate was identified as a blocky σ phase that also exists continuously at the grain boundaries. This brittle σ phase corresponding to the higher solute content (Cr, Mo) at grain boundaries causes a stress concentration, leading to the fracture. The intragranular striations are related to martensite ε phase with a profusion of stacking faults.⁵ Cr and Mo solutes can diffuse preferentially at the stacking faults with increasing temperature.⁶
Figures 2(a) through 2(d) show the microstructural changes brought about by the heat treatment for 6 h as a function of heat treatment temperature. An alloy heat-treated at 1170°C [Fig. 2(a)] shows the presence of the \( \sigma \) phase and intragranular striations. Figure 2(b) shows the resultant microstructure after 1200°C heat treatment. Main microstructural features were similar to the alloy heat-treated at 1170°C, but the morphology of \( \sigma \) phase changed from blocky shape into globular. Significant decrease in volume fraction of the \( \sigma \) phase is exhibited in the alloy heat-treated at 1230°C [Fig. 2(c)]. Furthermore, the dendritic structure disappears. Figure 2(d) shows the microstructure of an alloy obtained by the heat treatment at 1260°C. For longer heat treatment time (6 and 15 h) at 1260°C, the eventual disappearance of the interdendritic precipitates results in a homogeneous microstructure. The \( \sigma \) phase remains in an alloy heat-treated at 1200°C for longer than 6 h and an alloy heat-treated at 1230°C for 2 h, although the heat treatment temperatures were high enough above the \( \gamma \) equilibrium temperature.

### 3.2 Effect of heat treatment on X-ray diffraction patterns

Figure 3 shows the X-ray diffraction patterns of the as-cast alloy and heat-treated alloys at 1170, 1200, 1230 and 1260°C for 6 h. Alloys exhibit three strong diffraction peaks within the range of \( 2\theta = 40–80^\circ \). The relative intensities of the measured diffraction peaks are associated with \( \gamma \) phase and \( \epsilon \) phase of Co. No significant degree of peaks exists except the \( \gamma \) and \( \epsilon \) phase of Co, suggesting that no significant amount of additional phases exist. It is noteworthy that the diffraction
pattern of the as-cast alloy and alloy heat-treated at 1170°C showed γ (111) peak overlapped with ε (0002) peak. On the other hand, the ε (1011) peak is the strongest peak in the alloy heat treated at 1200°C. This indicates that the ε phase is preferential phase at room temperature in the alloy heat treated at 1200°C. Since the ε phase is formed by the athermal martensitic transformation under the condition of water cooling from temperatures where the γ phase is stable, the γ phase ↔ ε phase equilibrium temperature for this alloy can be estimated to be approximately in the range from 1100 to 1200°C. On the contrary, the γ (200) diffraction peak becomes sharper and more intense in the alloy heat-treated at 1260°C. This indicates that the γ phase stable in the temperatures higher than 1100°C is retained at room temperature, suggesting that the athermal martensitic transformation from γ phase to ε phase is suppressed by the heat treatment at higher temperatures like 1260°C. In addition, the volume fraction of γ phase estimated after Sage–Gillaud, 8) for an alloy heat-treated at 1260°C for 6 h and for 15 h was found to be 65.8 and 76%, respectively. This suggests that the prolonged annealing at the higher temperatures also affect the stability of γ phase. As shown in Fig. 4, the intensity of γ (200) diffraction peak of the alloy heat-treated at 1200°C for 15 h significantly increases. Accordingly, the higher heat-treated temperature as well as prolonged heat-treating time can suppress the athermal martensitic transformation from γ phase to ε phase, resulting in an increase in volume fraction of the retained γ phase at room temperature. This can be associated with reduction of the driving force for the martensitic transformation because of elimination of the intrinsic stacking faults and dislocations during higher temperatures and prolonged heat-treated time. In addition, the concentration of Cr and Mo solute in the γ phase is enriched and reaches the final composition of 28.54 and 5.43 mass%, respectively, by the heat treatment because of the dissolution of the σ phase containing higher amount of Cr and Mo than the γ phase. Thus it is likely that the athermal martensitic transformation from γ to ε phase can be affected by the variation in the chemical composition of the γ phase. As a result, the stability of the γ phase can be promoted by the heat treatment. However, further study is needed to clarify the relevant mechanism of the suppression of the athermal martensitic transformation.

3.3 Effect of heat treatment on mechanical properties

Figure 5 shows yield strength (0.2% offset proof stress) of as-cast alloy and heat treated alloys. The yield strength decreases with increasing heat treatment temperature and heat treatment time. In particular, the strength of the alloy heat-treated at 1170 and 1200°C slightly decreases or does not change, whereas significant decrease in the strength is found in alloys heat-treated at 1230 and 1260°C. The mechanical properties are related to the grain size, the volume fraction of γ and ε phase, 9) the dissolution of σ phase and the density of the crystal faults such as dislocation and stacking fault. The hcp striation restricts the dislocation glide operative in fcc phase during tensile deformation. As the volume fraction of ε phase and stacking fault density increases, the dislocation glide would be restricted so that a higher strength is expected. At higher temperatures, the increased volume fraction of γ phase as well as grain growth can be related to a decrease in strength, although the dissolution of the σ phase can slightly decrease the strength. On the contrary, elongation increases with increasing heat treatment temperature and time (Fig. 6). This is due to the fact that in general, an fcc crystal structure exhibits more ductility than an hcp crystal structure. However, considering the fact that the elongations of the as-cast alloy and the heat-treated alloy are 6.8% and 2.0–8.1%, respectively, it should be noted that the grain growth by a heat treatment as well as a volume fraction of γ phases affects the alloy ductility; excessive grown grain leads to a decrease in ductility.

4. Conclusions

In this study, effect of heat treatment on the microstructure and mechanical properties of Ni- and C-free Co–Cr–Mo alloys were investigated. The obtained results are summarized as follows:

1. The interendritic σ phase dissolved into matrix when the alloy was heat-treated at 1260°C for longer than 6 h.

2. The higher heat-treated temperatures suppress the γ →

Fig. 4 Effect of heat treatment time at 1200°C on the Co–Cr–Mo alloy.

Fig. 5 Effect of heat treatment temperature on the yield strength of the Co–Cr–Mo alloy.
Martensitic transformation, resulting in an increase in volume fraction of the retained $\gamma/C_13$ phase at room temperature.

(3) The volume fraction of $\gamma/C_13$ phase in the matrix increases with increasing heat treatment temperature and time. The volume fraction of $\gamma$ phase of the alloy heat treated at 1260°C for 15 h was 76%.

(4) Yield strength decreases with increasing the heat treatment temperature and the heat treatment time.

The elongation of heat-treated alloy exists in the range of 2–8.1%.

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