Effects of Zirconium Addition on Microstructures and Mechanical Properties of Co-29Cr-6Mo Alloy

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Co-29Cr-6Mo alloys consisting of 0~1.76% Zr were prepared and heat-treated at 1210°C for 2 h or 1230°C for 3 h. Three types of precipitates were identified. With more than 0.37% Zr content, precipitates are mixtures of σ phase and (Zr, Mo)-rich phase. The σ phase dissolves into a matrix and the (Zr, Mo)-rich phases change its composition into a Zr-rich phase with heat treatment. An alloy with a solid solution containing 0.01% Zr exhibits improved mechanical properties. [doi:10.2320/matertrans.48.1084]

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1. Introduction

Co-Cr-Mo alloys are widely used as surgical implant materials due to their excellent wear resistance, corrosion resistance, and biocompatibility.¹⁻³⁾ Several methods such as heat treatment, forging, and alloying are carried out to obtain reliable mechanical properties of Co-Cr-Mo alloys.⁴⁻⁶⁾ Besides, it is not only the major solute elements like Cr and Mo which influence mechanical properties and other functional properties required for implant materials, but also minor solutes. Carbon is a representative minor element facilitating the formation of $M_{23}C_6$ carbides and stabilizing an fcc Co matrix of cast Co-Cr-Mo alloy.⁷⁾ Ni, Fe, and Zr also stabilize an fcc structure of Co.⁸⁾ In addition, Kurosu *et al.* has reported that a 0.05% (all in mass%) Zr addition to Co-Cr-Mo alloys efficiently suppresses the release of Ni ions, which causes adverse biological effects.⁹⁾ Zr is known to exhibit no toxic or carcinogenic reactions to body tissue or cells.¹⁰⁾ Garza *et al.* reported that a 0.017% Zr addition greatly improves the mechanical properties of cast Co-Cr-Mo-C alloys.¹¹⁾ In this study, we investigated the effect of Zr addition on Ni-, C-free Co-29Cr-6Mo alloys for the possibility of new hot-forged alloys. Pre-heat treated microstructure and mechanical properties before the hot-forging process are investigated to understand the change of microstructures and mechanical properties of Zr added Co-Cr-Mo alloys.

2. Experimental Procedure

Co-Cr-Mo-Zr alloys were prepared by using a vacuum induction melting furnace and a metallic mold. The analyzed chemical composition of the alloy obtained is shown in Table 1. Some amount of added Zr reacted with oxygen or trace elements in raw materials during the melting and casting process. Therefore, chemically analyzed Zr contents

Table 1 Chemical composition of the experimental alloys (mass%).

Alloy	Cr	Mo	C	Si	Ni	Zr	Co
0Zr	28.80	5.61	<0.01	0.08	0.17	—	Bal.
0.1Zr	28.72	5.67	<0.01	0.08	0.17	0.01	Bal.
0.5Zr	28.72	5.68	<0.01	0.07	0.17	0.37	Bal.
1Zr	28.77	5.62	<0.01	0.07	0.17	0.82	Bal.
2Zr	28.70	5.76	<0.01	0.08	0.16	1.76	Bal.

are smaller than the nominal composition of Zr contents. However, the experimental alloys are referred to as 0Zr, 0.1Zr, 0.5Zr, 1Zr, and 2Zr alloy according to their nominal Zr composition in this study. Experimental alloys were heat-treated at 1210°C for 2 h or at 1230°C for 3 h in a tube chamber furnace using a halogen lamp heating system under an atmosphere of high purity Ar gas. Alloys were water-quenched immediately after heat treatment to examine their high temperature structure. The microstructures of as-cast and heat-treated specimens were determined by means of an optical microscope (OM), and an electron probe micro analyzer (EPMA) equipped with wave-length dispersive X-ray spectroscopy (WDS). The area fraction of the second phase was analyzed by using an image analysis program. X-ray diffraction patterns were measured between $2\theta = 40^\circ$ and 80° using Cu $K\alpha$ radiation. Tensile tests were performed at an initial strain rate of $5.2 \times 10^{-4} \text{ s}^{-1}$ using an Instron-type testing machine. At least three specimens were tested and the results were summarized as a mean value. The gauge size of the tensile specimens was 16 mm in length, 3 mm in width and 1.3 mm in thickness. Rockwell C scale hardness measurements were made on polished surfaces of as-cast and heat-treated specimens.

3. Results and Discussion

Figures 1(a) and 1(c) show optical micrographs of as-cast 0Zr and 1Zr alloys, respectively. The microstructure of as-

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Fig. 1 Microstructures of Co-Cr-Mo alloys with a different Zr content. Co-29Cr-6Mo-0Zr (a) as-cast, (b) 1230°C, 3 h Co-29Cr-6Mo-0.82Zr (c) as-cast, (d) 1230°C, 3 h.

cast 0Zr and 1Zr specimens shows a cored matrix with interdendritic precipitates. By increasing the amount of Zr added, a dense precipitation of the second phase is observed in the interdendritic region. However, there is no obvious change in the morphology of the second phase and casting structure of the alloys with the addition of Zr. Optical microstructures of heat-treated alloys at 1230°C for 3 h are also shown in Figs. 1(b) and 1(d). It is found that dendritic structure disappears and significant grain growth occurs in the heat-treated specimens. However, the heat-treated specimens with Zr content higher than 0.37% show reduced second phase in comparison with as-cast specimens, and the second phase does not achieve complete dissolution even after heat treatment at 1230°C for 3 h. In particular, a non-negligible amount of second phase remained along the grain boundaries and intergranular regions of 1Zr and 2Zr alloys after the heat treatment. The solubility limit of Zr in Co-29Cr-6Mo alloys is responsible for the remnant of second phase. According to a ternary phase diagram of Co-Cr-Zr alloy, the solubility of Zr is very limited (at most 1%).¹²⁾ Therefore, the solubility limit of Zr in Co-29Cr-6Mo alloy is much smaller than 1%. The area fraction of a whole second phase is illustrated as a function of Zr content and heat treatment condition in Fig. 2. 0Zr and 0.1Zr alloys show almost the same area fraction of second phase with each other. With a Zr content greater than 0.37%, the area fraction of second phase increases with Zr content. Figures 3(a) to (d) shows backscattered electron images and line analyses of 0.1Zr alloys. The second phase precipitating at the interdendritic region of as-cast alloy shows higher Cr and Mo content (Figs. 3(a) and (b)). It is well known that the solute elements Cr and Mo constitute an σ phase (topological close packing

Fig. 2 Area fraction of precipitates in Co-29Cr-6Mo alloys as a function of Zr content and heat treatment condition.

phase) which exists in the interdendritic region and grain boundaries of as-cast Co-based alloys.¹³⁾ From the above observations, it is confirmed that the second phase of as-cast 0.1Zr alloy is σ phase. In the case of 0.1Zr alloy heat-treated at 1230°C for 3 h (Figs. 3(c) and (d)), the alloy shows an almost homogeneous structure with a very small amount of σ phase. Figure 4 shows backscattered electron images and line analyses of 0.5Zr alloys. From the profile of line analyses, it is found that the composition of second phase of the as-cast 0.5Zr alloy (Figs. 4(a) and (b)) is different from that of the as-cast 0.1Zr alloy. The peripheral regions of the precipitates, colored in light grey, are separated from the interior region colored in dark grey. It is found that Zr and Mo are concentrated in the peripheral region, whereas Mo and Cr are

Fig. 3 EPMA-BEI micrographs and line analyses of Co-29Cr-6Mo-0.01Zr alloys. (a), (b) as-cast (c), (d) 1230°C, 3 h.

Fig. 4 EPMA-BEI micrographs and line analyses of Co-29Cr-6Mo-0.37Zr alloys. (a), (b) as-cast (c), (d) 1230°C, 3 h.

concentrated in the interior region compared with the concentration of those elements in the matrix. These observations indicate that the interior region and the peripheral region are σ phase and (Zr, Mo)-rich phase,

respectively. The inset micrograph of Fig. 4(a), *i.e.* the magnified image indicated by a square, shows a lamella structure. Table 2 shows the results of the quantitative analysis from the inset figure of Fig. 4(a) and from Fig. 4(c).

Table 2 EPMA quantitative analysis result of Co-29Cr-6Mo-Zr alloys scanned from regions shown in Fig. 4 (mass%).

Region	Phases	Co	Cr	Mo	Zr
a	σ phase	49.12	33.81	17.05	0.02
b	Light grey phase (outer)	54.64	9.75	11.27	24.34
c	Light grey phase (inner)	56.61	9.95	10.27	23.17
d	Dark grey phase	65.30	25.28	8.70	0.72
e	Zr-rich phase	59.77	9.37	1.25	29.61
f	Co-rich matrix	65.30	28.64	5.94	0.12

The quantitative results show the lamella structure consisting of (Zr, Mo)-rich phase (pointed by arrows b and c, light grey phase) and slightly Co-rich phase (pointed by arrow d, dark grey phase). The outer and inner side of (Zr, Mo)-rich phase show no difference in chemical composition. It is found from the table that the composition of Co-rich phase is almost the same as that of the matrix, although the Cr content is slightly lower in the Co-rich phase than in the matrix. Thus it is inferred that the lamella structure is formed by a eutectic reaction between the Co matrix phase, *i.e.* γ phase, and the (Zr, Mo)-rich phase during solidification. Therefore, this lamella formation can be described as following: During solidification, since the solubility of Zr and Mo is more limited in the Co-based alloy than that of Cr, the off-eutectic composition solidifies first forming dendrite, and the (Zr, Mo)-rich phase is formed along the interdendritic region in the remaining liquid. Then, the quasi-eutectic composition of (Zr, Mo)-rich phase and Co matrix phase constitute the lamella structure. At the same time, the σ phase precipitating adjacent to the (Zr, Mo)-rich phase would grow into a major second phase.

The resultant structure of 0.5Zr alloy heat-treated at 1230°C for 3 h mainly consists of an almost homogeneous matrix and second phase particles (Figs. 4(c) and (d)). The line analysis of the second phase (d) shows that although a slight decrease in Mo content and a significant decrease in Cr content are identified in the second phase particles, the Zr content exhibits a drastic increase. This indicates that heat treatment changes the composition of the (Zr, Mo)-rich phase observed in as-cast 0.5Zr alloy into Zr-rich phase. According to quantitative analyses in Table 2, the Zr content of 0.12% is detected from the Co matrix, indicating that approximately 0.12%Zr can be soluble in the Co-29Cr-6Mo alloy. This is coincidence with the result of area fraction of second phase in Fig. 2 that the second phase increases when the Zr content is greater than 0.37%. The Mo content of the Zr-rich phase is smaller than that of the Co matrix. The Cr content of the Zr-rich phase is the lowest level among the formed phases.

The effect of Zr content and heat treatment conditions on the tensile strength is illustrated in Fig. 5. 0.1Zr alloys show higher tensile strength in the as-cast and the heat-treated conditions than other alloys. Tensile strength decreases with increasing Zr content from 0.01%. As described above, Zr content greater than 0.37% caused second-phase precipitation in the intergranular region. Chiba *et al.* reported that a small addition of Zr greatly increases tensile strength and

Fig. 5 Effect of Zr content and heat treatment condition on the tensile strength of Co-29Cr-6Mo alloys.

Fig. 6 Effect of Zr content and heat treatment condition on the total elongation of Co-29Cr-6Mo alloys.

elongation in superalloy.¹⁴⁾ A small addition of Zr effectively suppresses the segregation of harmful impurity at grain boundaries. It can be thought that Zr has a similar effect on the Co-based alloys. This is why the yield of Zr amount is much smaller than the addition in this study. However, a small content (0.01%) of Zr react with any trace elements could not be detected by EPMA-WDS analysis, and 0.01% Zr added alloy has no distinctive structural features compared to other Zr added alloys except for smaller amount of second phase. Moreover, tensile strength decreases with increasing heat-treatment temperature. Increasing the heat-treatment temperature is responsible for grain growth. Although heat treatments eliminate a certain amount of intergranular second phase, larger grain size and residual intergranular second phase decrease tensile strength. The dependence of total elongation on Zr content shows a similar tendency to that of tensile strength (Fig. 6). On the contrary, hardness increases with increasing Zr content (Fig. 7). This is due to the fact that the increased second phase contributes to improvement in hardness. Both the second phase and grain size play an important role in determining the mechanical properties of the alloys. It is generally known that the precipitation of σ phase can cause embrittlement in Co-based alloys.¹⁵⁾ It is apparent from Figs. 6 and 7 that elongation was drastically reduced and hardness increased with increasing Zr content.

Fig. 7 Effect of Zr content and heat treatment condition on the hardness of Co-29Cr-6Mo alloys.

Fig. 8 Effect of Zr content and heat treatment condition on the 0.2% proof strength of Co-29Cr-6Mo alloys.

This means that the second phases associate with Zr are also brittle in the same manner as an σ phase. These brittle second phases in as-cast alloys and the Zr-rich phase in heat-treated alloys have a detrimental effect on the mechanical properties of these alloys. The 0.2% proof strength slightly decreases with Zr content after reaching a maximum value at 0.01%Zr content (Fig. 8). However, the 1Zr alloy heat-treated at 1230°C for 3 h and 2Zr alloys are so brittle that they show immature fracture behavior.

4. Conclusion

Microstructure and mechanical properties of Zr added Co-

29Cr-6Mo biomedical implant alloys are investigated and the following results are obtained:

- (1) The soluble limit of Zr in Co-29Cr-6Mo is approximately 0.12% by water-cooling from 1230°C to room temperature. The over-added Zr formed a second phase such as (Zr, Mo)-rich phase under an as-cast condition and Zr-rich phase under a heat-treated condition.
- (2) The tensile strength and the elongation increase with Zr content, showing maximum value at 0.01%Zr. The tensile strength and the elongation of the 0.01%Zr alloy are respectively 31.6% and 51% higher than those of the 0%Zr alloy under an as-cast condition.
- (3) The over-added Zr content (more than 0.37%) exhibits a detrimental effect on the mechanical properties of the abovementioned alloys, except for hardness.

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