Microstructure and Mechanical Properties of Co-29Cr-6Mo Alloy Aged at 1023 K

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Mechanical properties of Co-29Cr-6Mo alloys consisting of ε phase and σ phase were examined at room temperature. Solution treatment at 1523 K for 7.2 ks was carried out for cast Co-29Cr-6Mo alloy, followed by various aging treatments at 1023 K for up to 21.6 ks. The area fraction of the σ phase in the aged alloys increases with the aging time at 1023 K and reaches 0.6% after aging at 1023 K for 21.6 ks. However, mechanical properties such as 0.2% proof strength, ultimate tensile strength and plastic elongation of the aged alloys do not depend on the aging time. It is found that the σ phase less than 0.6% does not cause the deterioration of mechanical properties of the aged Co-29Cr-6Mo alloy. [doi:10.2320/matertrans.MRA2007606]

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1. Introduction

Cobalt chromium molybdenum (Co-Cr-Mo) alloys have been widely used for surgical prostheses such as hip and knee joint replacement due to their high mechanical properties, corrosion resistance and wear resistance. In as-cast condition, the alloys consist of γ phase (F.C.C.) and ε phase (H.C.P.) formed by martensitic transformation from γ to ε during cooling. As far as 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.¹⁻³⁾ On the other hand, the quantity of released metal ion tends to decrease with increasing the ε phase fraction.⁴⁾ In addition, wear resistance of Co-Cr-Mo alloys consisting of the ε phase are excellent under metal-on-metal condition.⁵⁾ 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 the γ phase have been reported so far,³⁾ the stability of the ε phase has not been investigated in detail yet.

At the composition of ASTM-F75(Co-(27~30)Cr-(5~7)Mo(mass%)), only the γ phase is stable at 1473 K, although the ε phase and the σ phase coexist at 1200 K.⁶⁾ Therefore, the σ phase inevitably precipitates when the ε phase is required as the matrix at the composition. 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),⁷⁾ the σ phase precipitates in the grain boundaries during aging treatment at 1123 K in the early stage. The Fe-29Cr-4Mo aged for 3.6 ks with the σ phase fraction of only 0.1% exhibited degradation of resistance to localized corrosion and significant ductility loss of 66%. Therefore the σ phase is supposed to affect corrosion and mechanical properties of Co-Cr-Mo alloys as well.

In previous study, we have investigated corrosion behavior of a Co-29Cr-6Mo alloy consisting of the ε phase and the σ phase in saline.⁶⁾ The σ phase mainly precipitates in grain boundaries. In addition, the size is less than 1 μ m and the shape is globosity.⁶⁾ The area fraction of the σ phase increases with increasing aging time at 1023 K and reaches 0.6% after the aging time of 21.6 ks. Corrosion resistance in saline such as breakdown potential, passive current density and the quantity of released Co ion of the aged Co-29Cr-6Mo alloys does not depend on the area fraction of the σ phase. Therefore, the effect of σ phase on the mechanical properties of Co-29Cr-6Mo should be investigated.

The objective of this study is to investigate microstructure and mechanical properties of Co-29Cr-6Mo alloy after aging treatment at 1023 K for various times.

2. Experimental Procedure

2.1 Alloys

The vacuum induction melting technique was employed to prepare Co-29Cr-6Mo (mass%) alloy. The chemical composition of investigated Co-29Cr-6Mo alloy was listed in Table 1. Each specimen was cut out by using electrical discharge cutting machine (EDM). The solution heat treatment was carried out at 1523 K for 7.2 ks. In our preliminary experiments, microstructure of the Co-Cr-Mo alloys was affected by cooling rate from 1523 to 1023 K. Thus the cooling rate from 1523 to 1023 K was settled at 0.166 K/s in the present study. The aging treatments were continuously conducted at 1023 K for 0, 1.8, 3.6, 7.2, 14.4 and 21.6 ks, followed by water quenching. Hereafter, these aged specimens are designated as 0, 1.8, 3.6, 7.2, 14.4 and 21.6 ks, respectively.

Table 1 Chemical composition of investigated Co-Cr-Mo alloy.

[mass%]					[mass ppm]	
Co	Cr	Mo	Ni	C	N	O
Bal.	28.68	6.01	1.06	<0.005	40	129

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2.2 Characterization of the aged Co-29Cr-6Mo alloys

Microstructures of the aged alloys were observed with an optical microscope (OM), a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Phase identification was performed with X-ray diffractometer (XRD) using monochromated Cu K α radiation over $40^\circ \leq 2\theta \leq 55^\circ$. For OM and SEM observation and XRD detection, the surface of specimens was polished by alumina powder with a diameter of 0.3 μm 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 σ phase was analyzed by using image analysis from backscattered electron images (BEI).

The specimens for TEM observation were cut into the disc by EDM with 3 mm in diameter. The disc was carefully polished up to 100 μm in thickness. Final thinning was achieved using a jet electrolytic polisher in a solution of 10% H $_2$ SO $_4$ -90% CH $_3$ OH, operating at 273 K and 12 V.

Tensile properties of the aged Co-29Cr-6Mo alloys were examined at room temperature and the initial strain rate of $6.4 \times 10^{-4} \text{ s}^{-1}$ using an instron type testing machine. The gauge size of the tensile specimens was 13 mm in length, 3 mm in width and 1 mm in thickness.

Fig. 1 X-ray diffraction patterns of Co-29Cr-6Mo 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.

Fig. 2 Optical micrographs of Co-29Cr-6Mo 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.

Fig. 3 Backscattered electron image (BEI) of Co-29Cr-6Mo 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.

3. Results

3.1 Microstructural characterization of Co-29Cr-6Mo alloys aged at 1023 K

Figure 1 shows X-ray diffraction patterns of Co-29Cr-6Mo alloys of (a) 0 ks, (b) 1.8 ks, (c) 3.6 ks, (d) 7.2 ks, (e) 14.4 ks and (f) 21.6 ks. As seen in Fig. 1, γ and ϵ phases coexist in the aged 0 ks, 1.8 ks, 3.6 ks and 7.2 ks. Only peaks from ϵ phase are detected in the aged 14.4 ks and 21.6 ks (Fig. 1(e) and (f)).

Figure 2 shows the optical micrographs of Co-29Cr-6Mo alloys of (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 striation is observed in the 0 ks, 1.8 ks, 3.6 ks, 7.2 ks and 14.4 ks in places. These striations are formed by the martensitic transformation from γ to ϵ during water quenching. However, the striation disappears in the aged 21.6 ks. It is noted that the jagged grain boundaries are

observed in all the aged alloys.

Figure 3 shows the back scattered electron images (BEI) of Co-29Cr-6Mo alloys of (a) 0 ks, (b) 1.8 ks, (c) 3.6 ks, (d) 7.2 ks, (e) 14.4 ks and (f) 21.6 ks. Figure 4 shows the area fraction of the σ phase in the aged alloys with different aging times. As seen in Fig. 3, the particles of σ phase (ca. 1 μ m) mainly precipitate in grain boundaries in aged alloys. The area fraction of the σ phase increases with increasing aging time at 1023 K and reaches 0.6% after the aging time of 21.6 ks.

Figures 5 and 6 show the transmission electron microscope micrographs of Co-29Cr-6Mo alloys aged at 1023 K for 0 ks and 21.6 ks, respectively. Diffraction patterns taken from the squared area in Figs. 5 and 6 revealed that both matrixes around the area consist of the ϵ phase with stacking faults. The density of stacking fault in the ϵ phase decreases with increasing the aging time.

Fig. 4 Area fraction of the σ phase in the aged alloys with different aging times.

Fig. 7 Stress-strain curves of Co-29Cr-6Mo alloy aged at 1023 K for 0 ks, 1.8 ks, 3.6 ks, 7.2 ks, 14.4 ks and 21.6 ks.

Table 2 Mechanical properties of aged Co-29Cr-6Mo alloys.

	Aged alloy					
	0 ks	1.8 ks	3.6 ks	7.2 ks	14.4 ks	21.6 ks
$\sigma_{0.2\%}$	363	385	427	415	390	380
[MPa]	(21.0)	(6.1)	(23.0)	(0)	(17.7)	(11.2)
σ_{UTS}	545	561	581	625	560	607
[MPa]	(22.4)	(16.4)	(24.8)	(18.7)	(15.4)	(6.5)
ϵ_p	8.3	8.9	9.3	13.4	10.1	17.1
[%]	(1.19)	(1.26)	(1.75)	(2.58)	(2.30)	(0.11)

(standard deviation)

Fig. 5 Transmission electron microscope micrographs of Co-29Cr-6Mo alloy aged at 1023 K for 0 ks.

Fig. 6 Transmission electron microscope micrographs of Co-29Cr-6Mo alloy aged at 1023 K for 21.6 ks.

3.2 Evaluation of mechanical properties

Figure 7 shows nominal stress–nominal strain curves of aged Co-29Cr-6Mo alloys. All of the aged alloys are ruptured after showing the peak stress. Table 2 summarizes the mechanical properties of aged Co-29Cr-6Mo alloys. In aged alloys, ultimate tensile strength and 0.2% proof strength are almost the same among them. In addition, the plastic elongation tends to increase with increasing the aging time.

4. Discussion

4.1 Microstructural change of Co-29Cr-6Mo alloy during aging treatment at 1023 K

As seen in Fig. 1, it is clear that the ϵ phase increases with increasing aging time. On the other hand, the area of the striation decreases with increasing aging time (Fig. 2). This striation is formed during quenching by the martensitic transformation from the residual γ phase which has not been transformed during aging at 1023 K. The ϵ martensite usually contains a large number of stacking faults.³⁾ However, ϵ phase with low density of stacking fault is also found in the aged 0 ks (Fig. 5), which is different from the ϵ martensite. This indicates that the ϵ phase is thermally transformed from the γ phase by diffusion, even in the period of cooling from 1523 to 1023 K. In addition, the aged alloys are characterized by the jagged grain boundaries. This is quite similar to the boundaries formed by massive transformation from the austenite phase (γ) to the ferrite phase (α) in the Fe-Ni and

Fig. 8 Ultimate tensile strength (σ_{UTS}) and 0.2% proof strength ($\sigma_{0.2\%}$) of aged Co-29Cr-6Mo alloys plotted against the amount of σ phase.

Fig. 9 Plastic elongation (ϵ_p) of aged Co-29Cr-6Mo alloys plotted against the amount of σ phase.

Fe-Mn system.^{8,9)} This suggests that massive transformation occurs during cooling from 1523 to 1023 K.

K. Rajan¹⁰⁾ reported the aging behavior of Co-26.7Cr-5.5Mo-0.15C alloy at 1023 K. The transformation from the γ phase to the ϵ phase proceeds through a complex two stage during the aging treatment. During the early stage of aging at 1023 K the alloy started appearing a heavily stacking faulted ϵ phase in the twin-twin boundaries. A heavily stacking faulted ϵ phase has Shoji-Nishiyama relationship against the γ phase, indicating that a heavily stacking faulted ϵ phase is isothermal ϵ martensite (hcp_1). In contrast, during the later stage of aging at 1023 K, a low stacking faulted ϵ phase (hcp_2) was transformed from hcp_1 or fcc into hcp_2 and the abundant nucleation of carbides coincident. In addition, the pearlite-like microstructure was observed in this alloy. Rajan suggested that the precipitation of carbide may play important role on the formation of pearlite-like microstructure.

The microstructural change is not agree with our observation, since the complex two stage transformation from γ to ϵ , a different stacking faulted density in ϵ phase (hcp_1 and hcp_2) and pearlite-like microstructure were not observed in the present study. The major difference is the carbon content in the Co-Cr-Mo alloy, although the content is quite small. Thus, carbon content may affect the microstructural change during aging at 1023 K.

4.2 Effect of aging treatment at 1023 K on the mechanical properties of Co-29Cr-6Mo alloy

Figure 8 shows the ultimate tensile strength and 0.2% proof strength of the aged Co-29Cr-6Mo alloys plotted against the amount of σ phase. Ultimate tensile strength (UTS) and 0.2% proof strength of the aged alloys exhibit almost the same values regardless of different amount of the σ phase. Thus the amount of the σ phase less than 0.6% hardly affects the UTS and 0.2% proof strength in the aged Co-29Cr-6Mo alloy.

Figure 9 shows the plastic elongation of the aged Co-29Cr-6Mo alloy plotted against the amount of σ phase. The plastic elongation hardly decreases with increasing the amount of the σ phase. It was reported that Fe-29Cr-4Mo alloy with the σ phase fraction of only 0.1% decreased the elongation

Fig. 10 Changes in work-hardening rate and true stress during tensile testing in aged Co-29Cr-6Mo alloys.

significantly.⁷⁾ The significant decrease of the elongation was caused by the precipitation of the network-like σ phase at grain boundaries. In the aged Co-29Cr-6Mo alloy, although the σ phase was precipitated at grain boundaries, the shape is globular (Fig. 3). Therefore, the plastic elongation of aged Co-29Cr-6Mo alloy is not affected by a small amount of precipitated σ phase less than 0.6%.

Figure 10 shows the changes in work-hardening rate and true stress during tensile testing in Co-29Cr-6Mo alloys. The aged alloys were ruptured near the intersection of the curves, indicating that the aged alloys show inhomogeneous defor-

mation after necking in spite of the existence of σ phase.

From these results, it can be concluded that UTS, 0.2% proof strength and plastic elongation of Co-29Cr-6Mo alloy aged at 1023 K are not affected by the σ phase less than 0.6%.

5. Conclusions

The effect of aging treatment at 1023 K on microstructures and mechanical properties of Co-29Cr-6Mo alloy was investigated. The obtained results are summarized as follows:

- (1) The $\gamma \rightarrow \varepsilon$ transformation occurs during cooling from 1523 to 1023 K and is completed at 1023 K for more than 21.6 ks.
- (2) The ε phase with low stacking faults density is formed by slow cooling from 1523 to 1023 K and aging treatment at 1023 K.
- (3) The σ phase precipitates in grain boundaries during aging treatments at 1023 K. 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.
- (4) The ultimate tensile strength, 0.2% proof strength and plastic elongation of Co-29Cr-6Mo alloy aged at 1023 K shows almost the same value regardless of different amount of the σ phase in the alloy.

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REFERENCES

- 1) A. Chiba, K. Kumagai, H. Takeda and N. Nomura: *Mater. Sci. Forum* **475–479** (2005) 2317–2322.
- 2) S. H. Lee, E. Takahashi, N. Nomura and A. Chiba: *Mater. Trans.* **46** (2005) 1790–1793.
- 3) S. H. Lee, E. Takahashi, N. Nomura and A. Chiba: *Mater. Trans.* **47** (2006) 287–290.
- 4) S. Kurosu, N. Nomura, K. Yamaguchi, S. Fujinuma and A. Chiba: *Japan Inst. Metals* **69** (2005) 886–891.
- 5) A. J. S. Garcia and H. F. Lopez: *J. Biomed. Mater. Res.* **74 A** (2005) 269–274.
- 6) S. Kurosu, N. Nomura and A. Chiba: *Mater. Trans.* **47** (2006) 1961–1964.
- 7) C. J. Park, M. K. Ahn and H. S. Kwon: *Mater. Sci. Eng. A* **418** (2006) 211–217.
- 8) A. Borgenstam and M. Hillert: *Acta Mater.* **48** (2000) 2765–2775.
- 9) W. C. Cheng and C. K. Lai: *Scr. Mater.* **55** (2006) 783–786.
- 10) K. Rajan: *Metall. Trans.* **13 A** (1982) 1161–1166.