



EFFECT OF HEAT TREATMENT AND ALLOYING ELEMENTS ON PRECIPITATION AND SURFACE BEHAVIOR OF Co-Cr-Mo ALLOYS

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ABSTRACT

The microstructures of as-cast and heat-treated Co-Cr-Mo with addition of C, Si and Mn have been investigated with a focus on phase and dissolution of precipitates. The heat treatment temperatures and heating periods employed ranged from 1448 to 1548 K and 0 to 43.2 ks, respectively. The precipitates observed in the as-cast and heat-treated alloys were carbides ($M_{23}C_6$, eta-phase, and pi-phase) and an intermetallic compound of chi-phase. Chi-phase was detected in the sample with lowest carbon content of this study, 0.15 wt%. The addition of Si seemed to increase the heating time for complete precipitate dissolution because of the effects of Si on the promotion of pi-phase formation at high temperatures and the increased carbon activity in the Co matrix. After polarization test in simulated body fluid to the single phase-contained specimens, it showed that chi-phase drastically decreased the corrosion resistance of the alloy. The alloys with chi-phase and $M_{23}C_6$ precipitates have lower corrosion resistance than those with pi-phase.

Keywords: Co-Cr-Mo, precipitate, heat treatment, dissolution, corrosion behavior.

INTRODUCTION

Co-Cr-Mo [1] alloys have been used for biomedical implants for a number of years. They are now frequently used for the metal-on-metal hip resurfacing joints due to their high corrosion and wear performance [2]. The corrosion and wear-resistant properties of cast Co-Cr-Mo alloys are related to the precipitates existence in the Co matrix [3]. In Co-Cr-Mo ASTM F75 alloys, the major precipitate was $M_{23}C_6$, wherein M is metallic elements of the alloys. Other precipitates were determined as a minor precipitates, such as eta-phase and intermetallic sigma-phase [4].

Thermal treatments are used on these alloys in attempt to alter the microstructure in terms of precipitates to improve the properties of the alloy [4, 5]. Several investigations have focused on examining the behavior of precipitates during solution treatment. It is known that the addition of some elements to biomedical Co-Cr-Mo alloys affects the phases of precipitates. Lee *et al.* reported the sigma-phase formation increases with the Fe addition in Co-Cr-Mo-(5-20wt %) Fe alloys [6]. The existence of metal carbides is revealed in Co-Cr-Mo alloy with zircon and carbon [7]. Moreover, nitrogen is known to suppress the formation of sigma-phase [8]. However, the effect of precipitates on the corrosion behavior is less well understood. There is a concern that corrosion processes are the cause of in-vivo failures, leading to retrieval operations. The release of metal ions due to corrosion is thought to have adverse affects on the surrounding body tissue and ultimately leads to failure of the implant [2].

This study was carried out to investigate the formation of secondary phases in Co-Cr-Mo F75 alloys before and after heat treatment. The effect of heat treatment and alloying elements on precipitation and corrosion of alloy's surface after polarization test were investigated.

EXPERIMENTAL

Specimens

The chemical compositions of the alloys used in this study are listed in Table-1. Alloy ingots were prepared by using an induction melting furnace under Ar atmosphere and cast in a copper mold.

Table-1. Chemical composition of as-cast alloys (wt%).

Sample	Cr	Mo	C	Si	Mn	Co
C15	27.1	5.61	0.13	1.33	0.02	64.19
C25	27.7	6.1	0.26	1.14	0.04	65.81
C35	27.7	6.0	0.38	1.20	0.01	64.71

Heat treatment and analysis

The alloys were inserted into a tube furnace at 1448-1548 K under Ar atmosphere for soaking time 0 to 43.2 ks. After heating, the alloys were quenched immediately in the water. The specimens was mechanically ground with emery paper and polished with 1 μ m diamond liquid. For microstructural observations, the specimens were electrolytically etched in 10% H_2SO_4 and methanol solution at 6 V.

Corrosion test of the alloys contains single phase of theta ($M_{23}C_6$), pi and chi was conducted in Kokubo solution. A saturated calomel reference electrode, SCE and a platinum plate as counter electrode were used. The potential was standardized versus SCE. The reference electrode was located in the same cell to the specimen because the salt bridge caused the delay of responses to the rapid change in potential of the specimen. The specimen was mounted by resin and it was charged at 0.85 V (vs. SCE) for 0.12ks using a potentiostat. The microstructures of the as-cast and heat-treated alloys and



after polarization test were observed using an optical microscope and a scanning electron microscope. The precipitates formed in the as-cast and heat-treated alloys were electrolytically extracted at room temperature in 10% H_2SO_4 aqueous solution at 2 V. The phases of the extracted precipitates were identified using X-ray diffraction, and the XRD patterns were obtained using $\text{Cu K}\alpha$ radiation.

RESULTS AND DISCUSSIONS

Precipitates in as-cast alloys

The content of the precipitates in the as-cast alloys, which was calculated from the OM images of the microstructure, is shown in Figure-1. The amount of precipitates increased with the addition of alloying elements. The relative intensity of XRD patterns of the precipitates that were electrolytically extracted from the as-cast alloys are shown in Figure-2. The precipitates detected in the as-cast alloys were M_{23}C_6 carbide, eta-phase, pi-phase, and chi-phase. The eta-phase was a minor precipitate in the as-cast alloys which shown as $\text{M}_6\text{C}/\text{M}_{12}\text{C}$ carbides [9] [10]. Pi-phase was the main precipitate in the as-cast C25 alloy. In the case of the as-cast C15 alloy, the XRD pattern of the extracted precipitates revealed the presence of chi-phase. Chi-phase exhibits a body centered cubic with $\alpha\text{-Mn}$ structure [11]. The formation of the chi-phase was first reported for Fe-C system [12]. Because carbon is an interstitial atom in chi-phase [13], chi-phase is considered to be a carbon-contained compound [14]. In alloying system, it was known that the carbon content in chi-phase was very low. Intermetallic sigma-phase was not detected. The carbon content of the alloys used in this study ranged between 0.15 and 0.35 wt%. It is known that sigma-phase reacts with the carbon atoms to form M_{23}C_6 carbide and eta-phase during the solidification of Co-Cr-Mo alloys [15] [16]. The carbon content of these alloys was sufficient for the reaction between sigma-phase and carbon atoms to proceed.

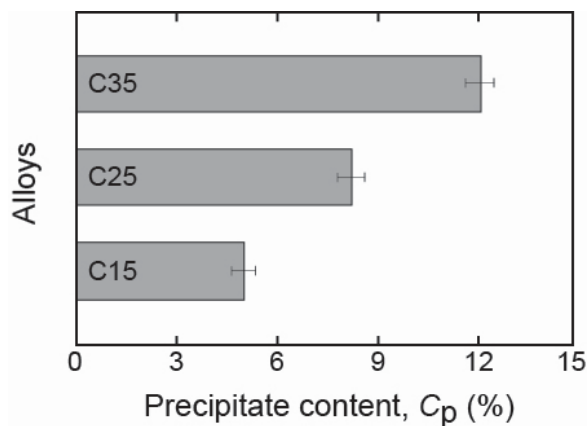


Figure-1. Content of precipitates in as-cast alloys.

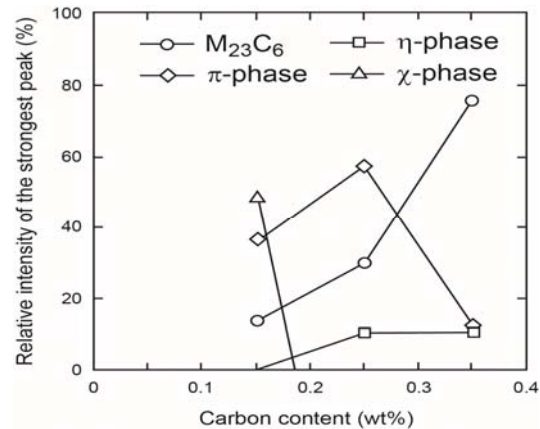


Figure-2. XRD patterns of precipitates electrolytically extracted from as-cast alloys expressed in relative intensity.

Precipitates in heat-treated alloy

The microstructures of C15 alloy after heat treatment at 1448, 1523, and 1548 K for a holding time of 1.8 and 7.2 ks are shown in Figure-3 the dissolution level of the precipitates and the morphology of precipitates formed depended on the temperature and heating time. In the C15 alloy, complete precipitate dissolution in the temperature of 1523 K was observed after 7.2 ks. Meanwhile, the precipitates in the lower and higher of this study were not completely dissolved in 7.2 ks, as shown in Figure-3 (b) and (f), respectively.

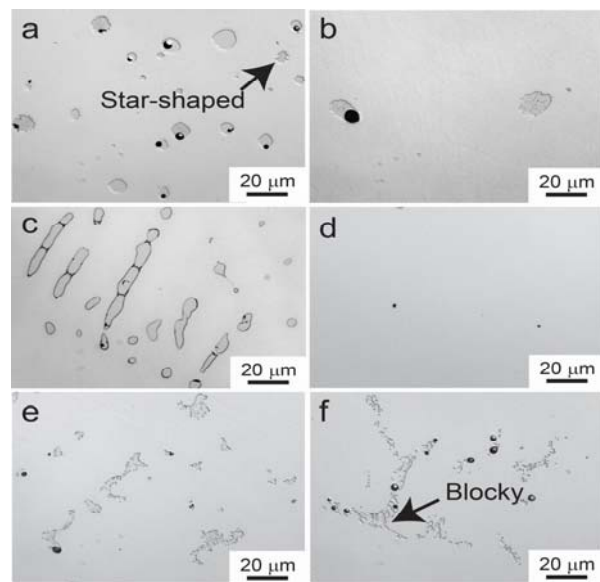


Figure-3. Microstructure of C15 alloy after heat treatment for (a, c, e) 1.8 ks and (b, d, f) 7.2 ks. Heat treatment temperatures were 1548 K (a, b), 1523 K (c, d) and 1448 K (e, f).

Figure-4 shows the phase of precipitate observed under as-cast and incomplete dissolution conditions after heat treatment. The main precipitates observed after heat



treatment at high temperatures such as 1548 K were pi-phase and $M_{23}C_6$ carbide, whereas $M_{23}C_6$ was mainly observed in all the alloys heat-treated from 1448 to 1498 K. After heat treatment, complete precipitates dissolution in C35 alloy was not achieved, even in heating temperature of 1548 K and 43.2 ks of heating time, as shown in Figure-4 (a). This was very understandable considering the as-cast C35 alloys had the highest content of precipitates because this alloys had the highest carbon content. This caused the precipitates did not have enough time to dissolved during heat treatment. Chi-phase was observed in the C15 alloy after heat treatment at 1448-1523 K for a short heating time, same as under as-cast condition. Particularly, the single phase of chi-phase was obtained at 1523 K for a heating time of 1.8 ks. However, in Co-Cr-Mo alloys, the formation of chi-phase can be found in limited heat treatment temperature and chemical composition, as shown in Figure-4 (c). Therefore, it is not very difficult to avoid the formation of chi-phase in the manufacturing process of Co-Cr-Mo alloys. At high temperatures, C15 alloy showed a longer heating time for complete precipitate dissolution, even though the carbon content of this alloy was the lowest. The difference in the precipitate phases and microstructures in the as-cast and heat-treated alloys appeared to affect the apparent dissolution rates. This might be has a correlations to the formation of pi-phase that found in the as-cast alloys.

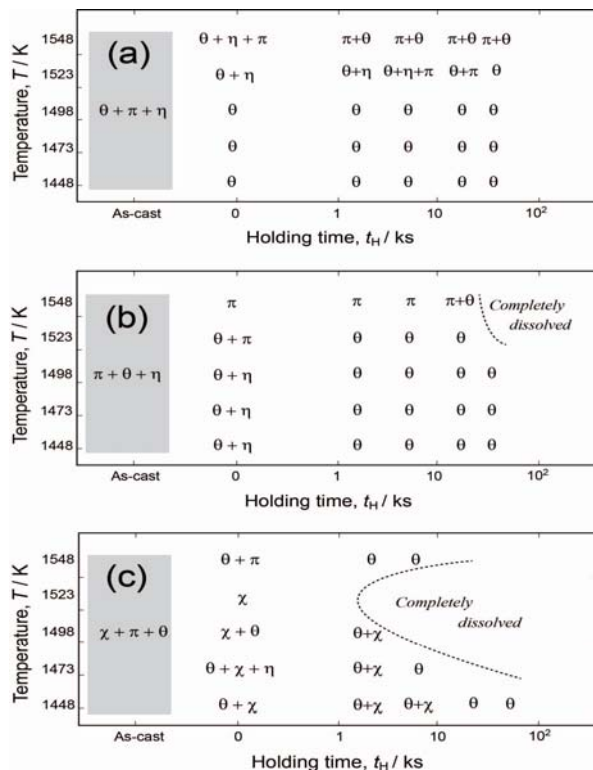


Figure-4. Phases of precipitate under as-cast heat-treated of C15, (b) C25 and (c) C35 alloy, show the formation of $M_{23}C_6$ carbide (θ), eta(η)-phase, pi(π)-phase, and chi (χ)- phase.

However, pi-phase appeared to form during the initial heat treatment at high temperatures and coexisted with the melt [16] [17], this caused an increase in the holding time for the complete precipitate dissolution of the C15 alloy at these temperatures. Moreover, it is known that the thermodynamic activity of carbon in iron-based alloys is increased by the addition of Si [18]. Although data on the carbon activity in Co-Cr-Mo alloys have not been reported previously, the increase in the carbon activity in the C35 alloy was another possible mechanism by which the dissolution rates decreased and the holding time for complete precipitate dissolution increased. In the case of the C15 alloy, the holding time for complete precipitate dissolution at 1548 K was longer than that at 1523 K. Hence, the C curve representing the boundary between the complete and incomplete dissolution conditions with a nose at 1523 K, as shown in Figure-4 (c). The C curve of the boundary has been reported for Co-Cr-Mo-C alloys [18] [19]. Partial melting in the alloys associated topi phase formation was caused by the non-uniformity of the cast microstructure around the nose temperature. This is considered to be related to the C curve. Two precipitate shapes, blocky and star-shaped, were observed as shown in Figure-3. In the alloys heat-treated over the temperature range of 1448-1498 K, the morphology of the $M_{23}C_6$ type carbide was blocky-dense. At 1548 K, the precipitate shape formed in the alloys was primarily a starlike. The starlike precipitate had two appearances: dense and stripe. This stripe-pattern consisted of $M_{23}C_6$ type carbide and metallic gamma-phase FCC [21].

Corrosion behavior of precipitates

To determine the corrosion properties of the precipitate with emphasis on changed in the surfaces of precipitate contained-specimen, polarization test has been conducted. After dipping the specimens for 0.12 ks, the surface of the specimens containing chi-phase and $M_{23}C_6$ carbide, (Figure-5 (b) and (c)), have the corrosive area which observed along the matrix. The specimen containing chi-phase exhibited low corrosion resistance. From the previous reports in stainless steel suggested that the chi-phase is considered to be a harmful precipitate in the manufacturing, as they can facilitate pitting or crevice corrosion [21]. Chi-phase was formed as a result from alloy element segregation during initial solidification and subsequent heat treatment. Since they contain large amount of Mo and Cr, they deplete the surrounding area in alloying element and reduce corrosion resistance. $M_{23}C_6$ carbide also has a responsibility on decreasing in corrosion resistance (Figure-5(c)). $M_{23}C_6$ carbide has extremely high content of Cr. These high Cr content in precipitate might causes the Cr depleted-zone surrounding the Co matrix. This matrix region might be corroded under the condition of 0.85 V in Kokubo solution. The effect of chi-phase on decreasing corrosion resistance of alloy is not fully understood yet. Chi-phase is an intermetallic compound with high in Co, Mo and Cr content. Non uniformity in chemical compositions and the morphology of precipitate were speculated to be the cause of the wide



corrosive area. The wider area for precipitation might decrease the corrosion resistance in the Co-matrix area.

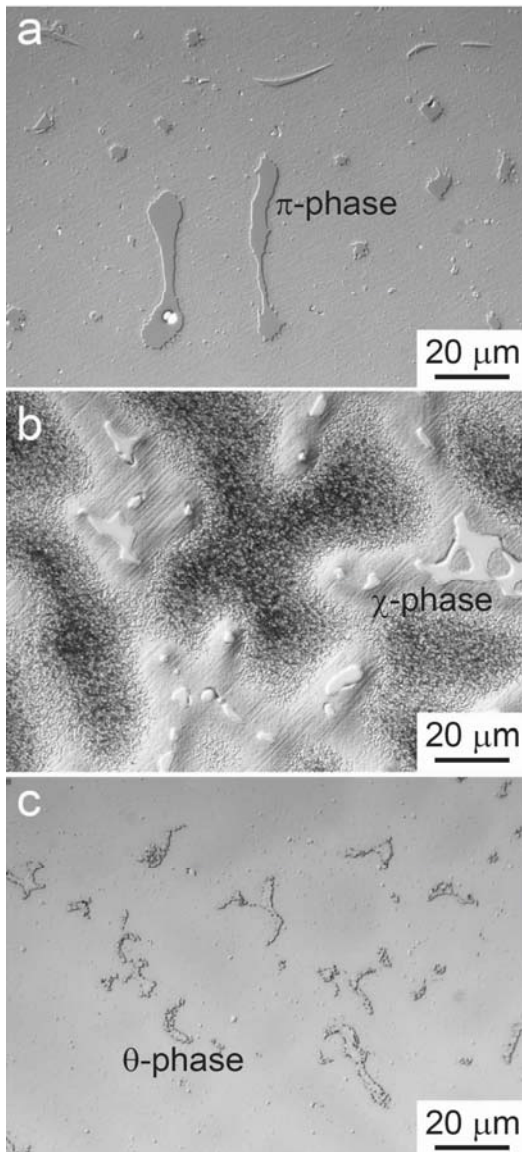


Figure-5. The surface of heat-treated alloys containing single.

- a) π (π)-phase/C25 alloy at 1548 K for 0ks,
- b) χ (χ)-phase/C15 alloy at 1523 K for 0ks
- c) $M_{23}C_6$ carbide (θ)-phase/C35 at 1448 K for 0ks after polarization test.

CONCLUSIONS

Precipitates and its corrosion behavior in biomedical ASTM F75 Co-Cr-Mo alloys with the addition of carbon were investigated. The precipitates observed in the alloys were $M_{23}C_6$ carbide, eta-phase, pi-phase, and chi-phase. During heat treatment, carbon increase the

heating time for complete precipitate dissolution. Blocky-dense $M_{23}C_6$ carbide was observed in the alloys heat-treated over the low temperature range of 1448-1498 K. At high temperatures such as 1548 K, two types of star-shaped precipitates, dense and stripe-patterned, were observed. The corrosion resistances of the alloys contained a single chi-phase and $M_{23}C_6$ carbide was inferior to those of pi-phase in simulated body fluids.

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