Characterization of intermetallic phase in as-cast Si-doped Co–Cr–Mo alloys

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Abstract. This research aims to investigate the effects of Si concentrations on the microstructure and formation of the intermetallic phase of Co–Cr–Mo–xSi alloys. The Si concentration (x) was varied between 0.1, 0.5, 1.0, 3.0 and 5.0 wt%. The microstructure and intermetallic phase of the solution heat-treated Co–Cr–Mo alloys were characterized using SEM-EDX, XRD and TEM. The microstructure analysis revealed that Si concentration played a role in the evolution of intermetallic phase precipitating in Co–Cr–Mo alloys. Two types of intermetallic phases were found in the Si-doped Co–Cr–Mo alloys. The σ phase was identified in the alloys containing Si between 0.1-1.0 wt% while the increase in Si (3.0-5.0Si) contributed to the formation of the χ phase. The calculated lattice parameters of the intermetallic phase precipitated in the 3.0Si and 5.0Si alloys correlated well with those of Co5Cr3Si2 phase.

1. Introduction

Cobalt-chromium-molybdenum (Co–Cr–Mo) alloys are extensively used in the manufacture of medical implants owing to their outstanding combination of mechanical properties and corrosion resistance as well as biocompatibility [1-4]. Such medical implants are expected to have a long lifetime and physically reliability. However, the as cast Co–Cr–Mo alloys usually contain the casting defects, for example, coarse dendritic structure, microporosity and cored matrix [5–7] which caused the early failure of medical devices. So, the deformation processes are applied to improve the mechanical properties. It has been reported that the appropriate hot rolling condition could produce an extremely high yield strength (1100-1400 MPa) with no reduction in ductility [8,9]. Furthermore, alloying element and heat treatment which are much more economical could be an effective method to enhance the mechanical properties of Co–Cr–Mo alloys.

In the Co–Cr–Mo alloys, the small amount of the σ phase, which is the common intermetallic phase, could improve the tensile strength. In addition, C is added to form the precipitate carbide, such as M23C6 and M6C which could simultaneously limit the formation of σ phase and enhance the tensile properties of Co-based alloys [10,11]. However, the carbide phases induce the surface fatigue when the alloys are used in the abrasive applications [12]. Therefore, to prevent the carbide precipitation, the carbon content in the Co-based alloys should keep below 0.1wt% [9].

Recently, Yamanaka et al. [13] suggested that the addition of Si could suppress the formation of the σ phase in Co–Cr alloys. It is well-known that the alloying elements would possibly change the precipitation behavior in Co–Cr–Mo alloys owing to the thermodynamic activity changes [14].
However, information on the effects of Si on the microstructure and precipitation behavior of Co–Cr–Mo alloys has not systematically investigated so far. Thus, the aim of present work is to investigate the microstructure and the evolution of the intermetallic phase of Si-doped Co–Cr–Mo alloys.

2. Experimental

2.1. Materials
The as-cast Si-doped Co–Cr–Mo alloys were prepared using high-frequency vacuum induction furnace in an Ar atmosphere. The Si concentrations were added in the Co–Cr–Mo alloys between 0.1, 0.5, 1.0, 3.0, and 5.0 wt%. The molten alloys were cast to be the rectangular ingots with the dimension of 20 × 30 × 150 mm³ in a steel mold. The nominal compositions of the as-cast Co–Cr–Mo–xSi alloys are tabulated in Table 1. Hereafter, the alloys are named as 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si in accordance with the concentrations of Si used in this study. Prior to analysis, the ingots were subjected to solution heat treatment at 1200°C for 24 h, followed by rapid cooling in the furnace using Ar gas.

| Alloy compositions (wt%) | Co  | Cr  | Mo  | Si  | Mn  | C   | N   |
|--------------------------|-----|-----|-----|-----|-----|-----|-----|
| Co–Cr–Mo–0.1Si           | Bal | 27.5| 6.10| 0.156| 0.614| 0.056| 0.135|
| Co–Cr–Mo–0.5Si           | Bal | 28.1| 6.15| 0.466| 0.521| 0.054| 0.148|
| Co–Cr–Mo–1.0Si           | Bal | 28.2| 6.17| 0.966| 0.593| 0.054| 0.128|
| Co–Cr–Mo–3.0Si           | Bal | 27.1| 5.89| 3.167| 0.75 | 0.067| 0.101|
| Co–Cr–Mo–5.0Si           | Bal | 27.6| 6.03| 4.445| 0.55 | 0.034| 0.111|

2.2. Microstructure and phase analysis
For the microstructure analysis, the heat-treated ingot was sliced into thin-sheet specimens using a wire electrical discharge machine (EDM). The specimens were ground off by abrasive paper and polished with 1-µm and 0.3-µm alumina suspensions (AP-D suspension, Struers). A 0.04-µm colloidal silica suspension was used for final polishing (OP-S suspension, Struers). The polished specimens were then cleaned with ethanol in an ultrasonic cleaner and air-dried. The microstructure of experimental Si-doped Co–Cr–Mo alloys was investigated using an electron backscatter diffraction (EBSD) under a field-emission scanning electron microscope (FEI, XL30S-FEG) operated at 20kV and a scanning electron microscope (SEM; S-3400N, Hitachi) coupled with an energy-dispersive spectroscopy (EDS). X-ray diffraction (XRD) patterns were acquired with a diffractometer (X’Pert MPD, PANalytical) using a Cu Kα (0.1547 nm) radiation source. The samples for transmission electron microscope (TEM) observation were prepared by mechanical polishing and ion slicer (EM-09100IS, JEOL). The detailed structure was observed on a TEM (EM-002B, Topcon) operated at 200 kV.

3. Results

3.1. EBSD and SEM analysis
Figure 1(a-c) illustrates the EBSD mapping analyses of the experimental 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys, including inverse pole figure (IPF) maps, phase maps and kernel average misorientation (KAM) maps. The EBSD analysis revealed that the experimental alloys have a coarse microstructure, consisting of large-columnar and small-equiaxed grains. The grain size varied from a few hundred micrometers to a few millimeters. The IPF maps in Fig. 1(a) show the maps with random colors indicating the variation in the crystallographic orientation of the individual grains. The EBSD phase maps (Fig. 1(b)) show that the microstructure of experimental alloys exhibited a nearly single phase of γ phase or face-centered cubic (fcc) structure. Since, the homogenizing process was carried out at 1200 °C following by rapid cooling, the γ-phase which is stable at high temperature was remained.
The KAM maps in Fig. 1(c) show the scattering of local distortion as indicated by the high different contrast of color within grains and at grain boundaries. This distortion might attribute to the remaining of local strain which would develop during the solidification and/or rapidly cooling stage [2].

![KAM Maps](image)

**Figure 1.** EBSD map of 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys (a) IPF map, (b) phase map, and (c) KAM maps.

Figure 2 shows the SEM images of the 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys and the corresponding EDS spectra acquired from the matrix and intermetallic phase. The EDS spectra of 0.1Si, 0.5Si and 1.0Si alloys revealed that the intensities of Cr and Mo in the intermetallic phase were higher than that of Co. On the other hand, the EDS spectra of 3.0Si and 5.0Si alloys showed the high concentration of Si as displayed in Fig 2(d) and (e). Quantitative EDS analysis of the intermetallic phase was summarized as tabulated in Fig. 3. The quantitative EDS analysis indicated that some Si dissolved in the intermetallic phase and the amount of Si in the intermetallic phase increased with increasing of Si in the initial compositions. Inversely, the amount of Cr and Mo are slightly dropped in the intermetallic phase. This results implied that the concentrations of Si affected on the evolution of the intermetallic phase precipitating in the Co–Cr–Mo–xSi alloys.

![SEM Images](image)

**Figure 2.** SEM images of the experimental as-cast 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys and the corresponding EDS spectra acquired from the matrix and intermetallic phase.

![Quantitative EDS](image)

**Figure 3.** Quantitative EDS analysis of the intermetallic phase precipitating in Co–Cr–Mo alloys.
3.2. XRD and TEM analysis

Figure 4 shows the XRD patterns of the experimental as-cast 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys. The XRD analysis revealed that the microstructure of alloys exhibited a dominant γ-phase, which was consistent with the EBSD phase map analysis. The weak peak of ε-phase or hcp structure was also detected in this analysis. The peak at 2θ ≈ 47.0° was identified as the σ phase. In addition, the peaks at 2θ ≈ 48.7° and 53.4° which were found in the XRD patterns of 3.0Si and 5.0Si alloys might be the σ and/or Co₃Cr₂Si₂ intermetallic phase.

Figure 5 shows the TEM bright-field images of the experimental 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys and the corresponding selected-area diffraction (SAD) patterns acquired from the intermetallic phase as indicated by an arrow in each TEM bright-field image. The SAD analyses revealed that the σ phase (space group P4₂/mnm) precipitated in the 0.1Si, 0.5Si and 1.0Si alloy. However, the SAD patterns of 3.0Si and 5.0Si alloys disclosed the formation of Co₃Cr₂Si₂ intermetallic phase and its lattice constant was calculated to be 0.8708 nm. According to the EDX, XRD and TEM analysis, the intermetallic phase precipitating in the 3.0Si and 5.0Si alloys could be confirmed to be a ternary intermetallic phase of Co₃Cr₂Si₂ (space group I43m) [15,16].

![Figure 4. XRD patterns of the experimental as-cast 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys.](image)

![Figure 5. TEM bright-field images of the experimental 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys and the corresponding selected-area diffraction (SAD) patterns taken from the intermetallic phase.](image)

4. Discussion

The intermetallic phases precipitating in Co–Cr–Mo–xSi alloys have been investigated in this study. The results revealed that an increase in Si concentrations has a significant influence on the evolution of intermetallic phase in the Co–Cr–Mo alloys. Two types of intermetallic phases, σ and Co₃Cr₂Si₂, were found in the experimental heat-treated Co–Cr–Mo–xSi alloys. Based on a study on the formation of intermetallic phase in Co-based alloys [17], a number of the intermetallic phases could possibly precipitate in the Co–Cr–Mo alloys. For instance, the σ and carbide M₃X₆ (M refers to the metallic elements and X refers to carbon C) were basically found in equilibrium with γ-fcc [18]. An increase in C promoted the formation of carbide phase and suppressed the σ phase in the Co–Cr–Mo system alloys. In addition, the precipitation of the other intermetallic phases in Co-based alloys such as η, χ, R and π phase has been found depending on the heat-treated temperature, cooling processes and alloying elements [2,17,19,20]. However, in this study, no carbide phase was observed in the experimental alloys due to the low concentrations of C added in initial compositions [20].

To clarify the impact of Si on the formation of the σ phase in Co–Cr–Mo alloys, the fraction of σ phase is plotted as a function of Si concentration using a thermodynamic calculation software, ThermocalC, as shown in Fig. 6. At 1200°C, corresponding the heat-treated temperature in this experiment, the fraction of the σ phase greatly decreases with increasing of Si concentrations and becomes near zero when the Si reaches 3.0 wt%. The reduction of the σ phase was consistent with the
XRD and TEM analysis in Fig. 4 and 5 in that the $\sigma$ phase was found in the 0.1Si, 0.5Si and 1.0Si alloys and almost disappeared when Si concentrations increased to 3.0 and 5.0 wt%. From the EDX analysis of in intermetallic phase of 0.1Si, 0.5Si and 1.0Si alloys, the amount of Co, Cr, Mo and Si was about 48 wt%, 35 wt%, 15 wt%, and 1 wt%, respectively, which closed to chemical compositions of the $\sigma$ phase, reported in the previous studies [3,21].

![Figure 6](image-url)  
**Figure 6.** Fraction of $\sigma$ phase as a function of Si concentration calculated using a thermodynamic calculation software, ThermocalC.

On the other hand, the Co$_5$Cr$_3$Si$_2$ ternary intermetallic phase formed in the alloys with Si concentrations over 1.0 wt%. However, information for the formation of the Co$_5$Cr$_3$Si$_2$ phase in the biomedical Co–Cr–Mo alloys is limited so far. Gupta [15] reported that the Co$_5$Cr$_3$Si$_2$, namely $\chi$, could be found to be in equilibrium with the $\gamma$ and $\sigma$ phase in the Co–Cr–Si system. Since the maximum solubility of Si in $\sigma$ phase was limited at 17 at% at 1175 °C, the extension of Si would lead to the formation of $\chi$ phase. In the present study, the amount of Si in the intermetallic phase of the 3.0Si and 5.0Si alloys phase was found to be 5.6 wt% (11.51 at%) and 7.8 wt% (15.37 at%), respectively. Thus, the $\chi$ phase should not be formed in the experimental 3.0Si and 5.0Si alloys because the concentrations of Si was below the maximum solubility limit in $\sigma$ phase. Narushima et al. [17] and Mineta et al. [22] similarly reported that the additions of 1.0 wt% Si significantly increase the heat-treatment temperature and time for complete precipitate dissolution of $\sigma$ phase in Co–Cr–Mo alloys. Therefore, the formation of Co$_5$Cr$_3$Si$_2$ phase in this study was possibly attributed to the insufficient heat-treated temperature and time. In contrast, Nová et al. [23] reported that the silicide (Cr$_3$Si) phase was observed in Si alloyed Co–Cr–Mo when the concentrations of Si in the initial compositions was reached 3.0 wt%. However, the lattice parameters, $a$, of Cr$_3$Si phase is 0.4564 nm (space group ($Pm\overline{3}m$)) which is different from the calculated lattice parameters of Co$_5$Cr$_3$Si$_2$ phase in this study. Thus, the intermetallic phase precipitated in the 3.0Si and 5.0Si alloys is $\chi$-phase.

5. Conclusions
In the present study, the microstructure of Co–Cr–Mo alloys with different Si contents was investigated. Alloying Si in Co–Cr–Mo alloys has no effect on the crystallographic orientations and phase presented. The two types of intermetallic compounds were found in the Si-doped Co–Cr–Mo alloys. The $\sigma$ phase was identified in the alloys containing Si between 0.1 and 1.0 wt% while the increase in Si from 3.0 to 5.0 wt% contributed to the formation of the $\chi$ phase. From the TEM analysis, a lattice parameter of the intermetallic phase precipitated in the 3.0Si and 5.0Si alloys was correlated well with those of Co$_5$Cr$_3$Si$_2$ phase.

Acknowledgements
The authors would like to thank Mr. Isamu Yoshii, Mr. Kouji Kuramoto and Mr. Kimio Wako of IMR, Tohoku University, for contributing to the alloy fabrication. A special thank you also goes to Mr. Shun Ito of IMR, Tohoku University, for valuable help in the TEM observation.
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