Effects of Si concentrations on microstructure and mechanical properties of as-cast Co–Cr–Mo alloys

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Abstract. This research investigates the effects of different Si concentrations on the microstructure and mechanical properties of Co–Cr–Mo–xSi alloys. The Si concentration (x) was 0.1, 0.5, 1.0, 3.0 and 5.0 wt%. The mechanical properties of the experimental heat-treated Co–Cr–Mo–xSi alloys was determined by hardness and tensile tests. The microstructure was analyzed using SEM. The microstructure analysis revealed that Si concentration played a role in the formation of the intermetallic phase of Co–Cr–Mo–xSi alloys. The presence of the intermetallic phase significantly decreased the ductility of the experimental alloys. However, the hardness was improved and was increased directly proportional to the fraction of the intermetallic phase precipitating in the Co–Cr–Mo–xSi alloys.

1. Introduction
Co-based alloys are extensively used as biomedical materials owing to their good biocompatibility and mechanical properties such as high tensile strength and high resistance to abrasive wear [1–3]. Recently, the Co–Cr–Mo alloys are the prospective candidate materials for replacing the currently used hot-working tool steels [4,5]. This is attributed to the excellent oxidation and corrosion resistance at high temperature [6]. Co–Cr–Mo alloys are divided into two groups, cast and wrought alloys. The cast Co–Cr–Mo alloys, referred to the ASTM F75, are the most common alloys for dentistry and artificial joints. The wrought or thermo-mechanically processed Co–Cr–Mo alloys (ASTM F799, F1537) are used as implant devices which require the superior strength [7]. The chemical compositions of Co–Cr–Mo alloys mainly consists of 27-30wt% of Cr and 5-7wt% of Mo and balance with Co. The microstructure of Co–Cr–Mo alloys possibly composed of $\gamma$-fcc and $\varepsilon$-hcp phase depending on the temperature [8]. The intermetallic phase, $\sigma$, phase is the common intermetallic compound precipitating these alloys. The Mo and Cr are added to enhance the solid solution strengthening as well as the corrosion resistance. The trace elements of N and C are also added to improve the mechanical properties of Co–Cr–Mo alloys due to the presence of fine Cr$_2$N and carbide phases. However, the fatigue and corrosion resistance would be deteriorated when the precipitates occupy at the grain boundaries of alloys.

Recently, the previous researches indicated that the addition of Si in Co–Cr alloys could stabilize the $\varepsilon$-hcp phase which is the harder phase compared to $\gamma$-fcc [9,10]. Moreover, the alloying Si suppressed the $\sigma$ phase formation and decreased the melting point of Co–Cr alloys. Besides, the oxidation resistance of Co–Cr–Mo and Co–Cr–W alloys was simultaneously improved by the small amounts of Si [6,11]. The previous studies on the oxidation behavior of Co–Cr–Mo–Si alloys have
indicated that Si effectively promoted the formation of a continuous Cr$_2$O$_3$ oxide film [6]. In addition, the internal oxidation of SiO$_2$ improved the bonding strength of Cr$_2$O$_3$ and matrix as well as the inhibition of further oxidation process [6]. The addition of Si would protect Co–Cr–Mo alloys from the oxidation or corrosion attack. In other words, the reliability of alloys is increased. However, there has been no related research on the effects of Si on the microstructure and mechanical properties of Co–Cr–Mo alloys. Therefore, the aim of the present work is to investigate the effects of Si on the microstructure and mechanical properties of Co–Cr–Mo alloys.

2. Experimental details

2.1. Materials

The as-cast Co–Cr–Mo–xSi alloys were prepared using high-frequency vacuum induction furnace in an Ar atmosphere, where x is the Si concentration 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 mm$^3$ 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 isothermally heat treatment at 1200 °C for 24 h, followed by rapid cooling in the furnace using Ar gas.

Table 1. The nominal compositions of the experimental Co–Cr–Mo–xSi alloys

| 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. Microstructural observation

In the microstructure analysis, the heat-treated ingot was sliced into round-shaped thin-sheet specimens with the dimension of 15 × 2 mm (Ø×t) 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 (OP-S suspension, Struers) was used for final polishing. The polished specimens were then cleaned with ethanol in an ultrasonic cleaner and air-dried. The microstructure of experimental Co–Cr–Mo–xSi alloys was investigated using a scanning electron microscope (SEM; S-3400N, Hitachi).

2.3. Mechanical testing

The mechanical properties of the experimental heat-treated Co–Cr–Mo–xSi alloys were characterized by hardness and tensile tests at room temperature. Vickers micro-hardness tester (HMV-2 Series, Shimadzu) with an applied load of 9.8 N and an indentation duration of 15 s was used for the hardness tests. The measurement was carried out five times for each specimen to obtain the reproducibility. The tensile tests and sample preparations were conducted according to the ISO 22674 standard: international standard for metallic materials for fixed and removable restorations and appliances. The tensile experiments were carried out using a uniaxial tensile testing machine (Autograph AGS-100kNX, Shimadzu) equipped with the extensometer system. The specimens were individually strained in triplicate until failure at a speed of 0.1 mm·min$^{-1}$ (corresponding to a nominal strain rate of approximately 1.5 × 10$^{-4}$ s$^{-1}$). The morphology of the fracture surface of the broken tensile specimens was observed using a scanning electron microscope (SEM; S-3400N, Hitachi).
3. Results and discussion

3.1. Microstructure analysis
Figure 1(a-e), respectively show back-scattered electron BSE-SEM images of the experimental 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys. The microstructure of experimental alloys shows a dendritic structure with the interdendritic intermetallic phase (bright phase), which uniformly distributed over the area. For 3.0Si and 5.0Si alloys, the interdendritic network of the intermetallic phase was clearly observed. The area fractions of the intermetallic phase precipitated in the 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys measured by the image processing software were 0.75%, 1.73%, 1.3%, 10.16% and 26.64%, respectively. The image processing analysis of intermetallic phase revealed that the elevated Si concentrations contributed to the increase in the fraction of intermetallic phase. This result is consistent to Çelik and Kaplan [12], reported in which the increasing fraction of intermetallic phases was due to the formation of various kinds of precipitates in high alloying Co-based alloys.

![Figure 1. BSE-SEM images of the experimental (a) 0.1Si, (b) 0.5Si, (c) 1.0Si, (d) 3.0Si and (e) 5.0Si alloys.](image)

3.2. Mechanical properties
Figure 2 illustrates the hardness and the standard deviation of the experimental 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys. The hardness of the experimental alloys increased with an increase in Si concentrations. The average hardness of the 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys was 287, 292, 295, 356 and 515 HV1, respectively. An increase in hardness is attributable to the presence of intermetallic phase which is naturally harder and stiffer than the surrounding matrix. However, the amount of Si below 1.0 wt% had a slight effect on the hardness evolution of Co–Cr–Mo alloys. The hardness of Co–Cr–Mo alloys was significantly elevated when the concentration of Si was greater than 1.0 wt%.

Figure 3 shows the representative stress-strain curves of the experimental alloys conducted at the room temperature. The tensile properties and hardness results along with the standard deviations of the experimental 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys were summarized in Table 2. The effects of Si on tensile properties is similar to the hardness analysis in that low content of Si in Co–Cr–Mo alloys (below 1.0 wt%) has a slight effect on the 0.2% proof stress, tensile strength and elongation of the Co–Cr–Mo alloys. The average 0.2% proof stress, tensile strength, and elongation to failure of 0.1Si, 0.5Si, and 1.0Si slightly increased. However, a high amount of Si over 3.0wt% significantly reduced tensile strength and elongation to failure of the alloys as seen in the stress-strain curves of 3.0Si and 5.0Si alloys. The stress-strain curves of 3.0Si and 5.0Si alloys show the linear elastic behavior with the extremely low elongation to failure (3.5 and 0.91%) indicating the ductility of the alloys was reduced. The diminished properties is attributed to the fraction of intermetallic phase precipitating in the Co–Cr–Mo alloys. The intermetallic phases which are brittle in nature deteriorates the ductility of alloys resulting in a significantly decrease in elongation to failure [13].
Figure 2. Hardness of the experimental 0.1Si, 0.5Si, 1.0Si, 3.0Si and 5.0Si alloys.

Table 2. Vicker hardness and tensile properties of the experimental alloys

| Alloys | 0.1Si | 0.5Si | 1.0Si | 3.0Si | 5.0Si |
|--------|-------|-------|-------|-------|-------|
| Hardness (HV1) | 287±10.3 | 292±12.0 | 295±14.0 | 356±28.0 | 515±51.0 |
| 0.2% proof stress (MPa) | 445.0±22.1 | 473.4±14.6 | 445.6±6.8 | 529.6±22.1 | N/A. |
| Tensile strength (MPa) | 778.6±23.4 | 773.7±7.4 | 796.3±9.6 | 592±65 | 194.1±26.5 |
| Elongation to failure (%) | 31.8±2.5 | 23.2±2.8 | 35.6±1.2 | 3.55±0.7 | 0.91±0.13 |

Figure 3. Stress-strain curves of the experimental alloys conducted at the room temperature.

Figure 4. Relationship between tensile strength, elongation to failure, hardness and the area fraction of intermetallic phase of Co–Cr–Mo as a function of Si concentrations.

Based on this finding, the relationship between the mechanical properties and the fraction of intermetallic phase of Co–Cr–Mo–xSi alloys could be summarized as shown in Fig. 4. The Co–Cr–Mo alloys with low Si concentrations between 0.1 and 1.0wt% pointed showed that the tensile strength, elongation to failure, hardness and the area fraction of intermetallic phase were almost constant. Inversely, alloys with high Si concentrations (3.0-5.0wt%), exhibited the extremely low ductility due
to the brittleness of the intermetallic phase. Thus, to suppress the formation of large intermetallic phase, the Si concentration in Co–Cr–Mo alloys should be of between 0.1 and 1.0wt%.

The fracture surface of tensile specimens induced by the tensile test was investigated as shown in Fig. 5. An intergranular quasi-cleavage fracture was observed in all alloys. For the alloys with low Si concentrations, crack initiation was possibly induced by the isolated particles of the intermetallic phase as indicated by the white arrow in Fig. 5(g-i). On the other hand, for 3.0Si and 5.0Si alloys, flat fracture surface together with the intergranular quasi-cleavage fracture was observed. The flat fracture observed in the 3.0 and 5.0Si alloys probably induced by the network of intermetallic phase as discussed in the microstructure analysis.

Figure 5. Fracture surface of tensile specimens (a) 0.1Si, (b) 0.5Si, (c) 1.0Si, (d) 3.0Si and (e) 5.0Si alloys and corresponding high magnification images (g) 0.1Si, (h) 0.5Si, (i) 1.0Si, (j) 3.0Si and (k) 5.0Si.

4. Conclusions
This research investigated the effects of different Si concentrations (0.1, 0.5, 1.0, 3.0 and 5.0wt%) on the microstructure and mechanical properties of Co–Cr–Mo–xSi alloys. The microstructure analysis revealed that Si concentration played a role in the formation of the intermetallic phase of Co–Cr–Mo–xSi alloys. The increasing of Si concentrations promoted the formation of the larger fraction of the intermetallic phase in Co–Cr–Mo–xSi alloys. The presence of the intermetallic phase significantly decreased the ductility of the experimental alloys. However, the hardness was elevated and was increased proportionally to the fraction of the intermetallic phase. To limit the formation of intermetallic phase, thus, the Si concentrations in Co–Cr–Mo alloys should be of between 0.1 and 1.0wt%.

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