

Effect of Si on Microstructure and Corrosion Behavior of CoCrMo Alloys

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Abstract: The aim of this research was to investigate the effect of silicon (Si) on the microstructure and corrosion behavior of CoCrMo alloys. The concentration of Si added in CoCrMo alloys was 0.1, 0.5 and 1 wt %. The corrosion behavior of the present alloys was investigated using potentiodynamic polarization measurements. The normal saline solution with 0.9 wt % was used as an electrolyte. Polarization curves obtained from the polarization test were used to evaluate in terms of corrosion current density (i_{corr}), corrosion potential (E_{corr}) and corrosion parameters that be used to compute corrosion resistant property of CoCrMo alloys. The microstructure of a sample during the polarization test was compared using X-ray diffraction (XRD) and optical microscope (OM). The results indicated that the increase in Si slightly changed the microstructure of CoCrMo alloys and could enhance the resistance to corrosion of CoCrMo alloys in NaCl solution. In addition, the reduction of Cr and Mo concentration in CoCrMo alloys was found to be a significant influence on the decrease in corrosion resistance.

1. Introduction

The CoCrMo alloys are widely used in implants owing to their excellent mechanical properties, good biocompatibility and high corrosion resistance [1–3]. In addition, they are recommended for use in metal-on-metal joint replacement applications because of their high wear resistance and hardness [4,5]. However, CoCrMo alloys which expose to the environment is undergone an oxidation as well as other metallic biomaterials. As well-known, the oxidation is one of the corrosion degradation mode in which the oxide films are formed at the interface of the alloy and environment. In the oxidation process, although, spontaneous passive film forms, the loss of metals are simultaneously taken place. In general, it is accepted that the good corrosion resistance of CoCrMo alloys is attributed to the high concentration of Cr which is play an important role on the formation of an inert Cr_2O_3 film [6]. In contrast, Cr and Mo were reported to be a cause of the formation of intermetallic phase, named σ phase, which decreased the corrosion properties of these alloys [7]. Therefore, the concentration of Cr and Mo should be controlled to obtain the high performance of alloys. Si is widely used as an alloying element to enhance the corrosion resistance of steels and alloys in various conditions. In addition Si adding to CoCrW could retard the precipitation of the brittle σ phase [8]. However, no research related to the effect of Si on corrosion resistance of CoCrMo alloys has been carried out. Thus, in this study, three kinds of CoCrMo alloys with different Si concentrations (0.1, 0.5 and 1.0 wt %) are investigated



the corrosion behavior in NaCl solution. For comparison, an alloy with reduced Cr and Mo is also performed the corrosion test in the same condition with the above-mentioned three alloys.

2. Materials and methods

Three kinds of Cobalt-Chromium-Molybdenum (CoCrMo) alloys with 0.1, 0.5 and 1 wt% Si and another alloy which has the lower Cr and Mo concentration were chosen for this study. Table 1 shows the chemical compositions of studied alloys. The all investigated alloys were cast using vacuum melting. In order to obtain the homogeneous structure, as-cast alloys were solution treated at 1250 °C for 24 hours followed by the thermo-mechanical process by hot forging at 1200 °C. Subsequently, alloys were rapidly quenched to room temperature in water. The disk samples were cut using wire electrical discharge machining (wire-EDM). The surface of sample was ground by silicon emery paper, polished with 1 and 0.3 μm alumina powder (AP-A suspension, Struers). Mirror-like surface was cleaned in alcohol ultrasonic cleaner for 10 minutes. Prior to corrosion tests, the phases identification of alloys used X-ray diffraction (XRD) analysis (Shimadzu labx xrd-6100) equipped with X-ray diffractometer (Cu K α radiation source). The microstructure of the alloy was characterized by optical microscope (OM; ZEISS Axio lab).

Table 1. The chemical compositions of investigated CoCrMo alloys

Alloy composition (wt %)	Co	Cr	Mo	Si	Mn	C	N
Co-28Cr-6Mo-0.1Si	Bal.	27.5	6.1	0.156	0.614	0.056	0.135
Co-28Cr-6Mo-0.5Si	Bal.	28.1	6.15	0.466	0.521	0.054	0.148
Co-28Cr-6Mo-1.0Si	Bal.	28.2	6.17	0.966	0.593	0.054	0.128
Co-26Cr-5Mo-1.0Si	Bal.	26.5	5.5	1.0	0.75	0.065	0.100

The potentiodynamic polarization measurement was performed in three electrode systems including the working electrode (sample), Pt counter electrode and activated carbon reference electrode. The applied potentials ranging from -0.8 V to 0.4 V (SCE) were generated using a Potentiostat/Galvanostat PGSTAT 302N (Autolab, EcoChemie, Netherlands). The polarization experiments were performed with a scan rate of 1 mV/s in 0.9 wt % NaCl solution. The polarization test of each alloy was repeated at least three times to confirm the repeatability of experimental results. The corrosion rate was calculated using the parameters obtained by Nova 1.11 software (Electrochemistry software; Metrohm Autolab).

3. Results and Discussion

3.1. Phase identification and microstructure

The phase diagram of Co-29Cr-6Mo-(0-2wt%)Si was predicted by the Thermo-Calc V5.0 as shown in Fig. 1(a). Two types of crystal structures: face-centered cubic (γ -phase) and hexagonal close-packed (ϵ -phase) were displayed depend on the temperature. In addition, two intermetallic phases were shown in the calculated phase diagram; σ and μ . The results of the XRD analysis in Fig. 1(b), revealed that the microstructure of alloys was dominantly composed of a nearly single γ -phase. No peak related to the intermetallic phase was observed. This attributes to the homogenized temperature and cooling process which are favorable for the presence of a single γ -phase. In previous study, Li et al. has demonstrated that the dominant presence of the γ -phase provided a higher resistance to corrosion than that of ϵ -phase [9].

Figure 2 shows the initial microstructure of the investigated CoCrMo alloys, observed using the optical microscope. Equiaxed grains along with the small fraction of twin boundaries which is typical microstructure after deformation processes were observed for all alloys. Moreover, finer grains were observed when the concentration of Si in the CoCrMo alloys was increased. The finest grain size was obtained in the Co-26Cr-5Mo-1.0Si alloys. Some defects in the form of microspores which possibly remained from the casting process were detected in all alloys. The corrosion behavior of CoCrMo alloys with different grain size has been reported by Li et al [9] in that increasing of the quantity of

grain boundaries would accelerated the anodic reaction resulting in the earlier occurrence of corrosion processes. To gain more details on the effects of different grain sizes causing by the Si addition, the corrosion behavior was performed and discussed in a next paragraph.

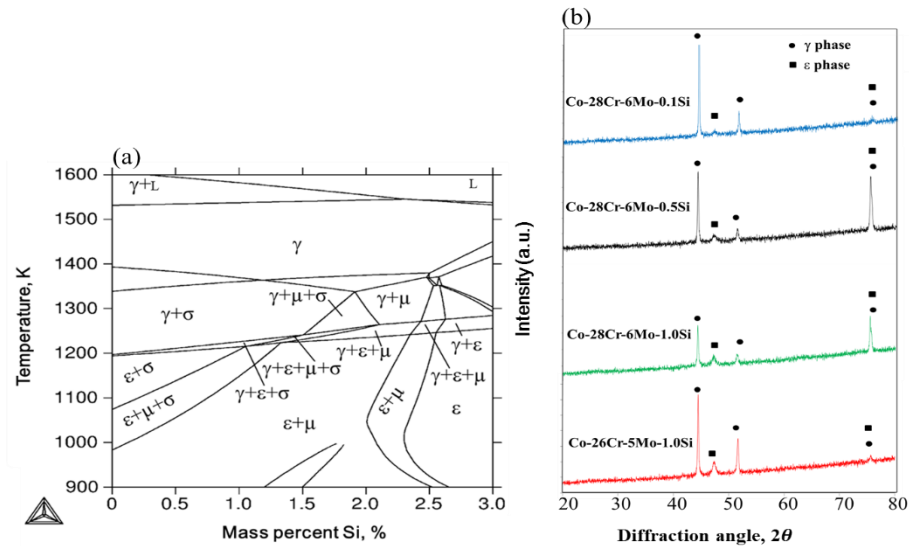


Figure 1. (a) Phase diagram of Co-29Cr-6Mo- x Si predicted by Thermo-Calc V5.0 and (b) XRD pattern of Co-Cr-Mo alloys with different Si contents.

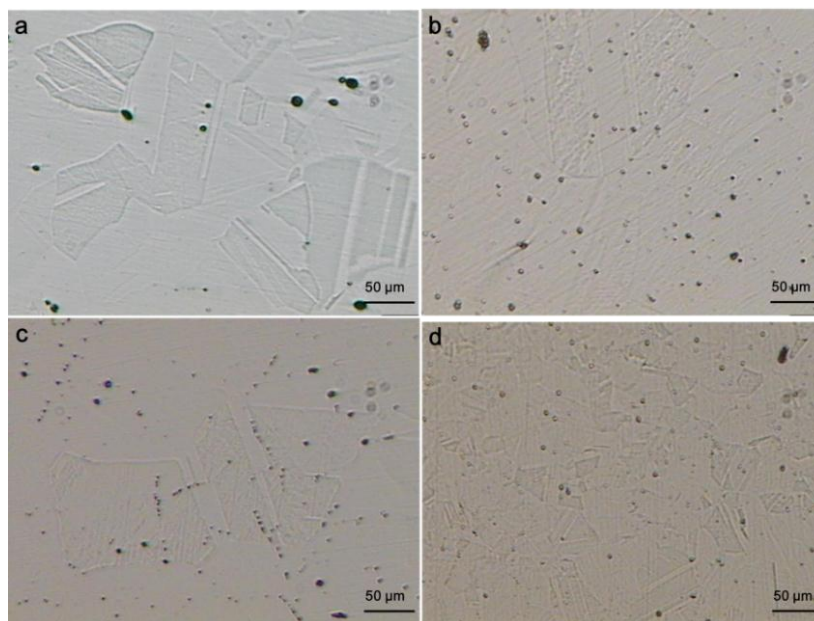


Figure 2. Optical micrograph of the investigated CoCrMo alloys: (a) Co-28Cr-6Mo-0.1Si, (b) Co-28Cr-6Mo-0.5Si, (c) Co-28Cr-6Mo-1.0Si and (d) Co-26Cr-5Mo-1.0Si.

3.2. Polarization testing

Figure 3 shows the polarization curves of Co-28Cr-6Mo-0.1Si, Co-28Cr-6Mo-0.5Si, Co-28Cr-6Mo-1.0Si and Co-26Cr-5Mo-1.0Si alloys in 0.9 wt % NaCl solution at room temperature. The shape of the curves exhibited a similar characteristic. The transition from cathodic to anodic regions of four alloys, generally referring to the open circuit potential (E_{ocp}), is located around the applied potentials ranging from -0.4 to -0.35 V (SCE). Among three alloys which have a similar Cr and Mo concentration, the

E_{ocp} of Co-28Cr-6Mo-1.0Si alloys was higher than that of Co-28Cr-6Mo-0.1Si and Co-28Cr-6Mo-0.5Si.

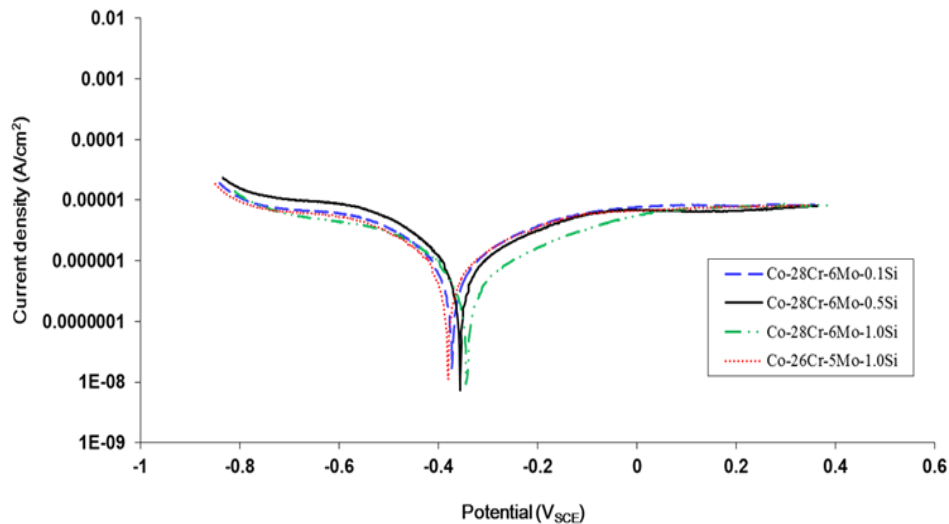


Figure 3. The polarization curves of CoCrMo with different Si alloys in 9 wt % NaCl solution.

This result indicates that the concentration of Si directly contributes to the enhancement of corrosion resistance although the higher concentration of Si reduce grain size of CoCrMo alloys. For the alloy with lower Cr and Mo concentration, the E_{ocp} was observed to be the most negative value, as seen in the polarization curve of Co-26Cr-5Mo-1.0Si in Fig. 3. This implies that reduced Cr and Mo leads to the decrease of corrosion resistance of alloys. This finding provides the interesting evidence on the influence of alloying elements on the corrosion resistance of CoCrMo alloys. Not only Cr/Mo but also Si plays a key factor in determining the corrosion behavior of investigated alloy series.

It has been reported that the high corrosion resistance of CoCrMo alloys is due to the formation of protective passive Cr_2O_3 -rich film although Co is a primary constitutional element [10]. Mo also significantly enhances the localized corrosion resistance [11]. In addition, Si promoted the formation of a compact and single Cr_2O_3 passive film [12]. Thus, the alloys with higher Si concentration would have a higher ability to resist the corrosion from surrounding environment.

Table 2. Corrosion parameter of CoCrMo with different Si alloys in 9 wt % NaCl solution.

Alloy	Parameter				
	b_a (mV/dec)	b_c (mV/dec)	E_{corr} (mV vs SCE)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate (mm/year)
Co-28Cr-6Mo-0.1Si	0.5552	0.2551	-385.17	1.68	0.0195
Co-28Cr-6Mo-0.5Si	0.2060	0.2833	-332.47	0.65	0.0075
Co-28Cr-6Mo-1.0Si	0.2840	0.2626	-353.90	0.82	0.0095
Co-26Cr-5Mo-1.0Si	0.6544	0.3504	-386.05	1.51	0.0175

The parameters from the polarization curve are summarized in the Table 2. The corrosion rate in the unit of mm per year was calculated. It is clear that the corrosion rate is reduced from 0.0195 to 0.0095 mm/year for Co-28Cr-6Mo-0.1Si and Co-28Cr-6Mo-1.0Si, respectively while the reduced Cr and Mo alloys exhibit the highest corrosion rate. This observation is consistent with the previous observation on the corrosion property of CoCrMo alloys at high temperature application [13]. The presence of Si could slow down the reaction and dissolution of passive film in severe environment due to a positive effect from the oxide film formation. The further research about the surface characterization of these alloys is required to clarify with regarding to the significant effect of such a chemical composition of passive film.

4. Conclusions

The effect of Si on the microstructure and corrosion behavior of CoCrMo alloys was investigated. The finer microstructure of alloys was obtained by increasing of Si concentration. The corrosion behavior of CoCrMo alloys in 0.9 wt % NaCl solution exhibited a similar cathodic and anodic characteristic. The presence of Si in CoCrMo alloys could slightly enhance the corrosion resistance properties. The transition from cathodic to anodic region of low Si alloys took place much faster than that of high Si alloys. The amount of Cr and Mo also played a key role on the determination of corrosion behavior. Considering future direction of this work, corrosion behavior of these alloys should be characterized at near the human body temperature which might increase the rate of corrosion and oxidation. Furthermore, with further optimization of compositions that might provide the higher performance of corrosion resistance, Co-based alloys would become a potential materials for biomedical applications.

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