Influence Of Heat Treatment On Crystal Structure And Corrosion Properties Of Co-Cr-Mo-Al Alloy In Simulated Body Fluid Solution.

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Abstract. One of the biocompatibility properties of cobalt alloys as a biomaterial is the corrosion resistance of the alloy to the biological environments such as Simulated Body Fluid (SBF). Cobalt alloys have two dominant crystal structures the FCC and HCP structures. The Co-Cr-Mo-Al alloy were subjected to the heat treatment at a temperature of 1000 °C, with various holding time, 4, 6, and 8 hours. Observation of the crystal structure of the alloy was conducted by using x-ray diffraction and the corrosion resistance was carried out by the voltammetry method, Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) in Simulated Body Fluid (SBF) at a temperature of 37 °C. From x-ray diffraction pattern, it is known that heat treatment increases the crystallite size of the alloy and alter the lattice parameters. The variations in the holding time of heating lead increase the concentration of the Face Centre Cube (FCC) crystal structures in the alloy. Observation of Cyclic Voltammetry show that the reaction of the formation of passive layers takes place spontaneously in an SBF environment. LSV data were used to determine the changes density current of corrosion of alloy. A low corrosion rate is found in alloy that untreated heat. It can conclude that heat treatment with different holding time affect on the crystal structure and corrosion properties of Co-Cr-Mo-Al alloys in the SBF solution.

1. Introduction
Cobalt alloy is one of the metal alloys used in medical implant materials because it has good strength, toughness and corrosion resistance [1]. This alloy can be applied as a biomaterial and is used as a prosthesis device, one of the application is hip joints replacement due to low wear rates [2]. The transformation of the allotropic phase of the face-centered cubic (FCC) to close-packed hexagonal (CHP) crystal structure in the cobalt alloy occurs at 422 °C [3]. The FCC crystal structure has a ductile properties while the CPH crystal structure has a brittle properties, which is because the FCC has larger glide systems than HCP [4]. The heat treatment process of the Co-Cr-Mo alloy, also known to increase the crystal size [5]. To understand the interaction of cobalt alloys with body fluids, the in-vitro method is one method that can be used [6]. Simulated body fluid (SBF) is a model of the solution used as a simulation of the inorganic part of blood plasma because it contains ions whose composition is close to human body fluids [7]. The defense of Co-Cr-Mo alloys against corrosive environments is by forming a passive layer of Cr₂O₃ [8]. Cobalt alloy has good mechanical strength as an implant material, but the use of metal implants in the body can cause the release of metal ions [9]. In-vivo studies recognize that the presence of metal ions can cause biological responses in the body, by
causing phagocytosis and biofilm growth on the implant surface [10]. This research will study the effect of heat treatment at 1000 °C with a holding time variation of 4, 6 and 8 hours on changes in crystal structure and corrosion behaviour of Co-Cr-Mo-Al alloys in a simulated body fluid (SBF). The heat treatment process for cobalt alloys also supports an increase in the volume fraction of the FCC crystal structure [11]. Concentrations of FCC and CPH crystal structures in cobalt alloys are known to have an impact on alloy corrosion behaviour [12].

2. Experiment Methods and Material

2.1. Sample and SBF Preparation
The raw material of Co-Cr-Mo-Al was provided to fabricate samples, their composition of alloy can be seen in Table 1. Co-Cr-Mo-Al alloys are formed with the dimensions of a cube 1 cm in length and thickness.

| Sample | Co | Cr | Mo | Si | Al |
|--------|----|----|----|----|----|
| CCMA   | Base | 16 | 6  | 1  | 5  |

Heat treatment on Co-Cr-Mo-Al alloys was carried out at 1000 °C with variations of holding time for 4, 6 and 8 hours, the specification of the heat process in the alloy can be seen in Table 2. After the alloy is heat treated, the alloy is subjected to quenching using water.

| Code | Sample Specifications |
|------|-----------------------|
| H0   | Without heat treatment |
| H4   | Heat treatment with holding time 4 hour. |
| H6   | Heat treatment with holding time 6 hour |
| H8   | Heat treatment with holding time 8 hour |

All SBF composition reagents were dissolved in 1000 ml of distilled water while maintaining a temperature of 37 °C and Ph 7.4 [7].

2.2. X-Ray Diffractometer (XRD)
The information provided by XRD includes crystal structure in the form of crystalline parameters and crystalline size. Bragg's law states that the distance between the crystal planes (d) is influenced by the diffraction angle formed by the scattering of x-rays on the crystal plane. Measurement of crystal size using the Williamson-Hall method, considering the broadening of the diffraction peak is influenced by the crystal size and strain factor.

\[
\beta_r \cos \theta = \varepsilon (4 \sin \theta) + \frac{k\lambda}{D}
\]

\( \beta_r \) (peak broad due to crystal size and lattice strain), \( \beta_s \) (peak broad due to lattice strain), \( \beta_c \) (peak broad due to crystal size), \( \varepsilon \) (lattice strain / strain), \( D \) (crystal size), \( k \) (Debye-Scherrer constant of 0.9), \( \lambda \) (x-ray wavelength using Cu Kα radiation of 0.154056 nm) and \( \theta \) (Bragg angle)
2.3 Voltammetry
Corrosion test is carried out using voltammetry. The methods used as a corrosion phenomenon are cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The CV and LSV methods use electrochemical cells in the form of Ag/AgCl as reference electrodes, counter electrodes in the form of platinum and working electrodes in the form of Co-Cr-Mo-Al alloy samples (surface area of 1 cm²).

The CV method is carried out by sweeping the potential from a low potential to a high potential then returning to a low potential of. The CV method is carried out to analyze the oxidation potential and the reduction potential that occur in alloys in an SBF environment (T = temperature 37 °C). Study of oxidation and reduction reactions using the Nernst equation.

\[ \Delta E = E_a - E_c = \frac{0.059}{n} V \]  

The \( E_a \) value represents the anodic potential peak (V), the \( E_c \) peak of the cathodic potential (V), and \( n \) represents the oxidation number involved in the redox event.

3. Results and Discussion

3.1. XRD Analysis
Figure 1 from the XRD data shows the diffraction pattern of Co-Cr-Mo-Al alloys that experience heating at temperatures of 1000 °C with variations of holding time for 4, 6 and 8 hours and alloys that are untreated heat (H0). The cobalt phase in the diffraction pattern has 2 crystal structures namely FCC and CPH, while for the aluminum phase it has an FCC crystal structure. Alloys without heat treatment seen 4 diffraction peaks while in alloys with heat treatment seen 6 diffraction peaks. This shows that the heating process supports the growth of the crystal structure phase. It is known that the FCC crystal structure is in-plane (111), (020), and (022), wherein the plane two atoms occupy namely cobalt and aluminum. whereas in-plane (100) and (101) are occupied by cobalt atoms with CPH crystal structures.

In the observation of diffraction peaks, it was observed that the heat treatment of the alloy resulted in a diffraction peak shift. The diffraction peak shift affects the value of the lattice parameter. Table 3 shows the changes in the lattice parameters and the volume of cell units to the alloy which are subjected to heat treatment, this is because the heat treatment process causes strain and stress in the arrangement of atoms, accompanied by rapid cooling causing residual stress that causes the distance between planar planes to decrease.

In observing the peak diffraction intensity it is known that the intensity of the diffraction pattern shows the observed phase concentration. Table 3 shows that the heating treatment accompanied by the holding time increased the concentration of the cobalt phase and aluminum FCC crystalline structure. Then observed a decrease in the concentration of the cobalt phase CPH crystal structure.

Calculation of crystal size can be observed through the diffraction peak broadening, diffraction peak broadening can be affected by broadening the crystal size (particle broadening) and broadening due to strain (strain broadening). Based on the diffraction peak pattern of Figure 1 and by looking at equation 1 (Williamson-Hall) a graph is made between \( \beta \cos (\theta) \) to \( \sin (\theta) \) which shows a linear relationship.

In Table 3 the crystal size calculation shows that the heat treatment on the alloy can increase the size of the crystal and detention the heating time increases the crystal size but on heating time 8 hours the crystal size decreases. Calculation of crystal size by the Williamson-Hall method considers the strain factor as a diffraction peak widening factor, the strain factor shows the presence of a residual strain in the crystal. The value of the expanding strain factor can affect the broadening of the diffraction peak which causes the crystal size to decrease.
Figure 1. XRD plot of Co-Cr-Mo-Al without Heat Treatment and with Heat Treatment

Table 3. Crystallographic parameters of the H0, H4, H6 and H8

| Sample | H0        | H4        | H6        | H8        |
|--------|-----------|-----------|-----------|-----------|
|        | Lattice Parameters (Å) |          |          |          |
| Cobalt (FCC) | a= 3.611  | a= 3.573 | a= 3.572 | a= 3.572 |
|          | b= 3.611 | b= 3.573 | b= 3.572 | b= 3.572 |
|          | c= 3.611 | c= 3.573 | c= 3.572 | c= 3.572 |
| Aluminium (FCC) | a= 4.050 | a= 4.050 | a= 4.050 | a= 4.041 |
|          | b= 4.050 | b= 4.050 | b= 4.050 | b= 4.041 |
|          | c= 4.050 | c= 4.050 | c= 4.050 | c= 4.041 |
| Cobalt (HCP) | a= 2.588  | a= 2.503 | a= 2.499 | a= 2.505 |
|          | b= 2.588 | b= 2.503 | b= 2.499 | b= 2.505 |
|          | c= 4.098 | c= 4.111 | c= 4.031 | c= 4.089 |
|        | Volume (Å³) |          |          |          |
| Cobalt (FCC) | 47.092   | 45.616 | 45.613 | 45.610 |
| Aluminium (FCC) | 66.528 | 66.430 | 66.430 | 65.988 |
| Cobalt (HCP) | 23.786  | 22.318 | 21.766 | 22.220 |
| Cobalt (FCC) | 80.0%   | 90.0% | 93.0% | 96.6% |
|        | Concentration (%) |          |          |          |
| Aluminium (FCC) | 1.8% | 2.2% | 2.9% | 0.5% |
| Cobalt (HCP) | 18.1% | 7.8% | 4.1% | 2.9% |
|        | Crystallite Size (nm) |          |          |          |
|        | 18.48 | 57.75 | 63 | 49.5 |
|        | Strain (%) |          |          |          |
|        | -0.0512 | 0.0214 | 0.0341 | 0.0194 |
3.2. Voltammetry

Observation of cyclic curves is seen by two observations, namely the reduction and oxidation reaction. Figure 2 shows a cyclic polarization curve that knows the potential value in reduction and oxidation. The more negative potential indicates the formation of a passive layer on the surface of Co-Cr-Mo-Al alloys that occurs due to the interaction of Cr on the aqueous environment to form Cr$_2$O$_3$. The more positive potential indicates the greater affinity of Cr$_2$O$_3$ for electrons, showing the behavior of the dissolution of the passive Cr$_2$O$_3$ layer in the solution in the form of CrO$_4^{2-}$.

![Voltammetry Diagram](image)

**Figure 2.** Tafel Polarization A) Reduction, B) Oxidation

In the calculation of the Nernst equation (3), it is known that the reaction is irreversible when the potential difference (∆E V) is greater than 0.0196 V, observed in Table 4. This identifies that the potential of oxidation and reduction interactions of the Co-Cr-Mo-Al alloy are irreversible and occur spontaneously when the alloy is in the SBF solution.

| Sample | $E_{\text{reduction}}$ (V) | $E_{\text{oxidation}}$ (V) | Potential Deviation (V) |
|--------|-----------------|-----------------|-----------------|
| H0     | -0.028          | -0.844          | 0.816           |
| H4     | -0.001          | -0.885          | 0.884           |
| H6     | -0.002          | -0.824          | 0.822           |
| H8     | 0.024           | -0.75           | 0.774           |

Table 5 provides information related to corrosion potential ($E_{\text{corr}}$), anodic tafel constant ($\beta_a$), cathodic tafel constant ($\beta_c$), and corrosion current density ($I_{\text{corr}}$). An increase in the density of anodic currents shows that the polarization curves of anodic regions are slower when compared to cathodic, this shows a reactive oxidation reaction to the SBF environment.
Table 5. Data from the corrosion test of the H0, H4, H6 and H8 in the SBF 37 °C

| Sample | $E_{\text{corrosion}}$ (V) | $\beta_a$ (V) | $\beta_c$ (V) | $I_{\text{corrosion}}$ ($\mu$A/cm$^2$) |
|--------|-----------------|-------------|-------------|-----------------|
| H0     | -0.838          | 0.211       | 0.293       | 11.281          |
| H4     | -0.894          | 0.475       | 0.179       | 14.648          |
| H6     | -0.734          | 363.3       | 0.298       | 24.872          |
| H8     | -0.757          | 0.358       | 0.277       | 23.043          |

The analysis of the corrosion current density of the alloys that are heating with a holding time of 4, 6 and 8 hours, it can be observed that the sample without heat treatment (H0) gives a smaller corrosion current density value, and along with the increase in heating detention time, it can be noted that the rate Alloy corrosion current density shows an increase. In the relation of the Faraday equation, it is known that the value of the corrosion rate is directly proportional to the corrosion current density [13].

Analysis of the increase in corrosion rate to the variation of heating hold time can be observed from the concentration of FCC and CPH crystal structures. In the analysis of x-ray diffraction, it is known that an increase in heating time results in an increase in the concentration of the FCC crystal structure and reduces the concentration of the CPH crystal structure in the alloy. The HCP crystal structure has fewer shear systems when compared to FCC, so that plastic deformation that causes reduced wear. The highest corrosion current density is shown in alloys that have a heating holding time of 6 hours with a greater FCC crystal structure concentration than non-heating alloys.

4. Conclusion
The heat treatment accompanied by the holding time of heating is known to affect the crystal size, lattice parameters, and the corrosion rate of the alloy. The increase in heating detention time shows that the observed FCC concentrations are increasing, and the CPH concentration decreases. The lowest corrosion current density was shown in H0 alloys which did not undergo heating and had the largest CPH crystal structure with a corrosion current density of 11.281 $\mu$A/cm$^2$.

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