The Effect of Manganese and Heat treatment on Structure and Corrosion Resistance of Cobalt Chrome Molybdenum

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Abstract. The selection of implant biomaterials must be based on the compatibility of the human body so that it has significant properties that will last long without experiencing rejection during use in the body. One of the commonly used biomedical implants is Co-Cr-Mo alloy. Since these alloy should also fulfill implant requirements such as high corrosion resistance. To increase corrosion resistance, the heat treatment temperature and time (heat treatment parameters) were 65 hours at 700 °C. Characterization was performed using X-ray diffraction and Potensio dynamic. The different X-ray diffraction patterns and corrosion resistance were obtained. The results show both structure and corrosion resistance are markedly influenced by the addition of Manganese after heat treatment.

1. Introduction

For economic reasons, as well as health issues, Co-Cr-Mo alloys have attracted the attention of researchers for surgical implants. These metal implants will be implanted in the body to replace the hip joint and artificial knee joint. [1] Co-Cr-Mo alloys have high durability, high corrosion resistance, superior wear behavior, and modest biocompatibility, so they are often used for metal-to-metal hip coatings. [2] Co-Cr-Mo alloy material consists of Cobalt (Co) as the main constituent element, where this element gives elastic modulus, strength, and hardness to the alloy. Chromium (Cr) provides alloy resistance to corrosion. Molybdenum (Mo) makes the surface of the grain smoother, increasing the strength of the atom.

The problem of using Co-Cr-Mo alloys as body implants is affected by corrosion and wear resistance. [4] Co-Cr-Mo alloys are considered to have good corrosion resistance, because it has a slow oxidation rate at room temperature. However, interactions between metal materials used as implants that interact with body fluids can cause tribocorrosion. [3] Tribocorrosion is a form of degradation of materials due to the combined effects of corrosion and wear. Also, tribocorrosion increases the possibility of releasing metal ions into the body which will harm the tissues in the body and the possibility of implant failure. A new study shows that heat treatment can affect its resistance to tribocorrosion and the release of metal ions. [5]

The behavior of the material can be determined by the composition of the alloying elements and the heat treatment applied. Cobalt as an alloying element in high-temperature applications will be discussed in this paper. Through the alloy design, it will be observed the possibility that occurs if the alloy is given heat treatment. Heat treatments are used to change microstructure to improve mechanical properties. Heat treatments are also applied to release stress and to remove crystal defects,
such as dislocation. The percentage of carbon present in the alloy will affect the hardness of the material. Co-Cr-Mo alloys with a low carbon percentage can be used as implants because the material is bio-compatible.

The present paper will deal with the study of the effect of manganese, heat treatment on corrosion resistance of Co-Cr-Mo based on experimental results supported by reference theory.

2. Experimental Procedure

The raw material of Co-Cr-Mo and W were provided to fabricate samples with different weight percentages (wt%) of Mn. The material used in this experiment is Co-Cr-Mo alloys type CDS 2, type G6, type G7, and type G8. All four samples received the same treatment, such as the XRD test, heat treatment test, and corrosion test. The composition of Co-Cr-Mo alloys which is used can be seen in Table 1.

| Type of alloys | Analyse (weight percentage) |
|---------------|----------------------------|
|               | Co  | Cr  | Mo  | Mn  | Si  |
| CDS 2         | Balance | 20.3 | 6.1 | 0.85 | 1.1 |
| G6            | Balance | 20.3 | 6.1 | 3   | 1.1 |
| G7            | Balance | 20.3 | 6.1 | 5   | 1.1 |
| G8            | Balance | 20.3 | 6.1 | 7.5 | 1.1 |

Cds2 is a material that has a manganese composition of 0.85%, G6 has a manganese composition of 3%, G7 has a manganese 5%, and G8 has manganese 7.5%.

2.1. XRD

By studying the crystal structure, phase identification is achieved by comparing the data obtained with that in the reference database. X-ray powder diffraction (XRD) analysis was carried out to see the characterization of Co-Cr-Mo alloys before and after heat treatment. [6]

2.2. Corrosion Testing

Corrosion test conducted in this study, an electrochemical test using a Digi-Ivy © DY2300 series potentiometer. The electrolyte used in the corrosion test in a 3.5 % NaCl solution. To determine the corrosion rate of each alloy sample, Faraday’s first law can be applied in this experiment. Mathematically, Faraday’s first law was defined as:

$$r = \frac{\sum C M i}{n \rho} = \frac{\Sigma C M}{n \rho A}$$

where
- $M$ = atomic weight (g.mol$^{-1}$)
- $i$ = current density (A/cm$^2$)
- $n$ = number of electron involved
- $\rho$ = density (g/cm$^2$)
- $C$ = constant (0.129 in mpy; 3.27 in mm/year; 0.00327 in mm$^3$/year)

The value of I from the information above has SI unit A/cm$^2$, where the cm$^2$ means the cross-sectional area of the samples which will be tested for the corrosion resistance.

2.3. Solution Heat Treatment

The heat treatment solution was tested for all samples at 700 °C for 65 hours. The initial temperature of the heating machine is 426 °C with a rate of 40. After 65 hours of heat treatment, the materials were followed by water quenching at room temperature. This treatment was done so that the constituents or
alloying elements enter into a homogeneous solid solution. Followed by rapid cooling or quenching in the room temperature water to hold the microstructure of materials.

3. Result and Discussion

3.1. XRD analysis

![XRD plot](image1.png)

**Figure 1.** XRD’s plot of the materials of Co-Cr-Mo alloys type CDS2, G6, G7, G8.

![Peak list](image2.png)

**Figure 2.** Peak list of Co-Cr-Mo in CDS2, G6, G7, G8
XRD identification through High Score using Cobalt HT and Cobalt Eta phase. 7 main peaks that can be identified, where 2 peaks (B,f) have 2 phases, namely Cobalt HT phase and Cobalt Eta phase in the same peak. There are a total of 9 peaks identified. For CDS2 material, 7 peaks can be identified with the following angles at 40.286; 43.066; 46.200; 50.412; 60.985; 74.515; 82.669. For G6 material has 7 peaks with each angle position as follows at 39.466; 42.611; 45.232; 49.775; 60.347; 71.967; 81.577. For G7 material has 7 peaks can be identified with the following angles at 40.520; 43.214; 46.447; 50.399; 61.356; 74.648; 82.911. And for G8 material has 7 peaks with each angle position as follows at 39.157; 42.805; 44.890; 49.580; 59.665; 71.555; 80.675.

Table 2. Crystallographic parameters of the materials of Co-Cr-Mo alloys type CDS2, G6, G7, G8

| Sample     | CDS 2 | G6    | G7    | G8    |
|------------|-------|-------|-------|-------|
| First peak’s Height (cps) |       |       |       |       |
| Cobalt HT  | 270.67| 389.24| 147.31| 487.48|
| Cobalt Eta | 181.85| 1087.91| 148.25| 122.62|
| First peak’s d (Å) |       |       |       |       |
| Cobalt Eta | 2.2086| 2.2111| 2.2058| 2.2140|
| Cobalt HT  | a= 3.58497 / 90| b= 3.58497 / 90| c= 3.58497 / 90| a= 3.62392 / 90|
| Cobalt Eta | a= 2.55147 / 90| b= 2.55147 / 90| c= 4.09735 / 120| a= 2.61008 / 90|
| Lattice Parameter (Å) |       |       |       |       |
| Cobalt HT  | a= 3.58497 / 90| b= 3.58497 / 90| c= 3.58497 / 90| a= 3.62392 / 90|
| Cobalt Eta | a= 2.55147 / 90| b= 2.55147 / 90| c= 4.09735 / 120| a= 2.61008 / 90|
| Volume (Å³) |       |       |       |       |
| Cobalt HT  | 46.07398| 47.40752| 45.53677| 47.59233|
| Cobalt Eta | 23.10015| 24.02044| 22.62928| 24.51559|
| Density (g/cm³) |       |       |       |       |
| Cobalt HT  | 8.49   | 8.26   | 8.59   | 8.22   |
| Cobalt Eta | 8.47   | 8.15   | 8.65   | 7.98   |
| Concentration (%) |       |       |       |       |
| Cobalt HT  | 37.8   | 16.7   | 48.4   | 16.3   |
| Cobalt Eta | 62.2   | 83.3   | 51.6   | 83.7   |
| Microstrain (%) |       |       |       |       |
| Cobalt HT  | 0.00   | 0.00   | 0.00   | 0.00   |
| Cobalt Eta | 0.00   | 0.00   | 0.00   | 0.00   |
| Crystallite Size (Å) |       |       |       |       |
| Cobalt HT  | 0.00   | 0.00   | 0.00   | 0.00   |
| Cobalt Eta | 0.00   | 0.00   | 0.00   | 0.00   |

The intensity of the X-ray diffraction pattern is directly proportional to the concentration of the components that produce it. As can be seen in Figure 1 that in the Cobalt HT phase and Cobalt Eta phase have maximum intensity, so there is a change in the concentration of Cobalt HT and Cobalt Eta in the sample. Based on the crystal structure, the cobalt HT phase has a cubic shaped crystal structure with the same lattice parameters in a, b and c. The size of the crystalline volume of the cobalt HT phase changes for each of the largest samples is G8, G6, G7, and CDS2. Whereas in the Cobalt Eta phase...
has a hexagonal-shaped crystal structure with a lattice parameter \( a \) equal to \( b \), but not equal to \( c \). The size of the crystalline volume of the Cobalt Eta phase changes from the largest G6, G8, CDS2, and G6. Meanwhile, if we compare the concentration of Cobalt HT with Cobalt Eta, the largest concentration of Cobalt HT is found in type G7, type G8, type CDS2, and type G6. This explains the composition of manganese contained in the Co-Cr-Mo alloys influences the cobalt composition of cubic and hexagonal structure.

3.2. Corrosion analysis

The electrochemical behavior can be known from the analysis of the corrosion mechanism and the corrosion rate values of the material of Co-Cr-Mo alloys used. Corrosion mechanism in this experiment, where Co-Cr-Mo was analyzed using electrochemical behavior in a solution of 3.5% NaCl. Since the chloride content of the environment is an important factor to consider when looking corrosion of an alloy. Chloride ions are an aggressive species that can cause local corrosion processes (attack occurs in specific sites where there are high local dissolution rates, which lead to high rates of penetration) in the form of pitting and crevice corrosion that are the most relevant types for artificial hip joints.

Figure 3 Tafel graph is presented to express the relationship between anodic reaction and a cathodic reaction. Corrosion E is the potential at which the rate of anodic reaction is proportional to the rate of cathodic reaction. The data presented in Table 3 contains the values of E corrosion (Volt), I corrosion (Ampere), and corrosion rate (mm/year).

Table 3. Data from the corrosion test of the materials of Co-Cr-Mo alloys type CDS2, G6, G7, G8 room temperature in the 3.5 wt% NaCl solution

| Wt % NaCl | Sample | R (ohm) | \( E_{\text{corrosion}} \) (V) | \( I_{\text{corrosion}} \) (A) | Corrosion Rate (mm/year) |
|-----------|--------|---------|-----------------|-----------------|-------------------------|
| 3.5 wt%   | CDS 2  | 1.530 x 10³ | -0.649         | 1.679 x 10⁻⁴  | 3.221 x 10⁻²     |
|           | G6     | 2.733 x 10³ | -0.808         | 9.402 x 10⁻⁶  | 1.804 x 10⁻²     |
|           | G7     | 3.839 x 10²  | -0.972         | 6.692 x 10⁻⁵  | 1.284 x 10⁻¹     |
|           | G8     | 4.007 x 10³  | -0.570         | 6.412 x 10⁻⁶  | 1.230 x 10⁻²     |

The reactions that occur during the corrosion process on Co-Cr-Mo alloys on NaCl electrolytes are shown below

Anodic reaction: 
\[ \text{Co} \rightarrow \text{Co}^{2+} + 2e \quad (2) \]
\[ \text{Co} \rightarrow \text{Co}^{2+} + 2e \quad (3) \]

The formation of \( \text{Co(OH)}^+ \) is mainly responsible for the sudden increase in current due to the dissolution of the Co metal. The electrons that are produced in the oxidation reaction must be consumed in a cathodic reaction of oxygen in a solution:

Cathodic reaction: 
\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (4) \]

Main reaction: 
\[ \text{Co}^{2+} + 2\text{Cl}^- \rightarrow \text{CoCl}_2 \quad (5) \]
\[ \text{CoCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Co(OH)}_2 + 2\text{HCl} \quad (6) \]

From table 3, the corrosion rate is influenced by potential E corrosion (Volt) and I corrosion (Ampere). Table 3 shows the greatest corrosion rate if the corrosion potential of I corrosion is getting negative, the fastest corrosion rate is the material of Co-Cr-Mo alloy types G7, CDS2, G6,G8.
Corrosion delays are caused by an anodic reaction which releases electrons to the metal, so that excess electrons in the metal shift the potential of the metal in a more negative direction and cause the anodic reaction to slow down and speed up the cathodic process.

3.3. Heat Treatment analysis
Table 2 can be seen if there is a difference in the first peak’s high in the state of cubic and hexagonal structure, indicating a structural change that occurs in the material of Co-Cr-Mo alloy.

4. Conclusion
The variation of manganese in the material of Co-Cr-Mo alloy effects the value of the corrosion rate. Co-Cr-Mo alloy type G7 with a manganese content of 5% has the greatest corrosion resistance. The material of Co-Cr-Mo alloy type G7 has the largest phase of cubic and hexagonal structures. The heat treatment has a considerable effect on structural change.

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