Influence of Manganese on Structure and Corrosion Properties of Cobalt Chrome Molybdenum (Co-Cr-Mo)

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Abstract. Co-Cr-Mo alloy are usually used as implant materials in biomedical application. Corrosion resistance is one of the properties needed to fulfill the requirement. The nature of material resistance in the body (biocompatibility) is determined by the corrosion resistance of a biomaterial. Corrosion which emits metal ions in the tissue directed at the implant and activates the system in the body. Manganese (Mn) were added to this alloy to enhance corrosion resistance. Addition of Manganese (Mn) might also affect to the structure of this alloy. X-ray diffraction and Electrochemical experiment were conducted to characterized the structure and corrosion resistance of this alloy. The addition of Manganese shows significant influence on the structure and corrosion resistance on the Co-Cr-Mo alloy.

1. Introduction
The Cobalt-Chromium-Molybdenum (Co-Cr-Mo) alloy is one of the metal alloys used in medical implant materials since the industrial revolution at the 19th century. This alloy is used in medical material implants because of its superiority in biocompatibility and mechanical properties[1][2]. Due to biocompatibility of this alloy, Co-Cr-Mo alloy can be used in orthodontic and dental applications. Co-Cr-Mo have two possible crystalline structures: face centered cubic (FCC) and close packed hexagonal (CPH) [3]. Co-Cr-Mo alloy material consisting of Cobalt (Co) alloy as the main constituent element, where this element gives elastic modulus, strength, and hardness [4]. Chromium (Cr) is the second constituent element, which gives corrosion resistance. The element chromium (Cr) in this alloy will form chromium oxide (Cr2O3) as a passive layer [5]. Molybdenum is the third constituent element, this element makes the surface of the grain finer so it increases strength [6] [7]. The problem of using Cobalt-Chromium-Molybdenum alloy (Co-Cr-Mo) in the implant is affected by corrosion and wear resistance. This alloy is considered to have a slow oxidation rate at room temperature, it implies had good corrosion resistance. However, interactions between metal materials used as implants that interact with body fluids can cause tribocorrosion (a form of metal degradation) [3]. The release of metal ions adversely affects body tissues around the implant and disrupts the system in the body. In the study a study was conducted on the effects of variations of manganese (0.85wt%, 3wt%, 5wt%, 7.5wt%) on Co-Cr-Mo on microstructure and corrosion behavior. X-ray diffraction is carried out to determine the material structure of the alloy. Electrochemical behavior using 3.5% NaCl solution, used to determine the corrosion behavior of the material. The addition of manganese (Mn) in the Co-Cr-Mo alloy can affect structural changes in the alloy[8]. Changes in the structure of the alloy can affect corrosion resistance.
2. Experiment Methods and Material

2.1. Sample Preparation

The raw material of Co, Cr, Mo and Mn were provided to fabricate samples with different weight percentages (wt%) of Mn. In Table 1, their composition of alloy can be seen. 4 types of sample were studied, which are called Mn0.85, Mn3, Mn5 and Mn7.5, containing 0.85%, 3%, 5% and 7.5% manganese, respectively. Co-Cr-Mo alloy was cut into 4 cubic shaped pieces with 0.8 cm in length, width, and their thickness.

| Sample | Co | Cr | Mo | Si | Mn |
|--------|----|----|----|----|----|
| Mn0.85 | Base | 20.3 | 6.1 | 1.1 | 0.85 |
| Mn3   | Base | 20.3 | 6.1 | 1.1 | 3    |
| Mn5   | Base | 20.3 | 6.1 | 1.1 | 5    |
| Mn7.5 | Base | 20.3 | 6.1 | 1.1 | 7.5  |

2.2. Corrosion Testing

Corrosion test were performed using Digi-Ivy © DY2300 series potentiostat. The method used as a corrosion fitting phenomenon is linear sweep voltammetry (LSV). The experiments were carried out in an electrochemical cell containing Ag/AgCl as reference electrode and Co-Cr-Mo alloy samples as working electrode (0.5 cm diameter) and platinum counter electrode. Corrosion studies were carried out in 3.5% concentration of NaCl solutions. The corrosion rate of each samples had been calculated after all data were collected from potentiostat. To determine the corrosion rate of each sample, first Faraday’s law could be applied in this case [9]. Mathematically, first Faraday’s law defined as:

\[
\text{Corrosion rate of alloy}, r = \Sigma C \frac{MI}{n \rho A} = \Sigma C \frac{MI}{n \rho A}
\]

where \(C\) is corrosion rate constant (3.27 × 10^-3 mm/year was used in this research), \(M\) is atomic weight of each element in the alloy (g/mol), \(i\) is current density in Ampere/cm², \(I\) is current passed the samples (Ampere), \(A\) is area exposed to NaCl solutions and ethanol solutions (cm²), \(n\) is number of electrons involved in corrosion process, \(\rho\) is mass density of each element in the alloy (g/cm³).

3. Results and Discussion

3.1. XRD Analysis

From XRD data, cobalt Ht and cobalt Eta phases are identified. In Figure 1 (a) there are 7 main peaks that can be identified. In Figure 1 (b) it can be identified, where there are 2 peaks (B and F) which have 2 phases, namely the cobalt Ht phase and the cobalt Eta phase in the same peak and it can be observed that peaks B and F have a dominant cobalt phase with a cubic structure.

There are 9 peaks identified, for sample Mn0.85 identified 9 peaks with angular positions of 40.8629°, 43.7273°, 44.5850°, 46.7972°, 50.9094°, 61.9868°, 74.2559°, 74.7773°, 83.5773°. For sample Mn3, it has 9 peaks with angular positions of 39.9843°, 43.2681°, 43.9808°, 45.8859°, 50.3942°, 60.9432°, 72.6375°, 74.0465°, 82.2442°. For sample Mn5, it has 9 peaks with angular positions of 41.0898°, 43.7098°, 44.3933°, 46.9779°, 50.9195°, 62.0918°, 74.8908°, 74.8943°, 83.6293°. For Mn7.5, it has 9 peaks with angular positions of 41.0146°, 43.7650°, 43.9028°, 46.7979°, 50.9914°, 61.6665°, 75.0307°, 74.7726°, 82.8472°. In Figure 1, there were 2 identified phases of the first maximum intensity, namely the cobalt Ht (peak B) and cobalt Eta (peak C) phases. In Table 2, the maximum cobalt Ht phase intensity at Mn0.85 is 187,502 cps, at Mn3 the maximum intensity is 303,925 cps, for Mn5 the maximum intensity is 239,778, and 139,629 cps for Mn7.5. Cobalt Eta phase
maximum intensity at Mn0.85 is 177.6851 cps, at Mn3 the maximum intensity is 615.8161 cps, at Mn5 the maximum intensity is 41.75745, and 90.53899 for Mn7.5.

![XRD plot of Co-Cr-Mo in Mn0.85, Mn3, Mn5, Mn7.5.](image)

**Figure 1.** (a) XRD plot of Co-Cr-Mo in Mn0.85, Mn3, Mn5, Mn7.5. (b) Peak list of Co-Cr-Mo on cobalt cubic and cobalt hexagon structure in Mn0.85, Mn3, Mn5, Mn7.5

A = Cobalt Eta [010]  B = Cobalt Ht [111]  C = Cobalt Eta [011]  D = Cobalt Ht [002]  
E = Cobalt Eta [012]  F = Cobalt Ht [022]  G = Cobalt Eta [013]
Table 2. Crystallographic parameters of the Mn0.85, Mn3, Mn5, Mn7.5

| Parameter                        | Sample   | Mn0.85  | Mn3     | Mn5     | Mn7.5    |
|----------------------------------|----------|---------|---------|---------|----------|
| First peak’s Height (cps)        | Cobalt HT (Cubic) | 187.5020 | 303.9251 | 239.7788 | 139.6297 |
| Comparison Peak (cps)            | Cobalt ETA (Hexagonal) | 177.6851 | 615.8161 | 41.7574  | 90.53899 |
| First peak’s d (Å)               | Cobalt HT (Cubic) | 1.0552  | 0.4935  | 5.7421  | 1.5422  |
| Lattice Parameter (Å)            | Cobalt ETA (Hexagonal) | 2.0684  | 2.0893  | 2.0693  | 2.0668  |
| Volume (Å³)                      | Cobalt HT (Cubic) | 1.9397  | 1.9761  | 1.9327  | 1.9397  |
| Density (g/cm³)                  | Cobalt ETA (Hexagonal) | 46.4222 | 47.3482 | 45.9745 | 45.7080 |
| Concentration (%)                | Cobalt HT (Cubic) | 23.0602 | 24.0917 | 22.6528 | 22.9202 |

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 Mn3, Mn0.85, Mn5 and Mn7.5. Whereas in the cobalt Eta phase has a hexagonal-shaped crystal structure with a lattice parameter a equal to b, and not equal to c. the size of the crystalline volume of the cobalt Eta phase changes from the largest for each sample from the largest Mn3, Mn0.85, Mn7.5 and Mn5.

In Figure 1, it can be observed that the cobalt Ht and cobalt Eta phases the maximum intensity shown at peak B and C shows the change in peak marked by an increase in peak intensity. Because the intensity of the X-ray diffraction pattern is directly proportional to the concentration of the component that produces it [10], it can be seen that there is a change in the concentration of cobalt Ht and cobalt Eta in the sample. In Table 2, it can be observed at the first maximum intensity the highest concentration of the cobalt Ht phase of the Cubic structure is found in Mn3, then Mn5, Mn0.85, and
Mn7.5. For the cobalt Eta phase, the highest concentration of Hexagonal structure was found in Mn3, Mn0.85, Mn7.5, and Mn5. The comparison of concentration cobalt Ht (cubic) to cobalt Eta (hexagonal), the greatest concentration of Cobalt Ht is found in Mn5, Mn7.5, Mn0.85, Mn3. This explains that the addition of manganese to co-cr-mo alloy affects the cobalt concentration of cubic and hexagonal structures [8], where the largest cobalt concentration of cubic structure is found in Mn5 with manganese composition of 5wt%.

3.2. Potentiodynamic Polarization Curve Analysis

Corrosion mechanism in Co-Cr-Mo was analyzed using electrochemical behavior in a 3.5% NaCl solution. In Figure 2. Tafel graph is presented stating the relationship between anodic reaction and cathodic reaction. The potential at which the rate of anodic reaction is proportional to the rate of the cathodic reaction is called E corrosion [3]. In presenting the data presented in table 3 which contains the values of E (V) corrosion, I (A) corrosion, and corrosion rate (mm / year). Some of the reactions responsible for corrosion in Co-Cr-Mo alloy at NaCl electrolytes are shown below[11]

**Anodic reaction**

\[ Co \rightarrow Co^{2+} + 2e \]  
\[ Co^{2+} + 2H_2O \rightarrow CoOH^+ + H_3O^+ \]  

Formation of CoOH\(^+\) is mainly responsible for the sudden increase in current due to the dissolution of Co metal. The electrons produced in the anodic reaction will be used in the cathodic reaction in the reduction of oxygen in solution.

**Cathodic reaction**

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]  

**Main reaction**

\[ Co^{2+} + 2Cl^- \rightarrow CoCl_2 \]  
\[ CoCl_2 + 2H_2O \rightarrow Co(OH)_2 + 2HCl \]  

### Table 3. Data from the corrosion test of the Mn0.85, Mn3, Mn5, Mn7.5 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%   | Mn0.85 | 9.040 x 10\(^1\) | -0.058                     | 2.842 x 10\(^{-4}\)    | 0.333                   |
|           | Mn3    | 8.216 x 10\(^1\) | -0.067                     | 3.127 x 10\(^{-4}\)    | 0.366                   |
|           | Mn5    | 2.242 x 10\(^3\) | -0.282                     | 1.146 x 10\(^{-5}\)    | 0.013                   |
|           | Mn7.5  | 2.726 x 10\(^1\) | -0.142                     | 9.427 x 10\(^{-4}\)    | 1.105                   |

Formation of Co(OH)\(_2\) increases the pH of the electrolyte, which induces further corrosion process. The corrosion rate is influenced by Potential E (V) corrosion and I (A) corrosion. The table states the greatest corrosion rate if the potential I (A) corrosion is getting negative, the fastest corrosion rate is the Mn7.5, Mn3, Mn0.85, Mn5 samples. The late corrosion rate is at a potential that has a more negative potential value of E (V) and I (A), namely in sample Mn5 with a corrosion rate of 0.013 mm/ year.
This is because the anodic reaction releases electrons to the metal so that excess electrons in the metal shift the metal potential towards more negatively which results in the anodic reaction being slow and accelerating the cathodic reaction [3].

4. Conclusion
Variation of manganese in the Co-Cr-Mo alloy influenced the phase composition, cobalt Ht (cubic) and cobalt Eta (hexagon), and the corrosion rate. The most corrosion resistance sample is Mn5 with 5% manganese composition, with the highest phase of cobalt cubic structure in the alloy.

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