Effect Of Mn On Structure And Corrosion Properties Of Co-Cr-Mo Alloys in Simulated Body Solutions

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Abstract. Metal alloys applied as biomedical materials have been developed for decade, due to the need for devices implanted into the human body. One of them is a cobalt-based alloy which commonly used as an orthopedic implant for total hip replacement. The biocompatibility properties of CoCrMo alloys make these alloys superior to corrosive resistance when making direct contact with the biological environment of the body where Simulated Body Fluid (SBF) solution is a solution often used to test its compatibility. The presence of manganese elements in CoCrMo Alloy and influence of heat treatment at temperature 700 oC for 65 hours were characterized by using X ray diffraction and Potentiostat. The structure and corrosion behavior in Simulated Body Fluid were discussed. The results show different crystal parameter and corrosion behavior observed. It concludes that, heat treatment and the presence of Mn affect the significantly on the properties of CoCrMo Alloy.

1. Introduction

There are many challenges and new demands in order to meet the needs of biomedical applications which are the basis for the development of standard-compliant biomedical implants to meet the modern success achievements [1]. This aims to create devices that have superior properties, so that when the device is implanted in the human body, it is expected to provide characteristics for implant materials that are safe and non-toxic, lightweight, durable and corrosion resistant [4]. Cobalt alloys have long been developed as prosthetic devices or artificial devices that resemble body parts, one of which is orthopedic implants in hip replacements.

Cobalt alloys contain cobalt and chromium, and significant amounts of molybdenum, nickel, iron, manganese, carbon and silicon [1]. Cobalt (Co) is the main constituent element of alloys that provides mechanical properties, such as strength, hardness and modulus of elasticity of the material. Chromium (Cr) contributes to the corrosion properties of the material by forming a passive layer in the form of Cr2O3, while molybdenum (Mo) is added to create a fine grain surface for increased strength. Problems that can occur in the use of the CoCrMo alloy as an implant material are influenced by the alloy's resistance to corrosion. The interactions that occur between metal alloys and body fluids can cause metal degradation.

This research was conducted and focused on the CoCrMo material with manganese variations of 5 and 7.5 wt%, as well as a description of the microstructure and corrosion behavior of the alloy. The XRD method is used to determine the structure of the alloy, and electrochemical testing using solution body fluids is used to determine the corrosion behavior of the material.
2. Experiment Methods and Material

2.1. Sample Preparation
Table 1 displays the composition of the alloy in percentage weight. The sample in this study consisted of 2 types of alloys with different manganese contents, namely 5 and 7.5 wt%.

| Type     | Analyse (weight percentage) |
|----------|-----------------------------|
|          | Co  | Cr  | Mo  | Mn  | Si  |
| CCM-1    | Balance | 20.3 | 6.1 | 5   | 1.1 |
| CCM-2    | Balance | 20.3 | 6.1 | 7.5 | 1.1 |

2.2. Solution Body Fluid Preparation
Table 2 shows the composition contained in the SBF solution used in this study.

| Number | Reagen                          | Composition (in 1000 ml) |
|--------|---------------------------------|--------------------------|
| 1      | NaCl                            | 8,035 g                  |
| 2      | NaHCO₃                          | 0,355 g                  |
| 3      | KCl                             | 0,225 g                  |
| 4      | K₂HPO₄·3H₂O                     | 0,231 g                  |
| 5      | MgCl₂·6H₂O                      | 0,311 g                  |
| 6      | 1,0 M HCl                       | 39,0 ml                  |
| 7      | CaCl₂                           | 0,292 g                  |
| 8      | Na₂SO₄                          | 0,072 g                  |
| 9      | ((HOCH₂)₃CNH₂)                  | 6,118 g                  |
| 10     | 1,0 M HCl adjusted to pH 7.4    |                          |

SBF solution is a solution containing inorganic ions with its composition which is adjusted to human body fluids.

2.3. X-Ray Diffraction
Through the XRD method, the results obtained in the form of crystal parameters and crystal size. Crystal size can be obtained using the Williamson-Hall method.

$$\beta_{tot} \cos \theta = \varepsilon 4 \sin \theta + \frac{K \lambda}{L}$$

Where $\theta$ is Bragg angle, $\lambda$ is x-ray wavelength using Cu Kα radiation, $k$ is Debye Scherrer constant of 0.9, and $\beta_{tot}$ is a combination of size widening ($\beta_L$) and strain widening ($\beta_e$).

$$\beta_{tot} = \beta_L + \beta_e = C \varepsilon \tan \tan + \frac{K \lambda}{L \cos \theta}$$

2.4. Potentiodynamic Polarization Methods
The instrument used for this test is the Digi-Ivy © DY2300 series Potentiometer. The method used is Open Circuit Potential and Linear Sweep Voltammetry body fluid simulator in the form of Simulated Body Fluid. The type of testing conducted is Linear Sweep Voltammetry. Faraday's Law is used to calculate the corrosion rate.

$$r = C \frac{M_i}{nF}$$
C = Constant corrosion rate = 3.27 x 10^{-3} \text{mm}^3, M = \text{Atomic weight of each alloy element (gr / mol)}, i = \text{Current (ampere / cm}^2\text{)}, n = \text{Number of electrons involved in the corrosion process}, \rho = \text{density of each alloy element (gr / cm}^3\text{)}

3. Results and Discussion

3.1. XRD analysis

Through the results of XRD data processing, it is known that the alloy has two phases, namely the cubic and hexagonal crystal structures.

From the figure above, a comparison diagram is shown between the sample of the alloy which has been homogenized by heating for 65 hours at 700°C with the alloy not undergoing heating treatment. The XRD results show that the sample phases formed are not homogeneous, which is characterized by the presence of more than one phase. Less homogenisation time and less high temperature can cause the porosity of the combining elements can not diffuse completely, so that the solubility is not homogeneous and may affect the mechanical properties of the alloy.
Table 3. Lattice Parameter From the Highscore Database

| Treatment | Type of samples | Phase formed | Lattice Parameter | Crystal Structure |
|-----------|-----------------|--------------|-------------------|-------------------|
|           |                 |              | a (Å)          | b (Å)          | c (Å)          |
| With Heat Treatment | CCM1              | ε            | 2.52884         | 2.52884         | 4.086         | Hexagonal |
|           |                  | γ            | 3.57098         | 3.57098         | 3.57098       | Cubic      |
|           | CCM2              | ε            | 2.61008         | 2.61008         | 4.15531       | Hexagonal |
|           |                  | γ            | 3.62392         | 3.62392         | 3.62392       | Cubic      |
| Without Heat Treatment | CCM1              | ε            | 3.60            | 3.60            | 5.15          | Hexagonal |
|           | CCM2              | ε            | 3.58            | 3.58            | 5.13          | Hexagonal |

In addition to being able to find out the phases formed, the XRD data results can also be used to review the average size of crystals owned by a material sample. In this case, the Williamson-Hall method is applied to obtain data on the average crystal size.

Figure 2. Williamson-Hall Plot Alloy Co-20.3Cr-6.1Mo-5Mn After Heat Treatment Phase ε

Figure 3. Williamson-Hall Plot Alloy Co-20.3Cr-6.1Mo-7.5Mn After Heat Treatment phase ε
Figure 4. Williamson-Hall Plot Alloy Co-20.3Cr-6.1Mo-5Mn After Heat Treatment (a) phase ε (b) phase γ

Table 4. Parameter for Average Crystallite Size of Co-20.3Cr-6.1Mo-xMn Alloy (x = 5; 7.5 wt%)

|                | Treatment | Phase | Average crystallite size (nm) |
|----------------|-----------|-------|------------------------------|
|                | Without Heat Treatment | ε      | 19.95                        |
|                |           |       | CCM1                         |
|                | With Heat Treatment | ε      | 20.09                        |
|                |           |       | CCM2                         |
|                |           | Γ      | 20.17                        |

3.2. Potentiodynamic Polarization Curve Analysis

Potentiodynamic polarization testing is based on tafel plot analysis. The voltage used in the Co-Cr-Mo alloy corrosion test is -2 V to 2 V. Tafel plot analysis shows that Co-Cr-Mo alloys with different manganese compositions have different potential values, so this can affect the rate of corrosion.
Figure 6. Potentiodynamic Polarization Plot Tafel Alloys Without Heat Treatment (a) at room temperature (b) at 36°C

Figure 7. Potentiodynamic Polarization Plot Tafel Alloys With Heat Treatment (a) at room temperature (b) at 36°C

In tafel plot, the results show the intersection of cathodic and anodic lines. The intersection between cathodic lines and anodic lines can identify corrosion current density (iCorr) and corrosion potential (ECorr) in Solution Body Fluid (SBF) solution.

The samples added with the elemental manganese showed different corrosion values in the solution body fluid. Samples with greater manganese application had a lower corrosion rate than samples containing less manganese. Based on the standard corrosion rate data for European medical applications, a material can be implanted into the human body if the corrosion rate is below 0.457 mpy.
Table 5. Effect of heat treatment and temperature on the corrosion rate of the samples

| Treatment       | Sample          | Temperature | $E_{corr}$ (V) | $i_{corr}$ (A) | Corrosion Rate (mm/year) |
|-----------------|-----------------|-------------|----------------|---------------|-------------------------|
| Heat Treatment  | Co-20.3Cr-6.1Mo-5Mn | Room Temperature | -0.357       | 1.512 x10^{-5} | 0.0012                  |
|                 | Co-20.3Cr-6.1Mo-7.5Mn | Room Temperature | -0.797       | 2.421 x10^{-5} | 0.0007                  |
|                 | Co-20.3Cr-6.1Mo-5Mn | 36 °C       | -0.670        | 2.707 x10^{-5} | 0.0014                  |
|                 | Co-20.3Cr-6.1Mo-7.5Mn | 36 °C       | -0.500        | 3.245 x10^{-5} | 0.0016                  |
| Without Heat Treatment | Co-20.3Cr-6.1Mo-5Mn | Room Temperature | -0.937       | 3.042 x10^{-5} | 0.0045                  |
|                 | Co-20.3Cr-6.1Mo-7.5Mn | Room Temperature | -0.928       | 8.617 x10^{-6} | 0.012                   |
|                 | Co-20.3Cr-6.1Mo-5Mn | 36 °C       | -0.562        | 4.418 x10^{-5} | 0.0065                  |
|                 | Co-20.3Cr-6.1Mo-7.5Mn | 36 °C       | -0.528        | 3.322 x10^{-5} | 0.0049                  |

4. Conclusion
The phases formed in the Co-20.3Cr-6.1Mo-xMn alloy (x = 5; 7.5 wt%) are present in the form of phases $\gamma$ (fcc) and phases $\epsilon$ (hcp) due to the heat treatment given to the alloys. Applying heat treatment to alloys will increase the size of the crystal when compared to alloys that do not receive heat treatment. Corrosion resistance of Co-20.3Cr-6.1Mo-xMn alloy (x = 5; 7.5 wt%) through heat treatment has a better corrosion rate than specimens without experiencing heat treatment.

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