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学位論文題目	In Vitro Corrosion Behavior of Co-Cr-Mo Alloys Prepared by Electron Beam Melting (EBM) in Inflammatory Artificial Blood Plasma (電子ビーム積層造形により作成した Co-Cr-Mo 合金の炎症性疑似血漿中での腐食挙動)		
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論文内容要約

The broad objective of this study is to investigate in-vitro corrosion behavior of Co-Cr-Mo alloys prepared by Electron Beam Melting (EBM) in inflammatory artificial blood plasma to the toxicity of Cr valence (Cr^{6+} and Cr^{3+}) contribution. It has argued that Cr valence (Cr^{6+} and Cr^{3+}) release from CoCrMo contributes to the carcinogenesis. Cr^{6+} contributed as number one carcinogenesis, while Cr^{3+} contributed as number three carcinogenesis regarding IARC (International Agency Research Center). Besides, the Cr valence release can cause inflammatory to become worse, thus affecting slower the wound healing process. Moreover, the Cr valence release induced osteolysis and aseptic loosening, due to produce the cytokines release that contributes 75% failure of the implant. CoCrMo fabricated by EBM promising for complexes design requirement and custom as well as better mechanical properties than conventional manufacturing (cast and forging). Further, investigation of biology condition induces corrosion process leading to the Cr release is essential. The biology of body solution is complexes such as inflammatory that involves reactive oxygen species (ROS), commonly produce hydrogen peroxide (H_2O_2). Also, the body solution consists of complex ions such in the blood plasma promote corrosion become faster. The release of metal ions from the metal implant can be as catalyze during an electrochemical process, which causes Fenton-like reaction. It can be worse when combining with Fe that contained in the blood, which induces the Fenton reaction. The effect of Fenton-like and Fenton reaction produces the $\text{OH}\cdot$ and $\text{O}_2\cdot$ radical that dangerous for the human body. This study, therefore, arises out of concern to investigation in-vitro corrosion behavior of Co-Cr-Mo alloys prepared by Electron Beam Melting (EBM) in inflammatory artificial blood plasma to the toxicity of Cr valence (Cr^{6+} and Cr^{3+}) contribution. The specific objective of this study outlined as follows:

1. The investigation of the microstructure of CoCrMo alloys prepared by EBM in various direct-built.
2. To investigate the relationship between potentiodynamic polarization test and Cr valence release (Cr^{6+} and Cr^{3+}) as well as the viability cell performance.
3. To examine the relationship between impedance test at the initial surface and after immersion, as well

as measure the Cr valence release after the immersion. In addition, the investigation of Degree of Sensitization (DoS) will use to predict localized corrosion.

4. Study of a redox reaction, oxide formation as well as Cr valence release using cyclic voltammetry method.

The microstructure of CoCrMo prepared by EBM showed evolution along the height due to the direct-built. The top part dominated by γ -phase, while the bottom part majority consist of ϵ -phase, except 90°. Crystallographic orientation also performed evolution along the height. The top part at 0° and 45° revealed strong orientation (001), while the bottom part depicted random orientation. In contrast, 55° showed random orientation both in the top and bottom part. The unique random orientation columnar only appeared in 90° both in the top and bottom part. All CoCrMo exhibited high boundaries ($15^\circ < \theta < 180^\circ$). EBM fabricated depicted different grain boundaries size distribution. The D_{average} (grain size average) influenced by direct-built during fabrication. At 0° and 45°, it showed less grain size average in the top part compare than the bottom part. The direct built 55° mean to reduce the height, the top part performed higher of grain size average compare than the bottom part. In contrast, 90° appeared the similarity. The low of carbon content in chemical composition CoCrMo still produce precipitates in grain boundaries and interior matrix grain, which called σ phase (intermetallic phase). EBM fabricated produced more precipitates in the microstructure compare than forging. The higher area fraction depicted in the bottom part compares than the top part. It has similarity trend when confirming with Thermo Cal software. Forging and EBM revealed two types of precipitates. Forging performed black spot that rich of Si, while grey blocky indicate rich-Cr and Mo. EBM fabricated, it appeared grey blocky precipitates that dominated Cr, Mo and Si, meanwhile the bright white exhibited rich of Mo and Si. EBM fabricated presented the martensitic transformation, which holds Shoji-Nishiyama (S-N) orientation relationship.

The potentiodynamic polarization was conducted to investigate the behavior of corrosion in inflammation artificial blood plasma after passivity film damage, thus measure the Cr valence release (Cr^{6+} and Cr^{3+}). All CoCrMo performed passivity region in alkaline and acidic artificial blood plasma (Simulated Body Fluid/SBF). However, only 45 bottom (ϵ_{45}) and 55 top (γ_{55}) continually exhibited passivity in various SBF condition, which not influenced by increasing of oxidizing power electrolyte due to H_2O_2 . Moreover, ϵ_{45} and γ_{55} permanently contributed to low of Cr valence release (Cr^{6+} and Cr^{3+}) during the electrochemical reaction. Both 45 bottom (ϵ_{45}) and 55 top (γ_{55}) were consists of two orientation combination, which each of the indicated planes with prefers of slip. The cell viability strongly influenced by amount Cr^{6+} release in alkaline SBF. Moreover, OH^\cdot and O_2^\cdot radical also contribute toxicity in SBF with H_2O_2 . The Cr^{3+} did not contribute to

the toxicity of fibroblast, and it performed in acidic SBF.

Impedance is useful to understand the metal/electrolyte interface. From the initial surface, impedance study revealed CoCrMo performed an excellent corrosion resistance in SBF both alkaline and acidic. The bode spectrum of initial spectrum exhibited a solution resistance at high frequency in all CoCrMo in various SBF condition, except 0 bottom (ϵ_0). The phase spectrum in the initial surface revealed 55 Top (ν_{55}) has excellent passivity at low frequency in SBF alkaline, SBF H₂O₂ 10 mM alkaline, SBF acidic, and SBF H₂O₂ 20 mM acidic. Moreover, 45 bottom (ϵ_{45}) and 55 top (ν_{55}) depicted excellent passivity at low frequency in SBF H₂O₂ 20 mM Fe and SBF H₂O₂ 40 mM with/without Fe. Nyquist spectrum performed the corrosion resistance. H₂O₂ with/without Fe increased the oxidizing power of artificial blood plasma thus depressed the quarter circles of Nyquist spectrum due to altered the passivity formation. Immersion a week in various artificial blood plasma, it performed passivity growth in all CoCrMo. However, some of CoCrMo depicted the loss of solution resistance after immersion in SBF H₂O₂ 10 mM alkaline, SBF acidic, and SBF H₂O₂ 20 mM acidic. The ν phase exhibited consistent excellent corrosion; however, the aggressive solution H₂O₂ 40 mM with Fe revealed ϵ phase perform excellent corrosion resistance. After immersion a week in various SBF, it dominated by release Cr³⁺, except forging (ν_f) in acidic SBF. Increasing concentration H₂O₂ 40 mM with/without Fe boosted the release of Cr⁶⁺ in all CoCrMo due to damage the passivity.

Study about redox employed by cyclic voltammetry. The oxidation reaction performed Cr₂O₃, Cr(OH)₃, MoO₂, precipitated Co(OH)₂ as secondary passivity in alkaline, and Co dissolution in acidic. After the transpassive, reduction reaction depicted some reverse oxide formation involve Cr₂O₃, Cr(OH)₃, MoO₂, and Cr reduction. It confirmed by the oxide formation using FTIR. Oxide dominated by Cr₂O₃, Cr(OH)₃, and MoO₂. The unique character of H₂O₂ is acting as oxidizing and reduction agent. During the redox reaction, it can predict the role of H₂O₂ to reduce Cr⁶⁺ become Cr³⁺. H₂O₂ 10 mM revealed release high Cr⁶⁺, and it indicates that the concentration H₂O₂ 10 mM could not reduce Cr⁶⁺ release after transpassive become Cr³⁺. From here, its suggested that H₂O₂ 10 mM is acting as oxidizing agent. Increasing the concentration H₂O₂ 20 mM and 40 mM, it can reduce the Cr⁶⁺ become Cr³⁺ during the reduction reaction. It suggested H₂O₂ acting as a reduction agent.

It can be concluded that the direct-built parameter to fabricate CoCrMo through EBM promising to metal implant production in the future due to the excellent of corrosion resistance and low of Cr valence release (Cr⁶⁺ and Cr³⁺). It related to the low contribution of Cr toxicity (Cr⁶⁺ and Cr³⁺).