Analysis of corrosion rate and surface characteristics in substitution bone implant material with corrosive media simulated body fluid (SBF)

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Abstract. Bone is a basic part of the human skeletal system which serves as the main foundation of the human skeletal system. Bone functions include providing a framework, bearing body weight, protecting vital organs, supporting mechanical movements, accommodating hematopoietic cells, and maintaining iron homeostasis [1]. Millions of people suffer from bone damage caused by natural disease and accidental damage which results in the treatment of bone damage being the main clinical operation [2]. Bones have the ability to grow and form their own parts in the healing process but bones also have a relatively long healing time [3].

Medical implants are the main structure that serves to help, replace or add to the biological tissue that is sick or injured [4]. Medical implants have many types according to the needs of organs that have damage, one of them is bone implants. Bone implants generally have 4 types with different materials and needs including: metals, ceramics, polymers, and composites [5].

Keywords: bone implant, ss 316 l, titanium nitride, biocompatible, simulated body fluid, apatite

1. Introduction
Bone is a basic part of the human skeletal system. Bone functions include providing a framework, bearing body weight, protecting vital organs, supporting mechanical movements, accommodating hematopoietic cells, and maintaining iron homeostasis [1]. Millions of people suffer from bone damage caused by natural disease and accidental damage which results in the treatment of bone damage being the main clinical operation [2]. Bones have the ability to grow and form their own parts in the healing process but bones also have a relatively long healing time [3].

Medical implants are the main structure that serves to help, replace or add to the biological tissue that is sick or injured [4]. Medical implants have many types according to the needs of organs that have damage, one of them is bone implants. Bone implants generally have 4 types with different materials and needs including: metals, ceramics, polymers, and composites [5].
Metal implants have advantages over other materials in the fields of strength, stiffness and toughness, capable of high loading [6]. In addition, ceramics (including bioglass) have low fracture resistance and high elastic modulus compared to bone [6]. Polymers have the advantage to follow the shape of human body tissue, polymer implants might increase inflammation in the tissues if monomers come out of implants [6]. The last is composite. Composite has the advantages of biocompatibility that can be adjusted as desired. In addition, composites have good physical and chemical properties [7]. Medical implants are often referred to as biomaterials so biomaterials must have criteria that must be met include: biocompatible, according to design and easy to manufacture, resistant to corrosion, resistance to wear and aseptic reduction [8].

Stainless steel is one material that is often used as a bone implant because it has a low corrosion rate and good mechanical properties. The biocompatibility of stainless steel has also been proven during decades for implantation. Stainless steels have better biomechanical properties compared to cobalt chrome or titanium alloys (alloys) but with their low corrosion rates and biocompatibility make stainless steels more limited in clinical applications.

Corrosion is a damaging attack on the metal that reacts with the surrounding environment and corrosion cannot be avoided. Corrosion process involves two simultaneous reactions namely oxidation and reduction (redox). The effect of this corrosion has a major impact because it can weaken the mechanical properties of a material and the quality of the material. Corrosion is divided into 2 types namely dry corrosion and wet corrosion. Dry corrosion occurs when direct contact between atmospheric gases such as oxygen gas and metals that can cause the formation of metal oxide layers or called “Theory of Wagnes”. As for wet corrosion, this corrosion occurs when the liquid media is involved or the metal is exposed to the liquid media. In this process, one part will act as an anodan and undergo an oxidation process, while the other part acts as a cathode and undergoes a reduction process. In the case of related bone implant corrosion is wet corrosion because the bone implant material comes in direct contact with human blood.

This study uses specimens from ST-41 low carbon steel coated with Titanium Nitride (TiN) as a trial material. Various types of materials that can be used such as stainless steel (SS316L), cobalt-chromium (Co-Cr) alloys, Titanium (Ti), and Ti-based alloys. So far, Ti and Ti-based alloys such as nitinol (TiNi) have proven to be suitable as implants because of their good mechanical properties, high corrosion resistance, and biocompatibility [4] [9]. This study discusses the surface characteristics of TiN specimens that have been carried out the immersion process on corrosive media Simulated Body Fluid (SBF) for 12 hours, 168 hours, 240 hours, 336 hours. SBF is an artificial blood solution that functions as a substitute for real human blood. SBF contains ions and chemical compounds that almost resemble real human blood. In addition, this test uses a Scanning Electron Microscope (SEM) to analyze the surface characteristics of the test specimen.

2. Methodology
This test was carried out to obtain the development of corrosion rates from alternative materials and the process of forming apatite layers in bone implant specimens. Test specimens were carried out immersion in SBF solution with immersion variations of 12 hours, 168 hours, 240 hours, 336 hours. After the immersion process, the specimens were tested with Potentiodynamic Polarization (PDP) and Scanning Electron Microscope (SEM). PDP and SEM tests are performed to obtain a correlation between the rate of corrosion of the material and changes in surface characteristics of the specimen.

Test specimens in the form of ST-41 and SS 316 L steel with the chemical composition according to Table 1. Cut with dimensions of 20 mm x 10 mm x 5 mm. Before the coating process is carried out, the specimen is sanding using 5 different types of roughness, namely 100, 200, 500, 1000, and 2000 mesh to obtain a fine specimen and polished using autosol until smooth. After that the ST-41
Steel will be treated with TiN coating process using PVD Coating method. The specimen coating by the PVD coating method is shown in Figure 1. In other words by vaporizing material from a solid or liquid form into the form of atoms or molecules and channeled in the form of a vapor into a vacuum or low pressure gas (or plasma) into the substrate where it condenses. The specimen is placed in a rotating holder or container in the entire vacuum chamber to produce the same thickness. PVD coating processing temperature is at a temperature of 500 °C (930 °).

| Table 1. Specimen chemical properties |
|--------------------------------------|
| ST-41 | Fe | C | Si | Mn | P | S | Cr | Mo | Ni |
| ST-41 | 98.9% | 0.19% | 0.18% | 0.6% | 0.021% | 0.015% | - | - | - |
| SS 316 L | 62.2% | 0.03% | 0.75% | 2.0% | - | - | 18.0% | 3.0% | 14.0% |

Figure 1. PVD coating process

Corrosive media SBF is made by dissolving a number of chemical compounds with reference to the Kokubo standard. The function of SBF is as a substitute for genuine human blood. In addition, SBF is used to see the formation of apatite on the surface of different materials so that it can predict the biological activity of material in bone [10]. Ingredients are in Table 2. Requires NaCl, NaHCO3, Na2HPO4.2H2O, MgCl2.H2O, CaCl2.2H2O, KCl, Na2SO4, and (CH2OH)3CNH2 compounds and are the compounds needed for the manufacturing process of SBF. Then the compound is dissolved with sterile aquadest until a volume of 1 liter is obtained. The pH of the solution was adjusted with 0.1 N HCL solution to 7.40.

| Table 2. Formula weights of reagents for preparing 1000ml of SBF |
|--------------------------|
| Reagent | NaCl | NaHCO3 | Na2HPO4.2H2O | MgCl2.H2O | CaCl2.2H2O | KCl | Na2SO4 | (CH2OH)3CNH2 |
| Amount (gram) | 6.547 | 2.268 | 0.178 | 0.305 | 0.368 | 0.373 | 0.071 | 6.051 |

The test begins by preparing a plastic container for immersion or immersion of the specimen. Specimens are immersed for 12 hours, 168 hours, 240 hours, 336 hours. The SBF volume needed for the immersion process is obtained using the Kokubo standard formula (equation 1).
\[ V_S = \frac{S_a}{10} \]  
(1)

Where \( V_S \) is the volume of SBF (ml) and \( S_a \) is the visible surface in the specimen area (mm\(^2\)). For porous materials, the SBF volume must be greater than the calculated \( V_S \). After calculating the SBF volume needed for immersion, pour it into a plastic or glass container for immersion. Place the specimen by the shape and position in Figure 2. Based on the reference Kokubo et al. [11] concerning the placement of specimens during immersion, it is recommended to lay specimens in Figure 2b, the formation of the tested apatite must be on the lower surface of the specimen.

![Figure 2](image)

Figure 2. a) immersion position for circular plate specimen, b) immersion position for square plate specimens

Tests are carried out using a Scanning Electron Microscope (SEM) to see the surface of the specimen until an apatite layer is seen on the surface of the specimen. SEM is carried out using a British Carl Zeiss (Evo MA 10) machine with an optical electron magnification capability of 25-50,000 times and can be enlarged up to 12 times. The resolution that can be achieved more than 10 micrometers and imaging analysis at 20 kV power. The magnification taken in this test was 2000 times. After an immersion process with 4 variations, the specimen is removed from the SBF and gently rinsed with pure water. Specimens must be dried using a desiccator without heating before being inserted into the SEM machine.

3. Result and discussion

3.1. Potentiodynamic Polarization (PDP)

In the Potentiodynamic Polarization test, the results of the corrosion rate of the specimens are obtained. The test was carried out after the immersion process on specimens with variations of 12 hours, 168 hours, 240 hours, and 336 hours. The solution used is the SBF solution resulting from the immersion of each specimen. Data on the results of the corrosion rate can be seen in Table 3. Obtained data for the highest corrosion rate that occurs in the ST-41 material is 0.17723667 mm year\(^{-1}\) at 168-hour immersion. Whereas in SS 316 L steel the highest corrosion rate was 0.0354924 mm year\(^{-1}\) at 168 hours immersion. For the lowest corrosion rate, ST-41 has a corrosion rate of 0.001645333 mm year\(^{-1}\) at 336 hours immersion while SS 316 L has the lowest corrosion rate of 0.008512167 mm year\(^{-1}\) at 12 hours immersion.
### Table 3. Potentiodynamic Polarization (PDP) test result

| Duration of Imersion | Material | $E_{a}$ (V/dec) | $E_{c}$ (V/dec) | $E_{corr}$ (V) | $I_{corr}$ (A) | $CR$ (mm year$^{-1}$) |
|----------------------|----------|----------------|----------------|----------------|----------------|----------------------|
| 12 Hours             | TiN      | 0.053426       | 0.04678        | -0.371883      | 0.00043296     | 0.00103356           |
|                      | SS316L   | 0.290843667    | 0.071102       | -0.19489       | 0.0041777      | 0.008512167          |
| 168 hours            | TiN      | -31.290        | 0.173820       | -0.574013      | 0.04718104     | 0.17723667           |
|                      | SS316L   | 0.022758       | 0.044537       | -0.313533      | 0.001543       | 0.0354924            |
| 240 hours            | TiN      | 0.062674       | 0.126877       | -0.63183       | 0.002385467    | 0.00569457           |
|                      | SS316L   | 0.028148667    | 0.047334       | -0.267493      | 0.0022887      | 0.0042448            |
| 336 hours            | TiN      | 0.162819333    | 0.18238        | -0.402837      | 0.0008871      | 0.001645333          |
|                      | SS316L   | 0.020117333    | 0.044902       | -0.402837      | 0.0008871      | 0.001645333          |

3.2. Scanning electron microscope (SEM)

In SEM testing using English Carl Zeiss (Evo MA 10) machine, surface images of TiN and SS 316 L specimens were obtained (Figure 3). The surface shape of the specimens with immersion for 12 hours had similar characteristics, namely, there were no signs of damage to the specimen surface or corrosion on the specimen. Also, there was no point or apatite layer attached to the surface of each specimen after the immersion process. Also, it was found on the surface image of the specimen with immersion for 336 hours that there was some damage to the surface of the TiN in the form of holes (yellow circle), but there were some apatite beads (red circle) attached to the surface of the TiN specimen. Whereas the SS 316 L specimen contained a point of corrosion (yellow circle) and no apatite granules attached to the surface of the specimen.

![Figure 3. Scanning Electron Microscope photo result: (a) SS 316 L with 12 hours immersion, b) TiN with 12 hours immersion, c) SS 316 L with 336 hours immersion, d) TiN with 336 hours immersion](image-url)
4. Conclusion
The conclusion from the research data is that the longer the immersion process in the specimen, the more corrosion layers will form and the formation of apatite layers on the surface of the specimen, especially TiN. The results of the corrosion rate of TiN and SS 316 L have almost the same pattern, namely the highest peak of corrosion rate occurs at 168 hours immersion while the lowest corrosion rate for TiN is at 168 hours immersion and SS 316 L at 12 hours. In the SEM test results, SS 316 L with an immersion duration of 12 hours and 336 hours contained no apatite granules covering the specimen. Whereas the 336 hours of TiN immersion contained apatite beads that protecting the specimen. So that further research is needed with a longer immersion process and the process of forming apatite granules on the surface of the specimen.

5. References
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