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Corrosion Behaviour of Collagen Coated and Uncoated Biomedical Titanium Alloy (TNTZ) Within Human Synovial Fluid

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Abstract. The corrosion behavior of uncoated Ti-29Nb-13Ta-4.6Zr (TNTZ) and collagen-coated TNTZ within human synovial fluid + NaCl 0.9% solution was investigated using immersion test in order to know the effectivity of collagen to increase bioactivity and also reducing corrosion rate as a coating material. Collagen was selected as coating material because of the ability of adhesion cell and increasing bone healing process. The immersion test has been used as corrosion method due to its simplicity and inexpensive. The immersion time in this study was for 2, 4, and 6 weeks. Surface morphology of material was examined by scanning electron microscope (SEM). Corrosion rate was calculated by measuring degradation of coating mass during the corrosion process. While mechanical property (hardness) of material was measured by microhardness testing. The result of this study showed that collagen coating has reduced the corrosion rate of TNTZ in the human synovial fluid where the corrosion rate of the coated TNTZ is 0.00125 mmpy and the corrosion rate of uncoated one is 0.00262 mmpy after 6 weeks immersion. On the other hand, the hardness of coated TNTZ is higher than the uncoated one. It can be concluded that the collagen coating increases both corrosion resistant and mechanical properties of TNTZ.

Keywords: Corrosion, Synovial fluid, TNTZ, collagen, immersion

1. Introduction

Metal alloys as biomaterials have to possess some characteristics such as corrosion and biocompatibility that really important especially for human utilization. Some kind of titanium alloys has been used in orthopedic like Ti6Al4V where is known to have high modulus



Young (100 GPa) than human cortical bone (30 GPa). Incompatibility of this modulus Young causes stress shielding that may cause bone resorption, moreover are loosening and premature failure implant [1]. In other hands, releasing Ti6Al4V compound (Al and V) will become toxic in the human body [2]. Based on this situation, type β titanium has all requirements that necessary that will be needed and they have β stable elements, such as molybdenum, silicon, zirconium, and tantalum.

Some of the titanium alloys have been reported closer to modulus elasticity of cortical bone, such as Ti29Nb13Ta4.6 Zr (TNTZ) [3], Ti25Ta25Nb [4], dan Ti35Nb4Sn [5] are 65 GPa, 55 GPa, dan 40 GPa respectively. Event another titanium alloy like Ti13Nb13Zr has been reported having significant value in cellular attachment than Ti4Al4V [6]. As the material in this research, TNTZ has some elements showed good performance. Other research found that Niobium element could increase the corrosion resistance of a material. Tantalum element [7] could be better in corrosion resistance because its oxidation stability highly [8,9] and its superior corrosion resistance also the biocompatibility of tantalum have been extensively evaluated [10]. Zirconium element (Zr) showed acceptable mechanical strength [11] and an in vivo study reports that zirconium implant exhibits good osteointegration [12,13].

Implant surface coating with a biomaterial that has bioactivity is really important to increase biocompatibility between implant and host. Coating with calcium phosphate (CaP) has been known to increase extracellular matrix (ECM) component and confirmed to upgrade osteoconductivity properties [14,15]. Though deposited CaP is one of natural composition of bone, it is different because the natural bone is not only consisted of the inorganic compound like CaP but also organic matrices like collagen and non-collagenous proteins. The organic part of bone ECM consists of collagen type 1 fibrils embedded in an amorphous substance, which consist of glycosaminoglycans and various bone proteins. ECM components participate actively in the regulation of cellular processes and responses. Therefore, implant surface modifications with components of bone ECM appears attractive to modulate specific intrinsic osteogenesis directly at the bone–implant interface [16,17]. The ECM works as a scaffold for bone forming cells and influences migration, adhesion, and differentiation of these cells [18,19]. Briefly, collagen type 1, major structural protein in ECM has been used as an organic implant coating material. Recent studies have referred to the role of a collagen coating in stimulating cellular responses, increasing bone growth and improving bone-to-implant contact [20,21,22].

Corrosion behavior classically focuses to material testing on simulated body fluid like phosphate buffer saline, sodium chloride solution, Hank solution, Ringer solution, and *bovine calf serum* and showed the essential purposed at gaining information on the involved corrosion mechanisms and analyzing the significant factors affecting the surface reactivity of biomedical alloys. Synovial fluid is a viscous fluid that is found in the synovial joints which are known to be composed mainly by inorganic salts like NaCl (Natrium Chloride) and organic molecules such as hyaluronic acid and lubricin, proteinase, and collagenase also cells [23] with alkali pH (7,4 – 10) [24]. These cells have been viewed as having a responsibility to release reactive chemical species that can change surface oxidation compositions of metal alloy [25]. Simulated body fluid disables to show the complexity of the in vivo electrolyte and the corrosion situation may determine through the contact between artificial joint and synovial fluid. Therefore, the aim of this study is to comprehend the corrosion resistance of one of new β type titanium alloy, TNTZ coated collagen in synovial fluid as attracted material.

2. Material and Methods

2.1 Material and Solution

Titanium type β Ti-29Nb-13Ta-4.6Zr (TNTZ) samples were provided in disk form, the thickness, 2-3 mm and diameters 6-7mm. All samples were polished and cleaned with nitric acid, acetone, and ethanol for 10 minutes for each solution, respectively using an ultrasonic cleaner for surface treatment. Corrosion testing was conducted within the synovial fluid (archived biological materials) that was found in human synovial joint and were added NaCl 0,9%. The temperature of the solution was kept at 37°C.

2.2 Collagen type I coating

After polishing and cleaning process, all samples were rinsed with distilled water, air dried and autoclaved process. For the coating process, 1 mg calf skin collagen type I/mL was added into 10 mM acetic acid and incubated overnight in 4°C. PBS 60 mM, pH 7.0 was added into solution (collagen + acetic acid) with ratio 1:1 and then the solution was incubated for 15 minutes in 37°C. The solution was centrifuged at 2000 rpm for 30 minutes in 27°C. The resulting gel was homogenized and the supernatant was removed. Next, adding PBS solution 1 mg/ml into solution and centrifuged for 15 minutes at 2000 rpm in room temperature (27°C). The supernatant was removed and the pellet was resuspended in 60 mM phosphate buffer, pH 7.0 to a concentration about 2 mg collagen/mL [18]. TNTZ disks were incubated in the suspension at 27°C for 15 min, washed with distilled water, and air dried.

2.3 Corrosion test

Corrosion method was immersion test with all samples were soaked into corrosion solution (synovial solution + 0,9 NaCl). samples consist of collagen uncoated dan coated TNTZ. The corrosion test was done for 2,4, and 6 weeks. All samples have measured the weight before and after corrosion test. The corrosion test was done in incubator 37°C with the stable variable. After the immersion process, the corrosion rate was measured with weight loss method based on ASTM G1 standard with the formula:

$$CR = (K \times W) / (D \times A \times T)$$

Where:

CR = corrosion rate (mmpy or milimetre per year)

W = lost of weight (gram)

K = constant factor of rate corrosion

$$= 8,76 \times 10^4$$

D = sample density (g/cm³)

A = surface area of sample (cm²)

T = time for immersion (hours).

2.4 Observation of microstructure, hardness, and thickness of samples.

The microstructure of samples was measured before and after corrosion process with a scanning electron microscope (SEM) (Hitachi High-Technologies Corporation, S-3400N Type II) with voltage was 230 Volt. The hardness value of samples was measured using Vicker hardness tester (Shimadzu HVM-2). The load was HV0.01 – HV2 (98.07N-19.614N) with pressuring time was 15 minutes and the voltage was 240V, 300VA 50/60Hz. The thickness was measured with Sanfix thickness gauge series type GF-280.

3. Results and discussion

3.1 Morphology of sample surface area

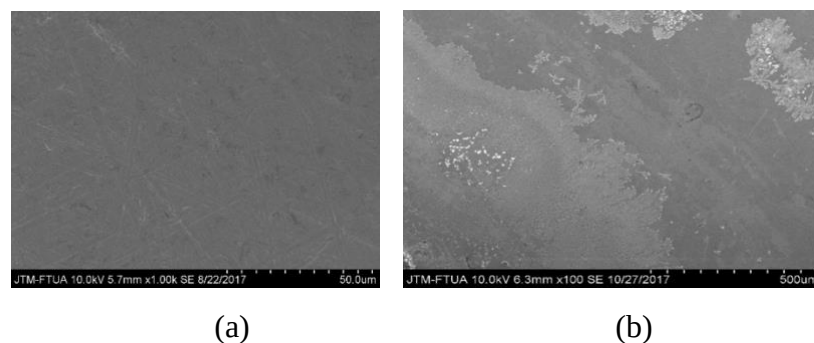


Figure 1. SEM photograph of samples before the coating process (magnification about 100x). (a) before the coating process, (b) after the coating process.

The sample surfaces have been observed in Figure 1(a) before coating process. The surface is average with a little scratch after the sanding process. Some white spot was assumed as tissue that has been recorded while cleaning process of surface area. After coating process (Figure 1 (b)), the collagen almost covers all of the surfaces but the spread of collagen in surface area is uneven and has different thickness. It is related to the position of a sample while the coating process and the collagen is fibrils that effect to how it covers the surface. Some areas look like a collection of dense dots and other areas like the fiber cluster. The collagen has well attached to the surface area and will reduce the corrosion process of material that has been showed in the result of the corrosion process. Corrosion areas are extensive in samples without coating process comparing to samples with coating process (Figure 2) for each week.

Corrosion process has increased along with the duration of the immersion process. Corrosion area of 6 weeks immersion period is wider than the area of 2 weeks immersion process for uncoated and coated process based on the SEM photograph. Collagen has degraded along with corrosion test slightly as time goes by corrosion process. Collagen has biodegradable features that will disappear by the time based on the corrosion process. The corrosion level of the solution also has an effect to collagen detached duration until it gets involved to the solution. Collagen coating reduces the duration of the corrosion process, so uncoated will be corrosive quickly than collagen coated. Based on Figure 2, the corrosion form is general, crevice and fretting corrosion where these corrosion types could operate in combination [26]. General corrosion is experienced by metallic biomaterial, include titanium alloy (TNTZ) because of releasing metal ion after exposing time in physiological fluid.

Metal ions release because dissolution of passive oxide film and ion transport passes the film. Another research found that exposure Ti-6Al-4V in human serum formed Ti complexes with serum protein [27]. This phenomenon has been experienced by coated and uncoated TNTZ when they soaked into synovial fluid.

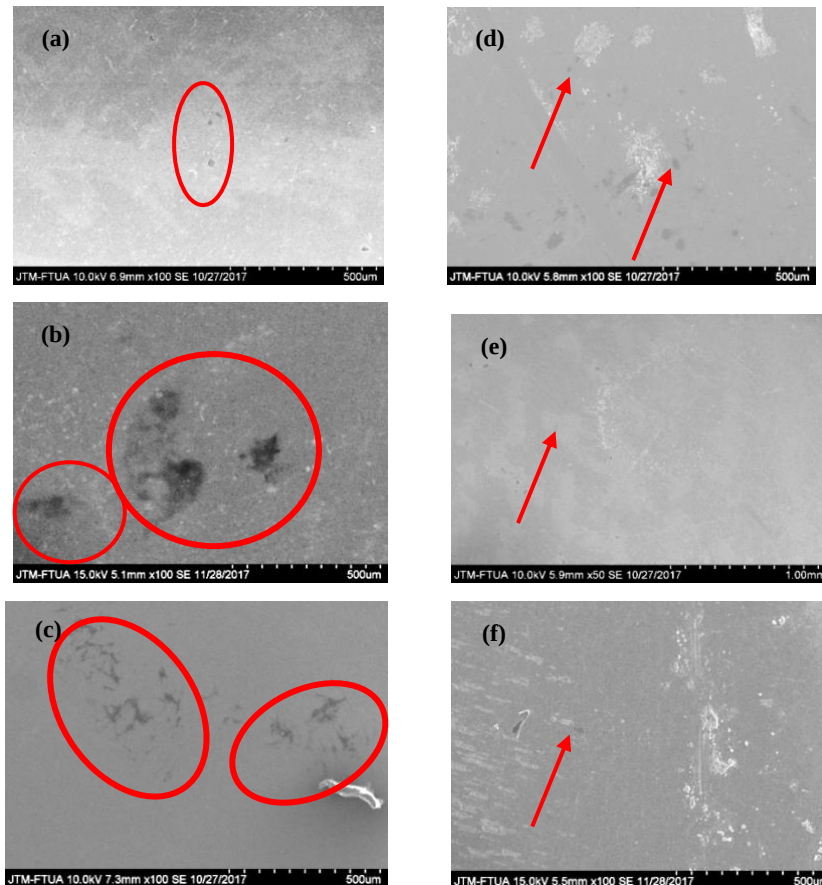


Figure 2. Morphology after corrosion testing for TNTZ uncoated, (a) 2 weeks, (b) 4 weeks, and (c) 6 weeks and TNTZ coated collagen (d) 2 weeks (e) 4 weeks (f) 6 weeks (magnification about 100x).

Pitting corrosion has been made due to surface heterogeneity generally like dislocation, inclusions, second-phase particles or mechanical strength and it all caused sites for pit initiation [28]. Uncoated samples showed more pitting corrosion than coated samples. Crevice corrosion has been found in some case of orthopedic devices [29]. It is created also at the boundary of markers fitted into the stent [26]

3.2 Corrosion rate

In Figure 3, the graphic shows that the corrosion test causes reducing the mass of TNTZ samples (Figure 3). Mass reductions tend to increase along with immersion time, respectively. The highest value of mass reduction belongs to uncoated TNTZ for 6 weeks immersion time that is 0.003 gram (Table 1). Based on all data from the graphic, we may assume that the coating process has an effect to reduce the corrosion process of samples and the value of mass reduction is directly proportional to the duration of corrosion time. Reducing of mass has

effect to corrosion rate where increasing of reducing mass makes the corrosion rate becomes higher (Figure 4). The corrosion rate of the uncoated sampel is higher than the coated one in synovial fluid. Overall, corrosion behavior of titanium TNTZ is better compared to other titanium alloys (Ti6Al4V) or pure titanium.

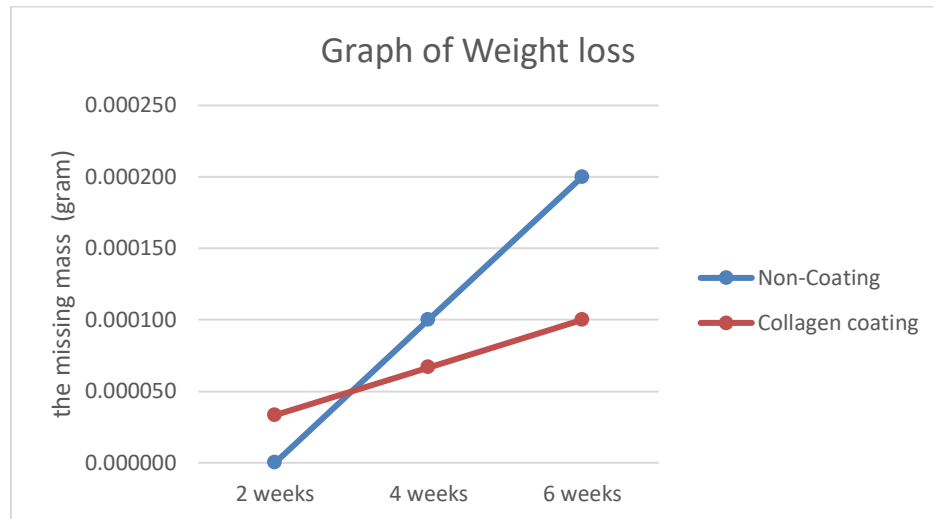


Figure 3. Graph of weight loss of TNTZ samples (coated and uncoated with collagen)

Table 1. The corrosion rate of coated and uncoated samples for each immersion time

Coating process	Weeks	Corrosion rate (mmpy)	Average of corrosion rate (mmpy)
Collagen uncoated	2	0.00165602	0.00205441
	4	0.00188331	
	6	0.00262391	
Collagen coated	2	0.00120125	0.00123278
	4	0.00124186	
	6	0.00125522	

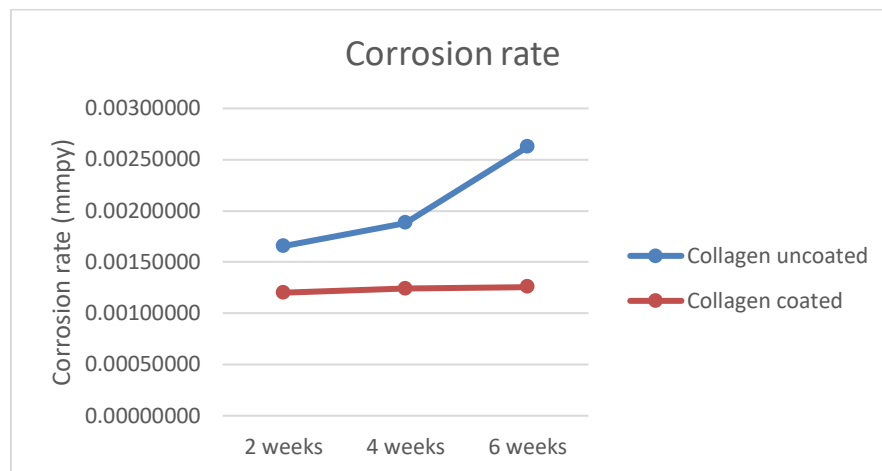


Figure 4. The corrosion rate of coated and uncoated samples for each immersion time

3.3 Hardness of samples

Hardness testing has a function to know the effect of corrosion test of TNTZ samples (coated and uncoated) to mechanical properties. Hardness values of coated and uncoated samples have been shown in Figure 5. The hardness value of the coated material is higher than uncoated samples except for time variation in 4 weeks. The hardness value of uncoated is higher than coated samples even the score is excessive to early hardness value samples before the corrosion test. It is because of the error process on taking a point of hardness test and focuses on the area with high hardness value but overall, decreasing of hardness value happened in each time based on the minimum distance of hardness value for coated and uncoated samples. The data shows that synovial fluid decreases the hardness value of all samples. It is because of degradation proses in the surface of samples and releasing of ions that cause damage in the surface of TNTZ based on SEM photograph (Figure 2).

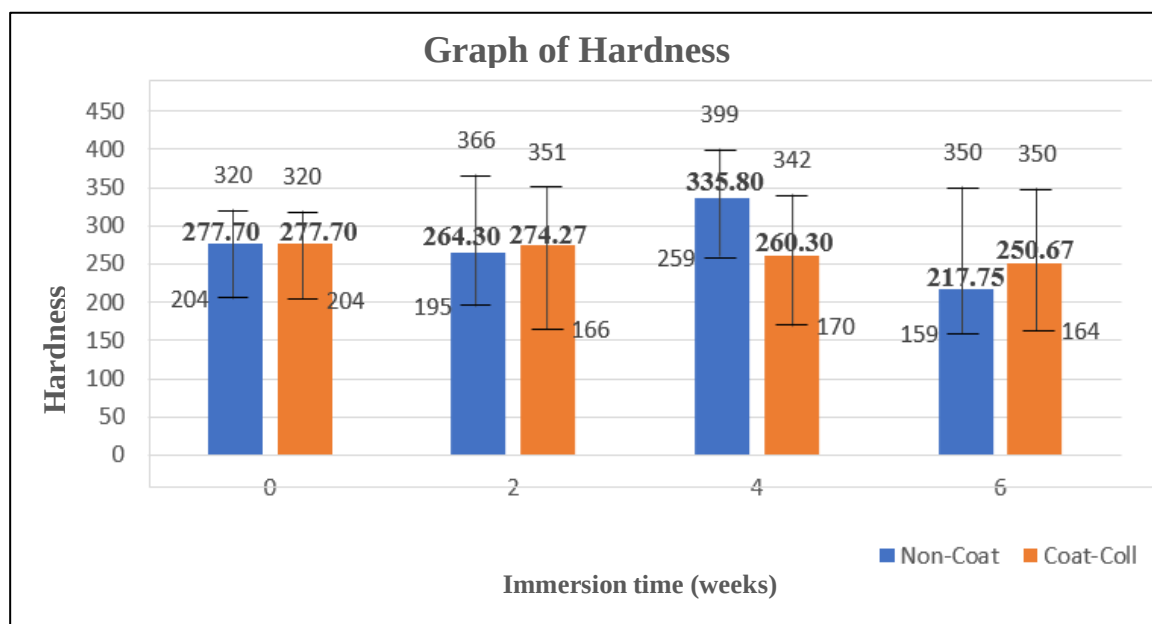


Figure 5. The hardness of each sample after corrosion process by the time

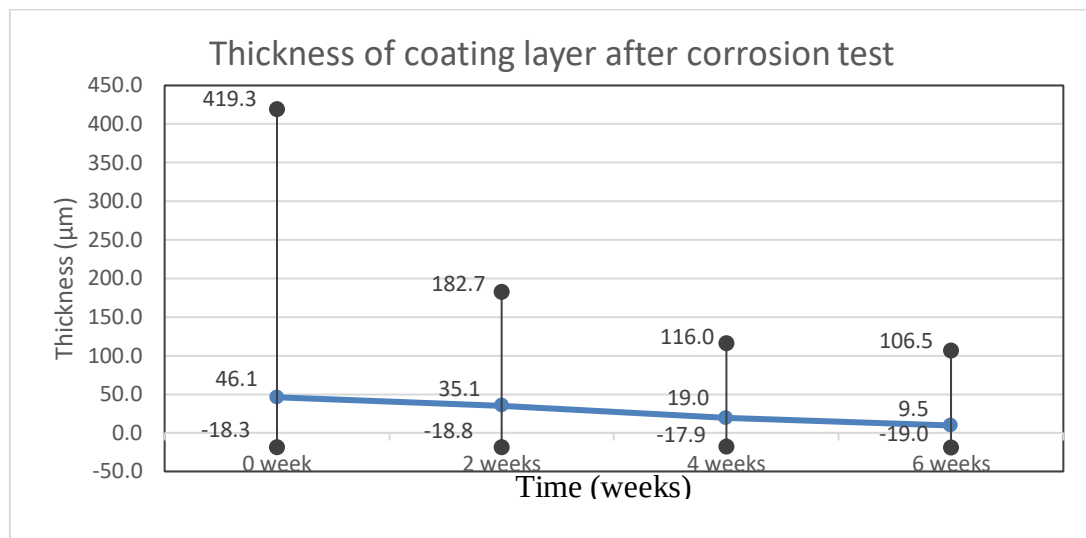


Figure 6. Graph of the degradation process of a coating layer after the corrosion test

Thickness testing of coating layer after immersion time has a function to calculate the residue of the coating layer. The data in the graph (Figure 6) have been calibrated and the result showed that the coating layer has been reduced along with the addition of corrosion time. In 6 weeks of treatment, the collagen layer still exists for about 9.5 μm. It proves that collagen coating as tissue layer does not drop off easily if it uses as a coating layer. It is assumed that collagen coating on TNTZ as joint prostheses is excellent because collagen induces cell adhesion after implantation.

4. Conclusions

The following conclusions are reached:

1. The corrosion rate of titanium TNTZ coated collagen is lower than the uncoated one. The corrosion rate of TNTZ coated collagen is $1,233 \times 10^{-3}$ mmpy and the uncoated one is $2,054 \times 10^{-3}$ mmpy.
2. Immersion time within synovial fluid has an effect to hardness value for coated and uncoated process where the hardness value becomes lower. In other hands, the duration of immersion treatment has an effect reducing the thickness of the collagen coating.

5. Acknowledgment

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