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The Effect of Plasma Nitridation on Surface Hardness of Titanium Alloy (Ti-6Al-4V) for Artificial Knee Joint Applications

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ABSTRACT. Nitriding has been carried out using plasma nitriding techniques for surface treatment of Titanium as a biomaterial component. The purpose of this study was to determine the effect of plasma nitriding on surface hardness that occurs in titanium. The material used is Titanium Alloy (Ti-6Al-4V) Grade 5 which is processed by plasma nitriding by varying nitrogen (N_2) and argon (Ar) gases of (100% N_2/0% Ar), (95% N_2/5% Ar), (90% N_2/10% Ar), (85% N_2/15% Ar), (80% N_2/20% Ar), and (75% N_2/25% Ar), and temperature 400ºC, time 5 hours and a pressure of 1.6 bar. The test results show that the optimum hardness is found in the gas composition with a ratio of 95% N_2: 5% Ar. Obtained a hardness of 371 HV/VHN or an increase of 159% of the raw material with hardness value of 143 HV/VHN.

Keywords: *Titanium Alloy, Plasma Nitridation, Hardness, gas, nitrogen, argon*.

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1. INTRODUCTION

The strength of the components in a mechanical structure is an important thing which the structure can hold in all conditions. Apart from its mechanical properties, as a biocompatible material it must have good corrosion resistance. In one case where good mechanical characteristic are required for the manufacture of the femoral component. As one of the most common implants in the application of this component is the replacement of the knee joint (see Figure 1).

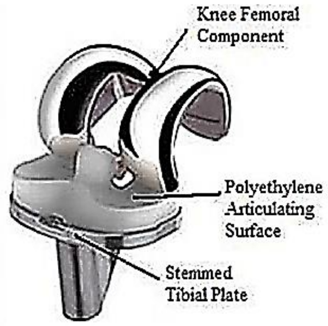


Fig 1. Knee implants in total knee replacement [1]

The process of engineering a body part (treating, adding, repairing or replacing the function of body tissues) starts from a basic understanding of restoration materials that can be applied directly or indirectly [2]. The biomaterial itself must have properties that are able to stimulate a response to biological properties in the body. The intended stimulation is where the material can bind well to living tissue or body fluids while dissolving itself into the body fluids and its surroundings, so that it is hoped that the selected biomaterials can also withstand damage such as wear and corrosion if inserted into the body.

The initial stage of damage to the material starts from the surface. When a material interacts with other objects either corroded or rubbed against other components, the coating can be eroded which can cause further damage if not paid attention. Surface damage problems cannot be avoided, but they can be prevented [3].

Surface treatment is one method that is often used to improve the quality of the surface of the material. Basically surface treatment can be achieved in two ways, the first is by adding other elements/changing the chemical composition, while the second is by changing the phase or crystal structure by heating at a certain temperature followed by quenching or slow cooling [4].

The Ion Implantation surface hardening technique is one of the developments in the use of plasma technology. Nitriding is a material surface hardening treatment involving diffusion of nitrogen into the metal surface at a certain temperature and time period, so that the thickness of the layer can be adjusted according to the application of the material used later. This nitridation process is carried out by pounding nitrogen ions on the hardened surface so that the surface atoms are splashed and compound with nitrogen ions and condensed to form a hard layer [5].

Biomaterials require corrosion resistance, therefore biocompatible materials that have good corrosion resistance are used, one of which is Titanium (Ti-6Al-4V) Grade 5. To increase its hardness, ion implantation is carried out using the plasma/ion nitriding method. A schematic of the plasma/ion nitriding device can be seen in Figure 2.

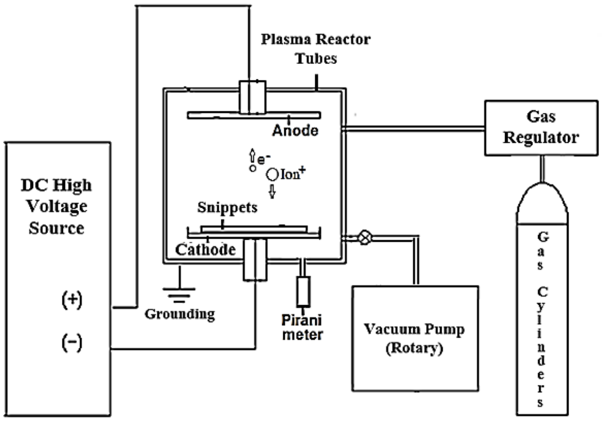


Fig 2. Schematic of plasma/ion nitriding device [5]

This nitriding process is carried out by pounding nitrogen ions on the hardened surface so that the surface atoms are splashed and compound with nitrogen ions and condense to form a hard layer. The formation of nitrogen ions is carried out by converting nitrogen gas into plasma which is in the plasma reactor tube so that nitrogen ions and electron pairs are formed. The formation of plasma uses a high DC voltage with positive polarity at the anode and negative polarity at the cathode resulting in incandescent discharge and plasma formation [5].

Sputtering argon gas and nitrogen

The nitriding process only requires nitrogen atoms. This research combines two different types of gas during the ion collision process, namely Argon (Ar) and Nitrogen (N_2) gas. The function of argon gas is used as sputter, where the argon ions will hit the surface of the sample but do not diffuse into the sample like nitrogen ions. This can happen because argon gas is an inert gas (non-reactive element) so that it does not combine with carbon atoms. In addition, the mass possessed by argon is greater than nitrogen, which is 1.784 g/l for argon and 1.251 g/l for nitrogen. As a result of the greater mass, in the process of colliding surface atoms, the atoms that are splashed onto the surface will be scattered in greater numbers. This process is usually carried out in a chamber or vacuum with the aim of reducing the effect of collisions with oxygen atoms which can interfere with the results of the coating process [6]. The sputtering process in plasma can be seen in Figure 3. Argon is also very good for suppressing gaseous pollutants such as oxygen in the reactor so that the nitriding process takes place efficiently [7][8].

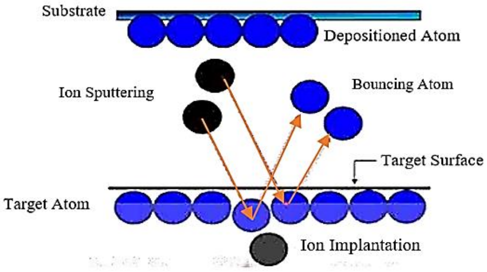


Fig 3.Sputtering process in nitriding samples [6]

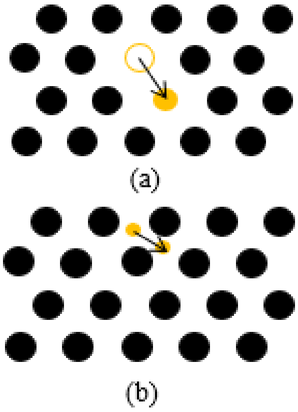


Fig 4. Atomic diffusion mechanism in (a) vacancy diffusion (b) interstitial diffusion [7]

The main of the sputtering process is the collision of the atomic ions in the sample. This is done to add certain elements to the surface which will make the surface increase in hardness, which is called the Diffusion process. There are two types of diffusion, namely vacancy diffusion and interstitial diffusion. The emptiness in the atomic structure of a material can occur as a result of heating, this emptiness occurs because these atoms change positions. The movement of atoms from the original region to another empty region is also known as Vacancy Diffusion. The second type of diffusion is interstitial diffusion, in which diffusion is when an atom inserts between the gaps in the two atoms. This mechanism occurs in compounds that are not pure or there are other elements such as nitrogen, carbon, hydrogen, and oxygen. These elements can enter the gaps between atoms due to the difference in size with other atoms in the bonds. The two diffusion mechanisms that have been mentioned can be seen in Figure 4.

2. MATERIALS AND METHODS

This study used a sample/material of Grade 5 Titanium Alloy (Ti-6Al-4V) in the form of a plate. Next, 7 plates were cut with dimensions of 10x10x4mm and glued using resin to make sanding easier. The number or grade of the sandpaper which is used sequentially is 100, 120, 500, 800, 1000, and 2000. Sanding is done for each grade accompanied by water. After the sanding process, polish the sample until it has a glassy sheen on the surface. Remove each sample from the resin and clean it using an ultrasonic cleaner.

The nitridation coating process by varying N_2 and Ar gases of N_2 100%/0% Ar, 95% N_2/5% Ar, 90% N_2/10% Ar, 85% N_2/15% Ar, 80% N_2/20% Ar, 75% N_2/25% Ar. For each sample with a temperature of 400 ºC, time 5 hours, and a pressure of 1.6 bars. Furthermore, the test was carried out with the micro vickers hardness test and Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) to determine the microstructure and chemical composition contained on the surface of the sample. From the various research flows carried out, it can be seen in the research flow chart as shown in Figure 5.

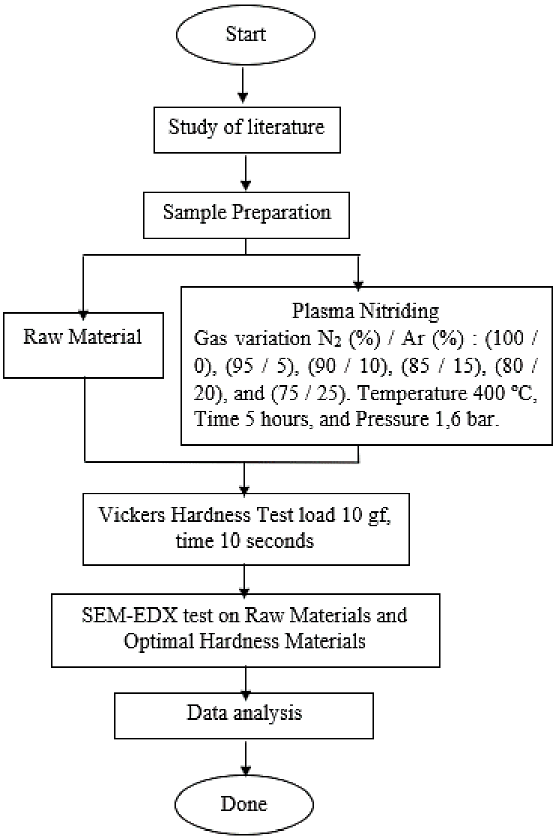


Fig 5. Research flow diagram

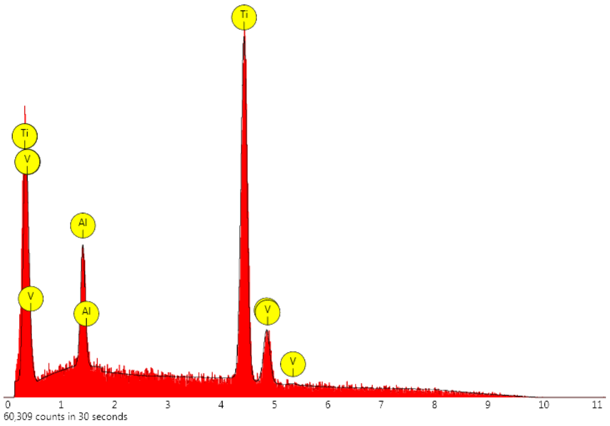


Fig 6. EDX test results on raw material

Table 1. The composition of the chemical elements contained in the material through the EDX test

Element symbol	Atomic Concentration (%)	Heavy Concetration (%)
Ti	83.32	87.47
Al	11.63	6.88
V	5.05	5.64

3. RESULT AND DISCUSSION

a. Composition Test

The composition test was carried out to determine the percentage of chemical elements contained in the sample using the SEM-EDX tool. Figure 6 shows the EDX test results on the raw material.

According to the EDX test results, the chemical composition of the materials used in this study is the right material. According to William [9], 6Al-4V Titanium has an oxygen content that can vary from 0.08% to more than 0.2% (by weight), nitrogen levels can be adjusted to 0.05%, and aluminum levels can reach 6.75 % and the vanadium content can be as high as 4.5%. When compared with the percentage of raw material EDX test results in Table 1, the materials used have almost the same elements.

b. Micro vickers hardness test

Hardness testing was carried out at the Physics Laboratory of the National Nuclear Energy Agency (PSTA-BATAN) Yogyakarta, the type of test used was Micro Vickers hardness with a loading of 10 gf, loading time of 10 seconds with 3 test points in each sample. This test aims to determine the hardness of Ti-6AL-4V material before and after nitriding, namely raw material, N_2 100%/0% Ar, 95% N_2/5% Ar, 90% N_2/10% Ar, 85% N_2/15% Ar, 80% N_2/20% Ar, and 75% N_2/25% Ar with a temperature of 400 °C, time of 5 hours, and a pressure of 1.6 bar. The results of the hardness test on the material before plasma nitriding and after plasma nitriding can be seen in Table 2. Based on this table, a graph is then obtained between the hardness and the percentage of mixing N_2 gas and Ar gas as is shown in Figure 7.

In this study, the nitriding process combines two different gases, namely argon and nitrogen gas. This process takes place when the two ions are fired onto the surface of the sample. The function of the argon ion is as a sputter ion combined with the nitrogen ion (reactive). The results of the comparison of the mixture of the two gases can be seen through the graph in Figure 7. The graph illustrates a condition where the higher the hardness of the sample, the less composition of the mixture in argon gas is given.

Table 2. The percentage is increase in the hardness value of Titanium before and after the plasma nitriding process.

No.	Composition of gas ratio (N_2 % : Ar %)	Hardness (HV)	Percentage increase (%)
1.	Raw Material	143	**0**
2.	Without Argon gas	305	**113**
3.	95 : 5	371	**159**
4.	90 : 10	310	**117**
5.	85 : 15	269	**88**
6.	80 : 20	250	**74**
7.	75 : 25	175	**23**

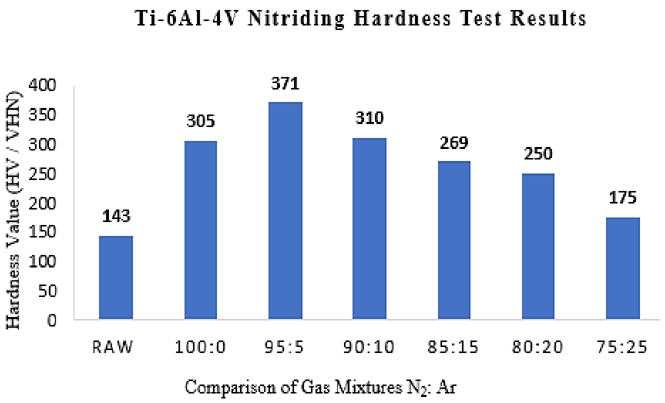


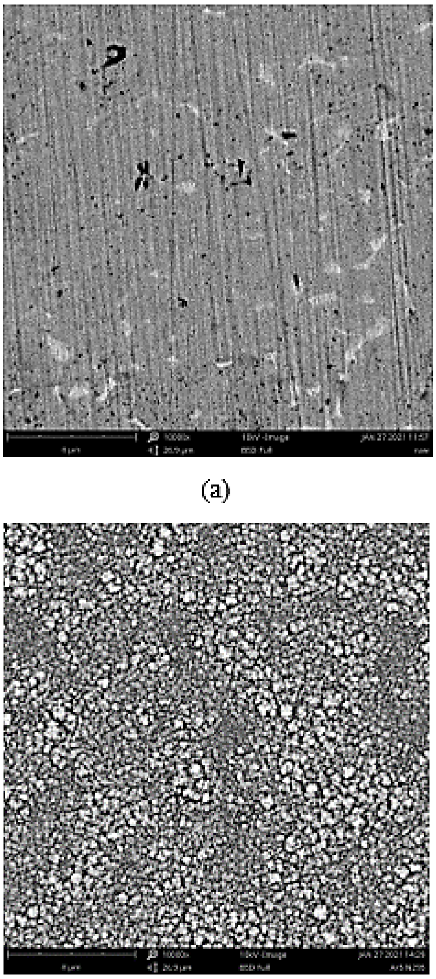
Fig 7. Graph of hardness values with percentage of N_2/Ar gas mixture

This is because the sputter process carried out by argon gas is relatively less than the deposition process [10],[11], considering that argon has a greater density when compared to nitrogen. Argon gas has a mass of 1.784 g/l and 1.251 g/l for nitrogen. Nitriding samples with variations in the ratio of the gas mixture N_2 and Ar get the optimum hardness in the gas composition with a ratio of 95% N_2 : 5% Ar. If the argon gas is increased, there will be an excessive sputtering process, so that the nitrogen ion deposition process to the surface decreases. For another reason the decrease in hardness in the sample besides the excessive composition of argon gas, namely the saturation phase. This decrease in hardness value occurs because the sample has reached the saturated phase and the mixed argon gas does not match the proportion anymore for sputtering [7].

c. SEM-EDX Test

Judging from the SEM test results with 10000x magnification, it can be seen that the microstructure morphology of the titanium samples before and after the nitriding process (as shown in Figure 8). It appears that there is a change in morphology on the surface of the sample from a striped structure (raw material) to a granular structure (samples with optimum hardness) which indicates the influence of the nitriding process. There was a change in morphology in the sample before and after nitriding, indicating the possibility of a change in the compound in titanium after undergoing the nitriding process.

The results of the chemical composition test (elemental content) on the sample with optimum hardness (90% N_2 : 5% Ar) shown by the SEM-EDX test can be seen in Table 3. The table shows that the Ti content is 23.39% (atom), Al 5.77% (atom), V 1.11% (atom), while N (nitrogen) from the plasma nitriding process is 32.82% (atom) or 11.93% (mass) and Fe (iron) 36.92% (atom) or 53.51% (mass). As a result of the addition (diffusion) of nitrogen into the sample interstitiously results in changes to the surface of the sample. This can be seen in Figure 8. (b) There is a change in the texture of the material which allows new compounds to occur on the surface of the sample. Metal compounds that may form during the plasma nitriding process on Ti-6Al-4V are iron nitride (FeN), titanium nitride (TiN), aluminum nitride (AlN) and vanadium nitride (VN) which have very high hardness properties [12-15]. The presence of Fe compounds after the nitriding process is possible due to the sprinkling of Fe atoms on the plasma reactor tube walls made of stainless steel, so that they also diffuse into the sample.


(a)

(b)

Fig 8. SEM test results (a) raw material (b) samples with a gas ratio of 95% N_2 : 5% Ar

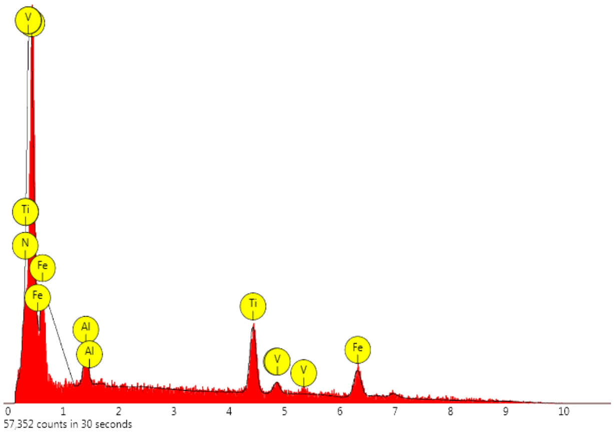


Fig 9. EDX test results on a sample gas ratio of 95% N_2 : 5% Ar

Table 3.The composition of the chemical elements contained in the sample with a gas ratio of 95% N_2 : 5% Ar through the EDX test

Element symbol	Atomic Concentration (%)	Heavy Concentration (%)
Fe	36.92	53.51
Ti	23.39	29.06
N	32.82	11.93
Al	5.77	4.04
V	1.11	1.47

4. CONCLUSION

Based on the research results obtained from testing and data analysis and discussion of the effect of plasma nitriding on the ratio of nitrogen (N_2) and Argon (Ar) gas mixture to Titanium (Ti-6Al-4V), it can be concluded that nitriding samples with variations in the ratio of the gas mixture get the optimum hardness on the gas composition with a ratio of 95% N_2 : 5% Ar. With this mixture, a hardness of 371 HV/VHN was obtained. In addition, an increase of 159% of the raw material with hardness value of 143 HV/VHN was observed.

Another conclusion is that the greater the dose of argon gas given, there will be an excessive sputtering process, so that the nitrogen ion deposition process to the surface of the sample decreases, and in turn, the hardness of the sample decreases.

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