Effect of Nitrogen-Based Ion Implantation on The Characteristics of 316L Stainless Steel for Implant Materials

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Abstract. The Effect of Nitrogen-Based Ion Implantation on the Characteristics of 316L Stainless Steel for Implant Materials has been performed. This study aims to determine the effect of variations in implantation energy on the characteristics of the surface mechanical properties, density, and corrosion resistance of 316L stainless steel. The 316L stainless steel plate was implanted with nitrogen ions with an optimum dose of 5 x 1016 ions/cm2 for various implantation energies of 70, 75, 80, 85, and 90 keV. The implanted samples were then characterized by density, hardness, corrosion resistance, and microstructure tests using SEM-EDX. The test results showed an increase in hardness and corrosion resistance in pieces implanted with nitrogen ions and reached the optimum point at an implantation energy of 80 keV. This was also supported by the results of the SEM-EDX analysis, which showed an addition of nitrogen content from the maximum limit of the ASTM 2000 standard for 316L stainless steel of 0.1% to 2.2%. Whereas in the density test, the density of the material tends to be constant at the energy variations carried out but has increased after implantation. Due to the lack of data used in training, the training data is less diverse, which causes when the program is tested, the program built is less training and gives an accuracy of 78—60%. However, referring to the original purpose of making the program for secondary opinion, practitioners can use the program.

INTRODUCTION

Metal is a material that is often used as an implant material in the medical world. The implant material must be biocompatible (acceptable by the body) and have mechanical properties to the human body's conditions. Clinical metals often used in implant materials are cobalt alloys, titanium alloys, and stainless steel (Giat et al., 2012). Stainless steel 316L is a type of stainless steel widely used for orthopedic surgery because of its corrosion resistance, good mechanical properties, and relatively low price (Sridhar et al., 2003). In addition, the availability of stainless-steel metal raw materials in the form of Ferro-Nickel in Indonesia is very abundant but has yet to be adequately utilized (Honest et al., 2013).

However, this stainless-steel material alloy has poor biocompatibility. Because based on previous clinical experience, it is known that 316L stainless steel is prone to local corrosion in the human body, which causes the release of metal ions around human implant tissue which can harm the patient (Sridhar et al., 2003). In addition, this type of stainless steel has lower mechanical properties than other implant materials (Park et al., 2007), so preventive efforts are needed to overcome this, one of which is by carrying out material engineering techniques on implant materials.

The ion implantation technique is the most effective way to modify surface properties without destroying the material's bulk properties. This technique is carried out by inserting high-energy foreign ions (dopants) into the surface of the target material at low temperatures so that the possibility of thermal stress can be avoided because material distortion can occur. In addition, the dimensions of the material did not change after ion implantation (Hongxi et al., 2012). The depth of ion insertion can also be controlled by controlling the voltage of the implanted ion accelerator (Sujitno, 2006). The maximum ion energy deposited in the material is strongly influenced by the mass of the ion and the target atom, so that it will determine the number of inserts forming a new phase (Susita et al., 1996).

The type of nitrogen ion is one type of dopant ion often used for biomedical applications (Pudjorahardjo et al., 2003). Nitrogen ions implanted in stainless steel will change the microstructure on the surface with a certain depth. The change in microstructure occurs due to the interaction of high-energy ions with the target, causing the formation of pairs of vacancies and interstitions which, under certain conditions, form the Fe-N phase (Susita et al., 1996). Sudjatmoko et al. (1999) stated that changes in the mechanical properties of a metal material occurred at doses between 1016 ions/cm2 to 1017 ions/cm2. At the same time, the variation of energy often used for ion implantation is 10 to 100 keV. The depth of insertion of atoms that is too deep can cause the material to become brittle (Susita et al., 1996).

In a previous study (Sudjatmoko et al., 2013), a nitrogen ion implantation process was carried out on stainless steel with ion energy variations of 60 keV, 80 keV, and 100 keV. At these ion energy variations, there was an increase in both hardness and corrosion resistance at the optimum energy of 80 keV. The optimum hardness of the material does not occur at a more incredible energy but at a specific ion energy. This is because the more significant the energy, the material’s surface will form an amorphous structure which will reduce the surface hardness value of the material. The new phase formed can potentially increase the corrosion resistance of the stainless-steel surface. The ion implantation process with nitrogen dopants is expected to increase its hardness and corrosion resistance. So ion energy is needed with the right nitrogen dopant to get the best characteristics.

Based on research conducted by Sudjatmoko et al. (2013), the range of ion energy variations is reduced at energies of 70 keV, 75 keV, 80 keV, 85 keV, and 90 keV at an optimum dose of 5x1016 ions/cm2. The characteristics of stainless steel resulting from nitrogen ion implantation can be seen through several tests. The test includes a density test to see the density of a sample, a hardness test to know the sample's resistance to pressure, a microscopic test to see the microstructure and determine the elemental composition, and a corrosion test to know the sample's resistance to corrosion.

Biomaterials are materials that are used in the medical world. Sudjatmoko (2008) in John (2005) states that biomaterials are used as a substitute or to improve the function of parts of the human body that are related on an ongoing or temporary basis, and while there is no contact in human body fluids in the short or long term. Therefore, a biomaterial must meet the requirements, including biocompatible; its mechanical and chemical properties must be acceptable to the body. In practical application, machines must quickly form biomaterials into several forms, have relatively lower prices, and these raw materials are widely available in the market (Cahyanto, 2009).

These requirements narrow down several other materials to be used in orthopedic surgery. Material applications in the medical field are divided into several types, including metals, ceramics, polymers, and composites. Each type of material has its characteristics, so its application in the body is adjusted to the features of the material.

Regarding wear and tear, stainless steel material has low hardness and poor tribological properties, thus shortening its service life. Tribological properties are related to the interaction between moving material surfaces resulting in friction, wear, and abrasion (Sudjatmoko et al., 2008). Wear on stainless steel can be repaired by surface treatment, one of which is by using ion implantation techniques.

Ion implantation is a surface modification technique by inserting dopant atoms into a target material with an accelerating voltage in units of electron volts. All mechanical, optical, magnetic, and superconducting properties are influenced and dominated by the presence of the dopant atom (Nastasi & Mayer, 2006).

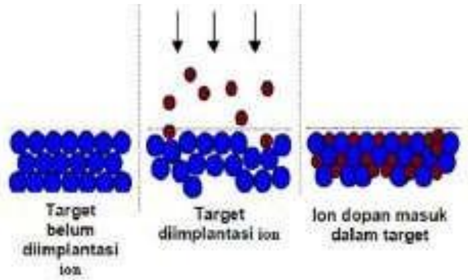

Figure 1. The arrangement of target atoms due to ion implantation

Each part of the ion implanter has the following functions:
1. Ion implants or ion sources produce ion types in gas or solid materials (Sujitno, 2006).
2. High voltage power source, each voltage has a different function. High voltage 0-5 kV is used for ion source supply. A 0-15 kV voltage feeds the extractor system (removing ions from the ionization chamber into the accelerator tube). A 0-200 kV voltage accelerates the dopant ions inside the accelerator tube (Sumaryadi, 2008).
3. Accelerator tube is a tube that is emptied to accelerate an ion before it hits the target material. This accelerator tube is made of ceramic material with many electrodes that focus charged ions that will hit the target material (Harianto et al., 2000).
4. Ion beam separating system, composed of magnets that separate ions from their elements (Nastasi & Mayer, 2006).
5. The sweeping beam system is a system that functions so that ion beams can be spread uniformly on the surface of the target material (Nastasi & Mayer, 2006).

6. Target site, the material to be implanted is placed in the target space.

This accelerator works by injecting ions from an atom into the surface of the target material. According to Sujitno (2006) in Djaloeis (1998), this process begins with the ionization of the atoms or molecules to be injected, accelerated in the accelerator tube by an electric field, focusing in an electromagnetic field, and then fired into the surface of the target material.

The ion implantation results on a material surface are strongly influenced by two parameters, ion energy and ion dose. The number of ions implanted per cm2 is given by equation :

$$D = \frac{it}{eA}$$

i = flowing current
t = duration of the implantation process (seconds)
e = electron charge (1.602 x 10^{-19} C)
A = cross-sectional area (cm^2)

The energy of the fired ions affects the distance of the ions. The length of the ion in the target measured from the ion entering the target until it stops at a location can be mathematically formulated by Equation :

$$R_i(nm) = \frac{13\,E_0}{\rho} . \frac{1 + \frac{m_i}{m_s}}{{Z_i}^{2/3}}$$

mi = masion dopan (sma)
ms = Massa atom target (sma)
Zi = nomor atom ion dopan
ρ = rapat massa target (gr/cm3)
E0 = energi ion datang (keV)

The process of implanting nitrogen in iron-based samples can increase the hardness of iron. This is possible due to the presence of impurities in the material. There are two types of impurities in materials, substitution and interstitial. The process of substitution in materials can occur when impurity atoms replace host atoms because their sizes are almost the same. Meanwhile, the interstitial process can occur when impurity atoms fill the gaps/cavities between the host atoms. In this process, the impurity atoms are smaller than the host atoms.

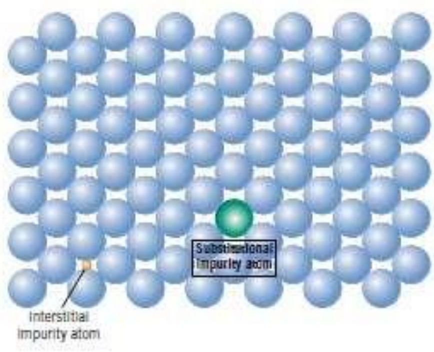

Figure 2. Interstitial Mechanism

Iron is a metal that has an atomic size larger than nitrogen atoms. In the process of implanting nitrogen ions, it is possible for nitrogen atoms to be inserted between the supporting atoms which are much larger than nitrogen atoms. The formation of this interstitial interaction mechanism makes it possible to improve the mechanical properties of a material.

EXPERIMENTAL METHOD

In this study the material used was SS 316L metal material which is widely available in the market. For sample preparation, namely diamond paste and alcohol. Nitrogen dopant material in gaseous form. To test the density of the material needed distilled water. Whereas in the corrosion test the materials needed for a solution are SBF (Simulated Body Fluid) solution with a composition of 1 liter of distilled water (Hank Solution). SS 316L material available in the market in the form of bars is prepared into cylindrical pieces with a diameter of 15 mm and a thickness of 2 mm.

Then the sample is smoothed on one surface using abrasive paper measuring 600 to 1800 to obtain a flat surface. The sample is then given diamond paste to make it look smoother and shiny. After that, the samples were washed with distilled water and alcohol to remove dust and residue from the previous abrasive powder.

Then the samples were fired with nitrogen dopant material with energy variations of 70 keV, 75 keV, 80 keV, 85 keV, and 90 keV, respectively. The amount of ion fired was maintained at a dose of 5 x 1016 ion/cm2 with a flowing ion current of 20 µA. It is hoped that optimal results can be obtained at the dose and ion current.

The implanted sample was weighed in water. Then compare its mass when it is in the water. The test is adjusted to the ASTM A378-88 test standard with the following equation :

$$\rho_{sampel} = \frac{Mu}{Ma}\rho_{air}$$

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The implanted sample was weighed in water. Then compare its mass when it is in the water. The test is adjusted to the ASTM A378-88 standard test with the following equation; then, a hardness test is carried out with a compressive force of 10 gf slowly for 15 seconds so that the results of the indentation are visible. After the force is removed, the indentation results are measured by the average length of the diagonal and then converted to the Mitutoyo table.

For corrosion testing with the Immersion Corrosion method, it is done by calculating the sample weight before and after ion implantation. Samples were weighed using a digital balance to determine the initial weight. Subsequent testing of the sample is put into a corrosive solution of SBF (simulated body fluid) and placed in a furnace at 37 degrees Celsius, representing human body fluids. The sample was immersed in SBF solution for 10 hours and weighed with a digital balance to determine the final weight of the piece. Then from the data obtained, the corrosion rate is calculated using equation :

$$Corrosion\ Rate\ \left(\frac{mm}{year}\right) = \frac{K.W}{A.t.D}$$

Furthermore, SEM testing was carried out to determine the microstructure formed from ion implantation samples, especially the morphology and layers formed on the sample's surface. Before the SEM characterization, the SEM-EDX type EVO.MA10 was vacuumed at a pressure of 2x10-6 mbar for five minutes. Furthermore, the sample to be used is prepared in advance. After the sample is ready, it is put into the specimen chamber to be observed for its microstructure on the SEM screen and analyzed. The results of the SEM image will display the topography (surface texture of the sample) and morphology (shape and size of the particles that make up the sample).

RESULT AND DISCUSSION

The prepared samples with a diameter of 25 mm and a thickness of 2 mm were implanted with nitrogen ions with various implantation energies of 70 keV, 75 keV, 80 keV, 85 keV, and 90 keV with ion doses maintained at 5 x 1016 ions/cm2. The implanted samples were then characterized by using several tests. The tests included a density test, hardness test, corrosion test, and microstructure observation using SEM-EDX.

From the results of the density test, it can be seen that the difference in outcomes between the control sample without implantation and the sample after implantation. This is because, in the nitrogen-doped implanted sample, smaller nitrogen ions with a diameter of 56 pm will diffuse between the target atoms (316L stainless steel), mostly dominated by larger Fe atoms (diameter 156 pm). With a fixed volume and increased mass due to the diffusion of these nitrogen ions, the empty spaces in the target material will be filled to increase density. The greater the density value, the more the material's mechanical properties will tend to increase.

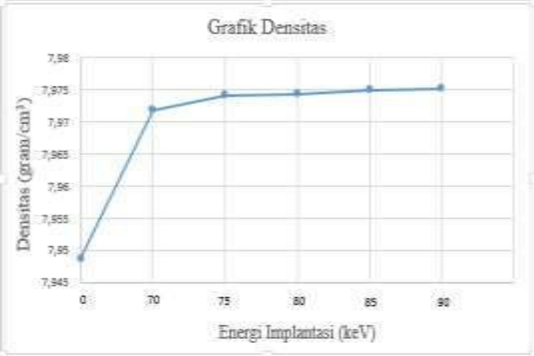


Figure 3. The density of The Sample Based on Implantation Energy

In Figure 3, it can be seen that the effect of variations in implantation energy on density shows a graph that tends to be constant. This is because the number of nitrogen ions fired at the target material is fixed, even though the implantation energy fired is different.

The hardness test results (in Figure 4) show the relationship between the variation in the implantation energy and the hardness value of a sample.

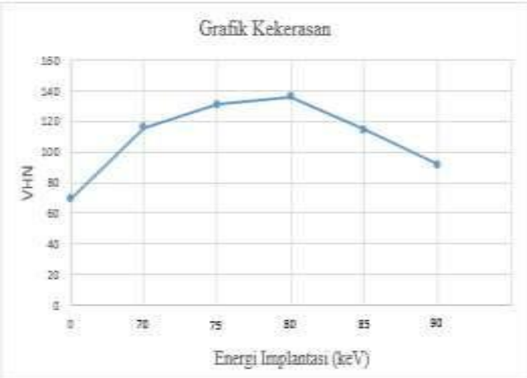


Figure 4. The Hardness of The Sample Based on Implantation Energy

These results indicate that the optimum hardness value in the 316L stainless steel sample occurs at an implantation energy of 80 keV, which is (136 ± 2) VHN. The figure also appears that the hardness value of the sample has increased along with the increase in the ion implantation energy fired into the sample. This is because the energy of the dopant ions fired into the target atoms shifts the target atoms from their original lattice position. Displaced atoms can also shift other atoms, resulting in successive collisions (Sudjatmoko et al., 1999). This event resulted in the accumulation of interstitial dopant ions (crystal defects) into the empty spaces of the target atoms. The higher the residual voltage of the dopant ions that hit the target material on the surface, the more density will increase because the empty spaces in the target material have been filled. As a result, the atoms in the target material will interlock (Giat et al., 2012).

At the optimum implantation energy, the defects formed on the target material have an optimum density level. The atoms in the target material will also be more and more interlocked. The consequence of this interlocking is that the grains cannot move anymore, so the hardness will increase.

In addition, Shen et al. (2004) increased the hardness of the samples resulting from nitrogen ion implantation because it was believed that a new nitride layer was formed in the modified layer. This is in line with research conducted by Sudjatmoko (2013), which stated that the increased hardness in the ion implantation process was due to the formation of a new nitride layer on the surface of the sample. However, in this study, it was impossible to prove the presence of a nitrogen layer on the sample's surface because no XRD test was carried out to see the bonds formed from the implantation of the nitrogen ion.

Figure 4 shows that the hardness value decreased at the variation of the implantation energy of 85 keV and 90 keV after reaching optimum conditions. This is because the more significant the implantation energy, the more amorphous the atomic structure will occur at a certain depth (Sudjatmoko, 2000). The emitted ion energy radiation is too high compared to the binding energy of the atoms on the surface of the target material, thus damaging the atomic structure in the surface layer (Susita et al., 1996). This event causes a decrease in the hardness value on the surface of the material.

The results indicate that the optimum hardness value can be used as a bone implant at the right ion implantation energy. By the ASTM F138 standard, the hardness of 316L stainless steel for bone implant applications has a maximum value of 95 HRB (Park, 2007), or in the Vickers test standard, a maximum value of 210 VHN. The test results above show that the optimum value of violence in samples with an implantation energy of 80 keV is still within the permitted standard limits. However, to obtain an increase in hardness closer to the standard, it is possible to increase the hardness by varying the ion doses fired. As for the corrosion test, it can be seen that the optimum corrosion rate occurs at a variation of 80 keV implantation energy with a corrosion rate of (0.0096 ± 0.0048) mm/year.

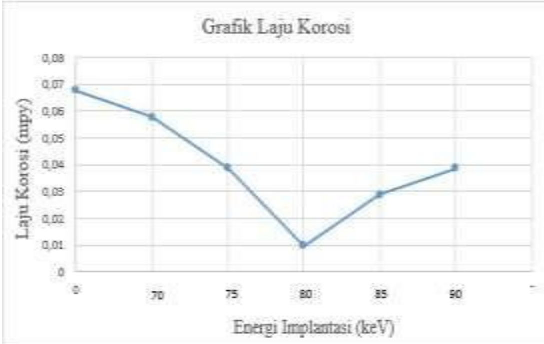
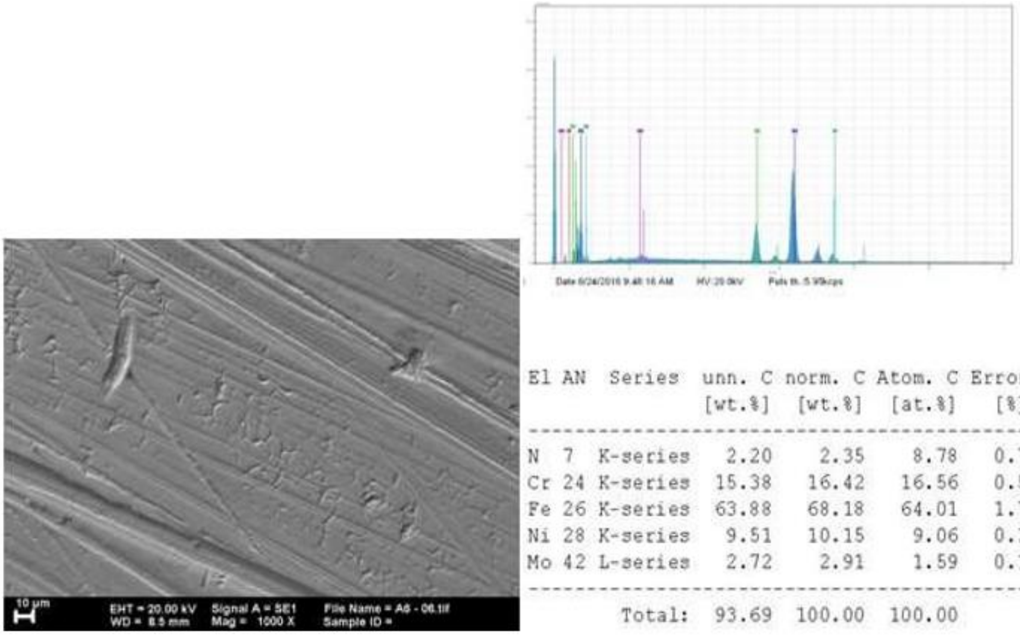


Figure 5. The Corrosion of The Sample Based on Implantation Energy

Figure 5 showed the value of the corrosion rate would decrease as the implantation energy increases. This is because the smaller nitrogen ions (56 pm in diameter) occupy the space in the target material, predominantly occupied by Fe atoms (156 pm in diameter). The implanted dopant ions cause the arrangement of atoms in the target material to become denser. The denser arrangement of atoms becomes a protective layer for the metal layer underneath so that it avoids direct corrosive media, which causes the corrosion rate to decrease.

However, in Figure 5, after reaching optimum conditions, the corrosion rate of the samples has increased at various ion energies of 85 keV and 90 keV. The increase in the corrosion rate of the samples after reaching these optimum conditions was because, in samples A4 and A5, the ion implantation energies were too large, which resulted in the dopant ions being shot, destroying the surface structure of the target material into an amorphous layer. The surface of this amorphous layer is easily oxidized (Pribadi, 2011), thus making the metal layer underneath unprotected. The corrosion rate will increase if the implantation process is continued with more incredible energy. The appearance of the microstructure after implantation in Figure 6 shows the morphological structure of the surface of 316L stainless steel implanted at an implantation energy of 80 keV, which looks rough with some domain boundaries that have crystal defects but are not so clearly visible.



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
N	7	K-series	2.20	2.35	8.78	0.7
Cr	24	K-series	15.38	16.42	16.56	0.5
Fe	26	K-series	63.88	68.18	64.01	1.7
Ni	28	K-series	9.51	10.15	9.06	0.3
Mo	42	L-series	2.72	2.91	1.59	0.1
		Total:	93.69	100.00	100.00	

Figure 6. The SEM-EDX result of The Sample Based on Implantation Energy

The appearance of the microstructure after implantation in Figure 6 shows the morphological structure of the surface of 316L stainless steel implanted at an implantation energy of 80 keV, which looks rough with some domain boundaries that have crystal defects but are not so clearly visible. The results of elemental composition analysis using EDX shown in Figure 6 also show a significant increase in nitrogen content of 2.2%. The maximum nitrogen content that makes up stainless steel, according to ASTM 2000 standards, is 0.1%.

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CONCLUSION

Based on a series of studies, analyses, and discussions that have been carried out regarding the effect of nitrogen-based ion implantation with variations in implantation energy, it can be concluded that variations in nitrogen ion implantation energy affect the characteristics of 316L stainless steel in terms of hardness and corrosion resistance of the material. Meanwhile, the density of the material tended to be constant but increased between before and after implantation. This can be seen from the rough surface morphology of the sample due to crystal defects. Samples owned the best variation of implantation energy with an implantation energy of 80 keV with optimum hardness and corrosion rate values of (136 ± 2) VHN and (0.0096 ± 0.0048) mm/year, respectively.

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