Analysis of nitrogen ion implantation on the corrosion resistance and mechanical properties of aluminum alloy 7075

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Abstract. The present work reports the effect of nitrogen ion implantation on aluminum alloy 7075. The microhardness, corrosion resistance, and surface nanostructure were investigated. The implantation was carried out at energy 60 keV with the ion doses used were $1.70 \times 10^{17}$ ion/cm$^2$, $1.86 \times 10^{17}$ ion/cm$^2$, $2.02 \times 10^{17}$ ion/cm$^2$, $2.17 \times 10^{17}$ ion/cm$^2$, and $2.33 \times 10^{17}$ ion/cm$^2$. The microhardness test was performed to study the hardness of the implanted layer which was characterized by X-ray Diffraction (XRD). The potentiodynamic corrosion test was performed in a 0.5 mol/l NaCl solution. The surface nanostructure was investigated by atomic force microscopy (AFM) to study the surface roughness after implantation. The results showed that the microhardness after implantation at $2.17 \times 10^{17}$ ion/cm$^2$ increased by 90.81%. The increase was attributed to the formation of the AlN phase. The AlN phase was confirmed at 2-theta peaks of 39.53°, 45.84°, 66.90°, and 80.54°. The corrosion test showed the improvement of corrosion resistance by the decrease of corrosion rate from 4.49 mpy to 1.43 mpy. The atomic force microscopy showed the arithmetical mean height (Sa) value was 37.5 nm and the root means square (Sq) value was 47.6 nm. The ion implantation induced the change of material surface due to the penetration of nitrogen ion into the material.

1. Introduction

Aluminum and its alloy are widely used in life. Aluminum alloy 2xxx, 6xxx, 7xxx, and 8xxx series are known as common material used in aerospace applications [1]. The fuselage, the upper wing surface, and the spars are commonly used 7xxx series which is aluminum alloy 7075 [2]. Aluminum alloy 7075 is chosen due to the lightweight and high strength. However, the aluminum alloy 7075 contains zinc which is anodic so the material is susceptible to stress corrosion cracking (SCC) [3]. This material also susceptible to some form of corrosion such as pitting corrosion, intergranular corrosion, and exfoliation corrosion [4], [5]. High operating hours and various kinds of weather can also affect the lifetime of material and the corrosion rate of the material.

Ion implantation is well known to improve the properties of a material without changing its bulk properties. This technique works by injecting ion to the material using an accelerator tube so the dopant ion will interact with the target atoms [6]. The implantation technique has a number of advantages, for example the implantation fluence can be controlled and no needed for high temperature during the process [7].
Several works showed the benefit of the ion implantation technique. The formation of the aluminum nitride (AlN) layer indicated the increase of hardness and high wear rate along with the increase of ion dose. This improvement occurs until it reaches the optimum dose. Another work has shown the effect of nitrogen ion implantation on the corrosion resistance of aluminum and its alloys. The result presented the improvement of corrosion resistance on the material [4], [5], [8]–[14].

Based on the previous works, therefore it is known that the ion implantation technique at optimum dose can improve the properties of the material. So, the aim of this work is to know the effect of ion implantation on mechanical properties and corrosion resistance of aluminum alloy 7075.

2. Experimental Procedure

The sheet of aluminum alloy 7075 was cut into a disc shape with a 14 mm diameter and 5 mm thick using a water jet cutting machine. The composition of material obtained from the spectrometer test was 87.47% Al, 7.5% Zn, 2.6% Mg, 0.33% Ti, 2.1% Cu. Samples were ground using SiC papers from 1000-grade up to 3000-grade. After ground, samples were polished with diamond paste. Samples then washed using liquid soap and alcohol by ultrasonic cleaner for 5 minutes and 20 minutes for each process.

Simulation using Stopping and Range of Ions in Matter (SRIM) was done before the ion implantation process to see the simulation of ion distribution. The ion implantation process was carried out at PSTA – BATAN, Indonesia. The energy used was 60 keV with the ion doses used were 1.70 \times 10^{17} \text{ion/cm}^2, 1.86 \times 10^{17} \text{ion/cm}^2, 2.02 \times 10^{17} \text{ion/cm}^2, 2.17 \times 10^{17} \text{ion/cm}^2, and 2.33 \times 10^{17} \text{ion/cm}^2. The vacuum level obtained was 2 \times 10^{-7} \text{Torr} to minimize contamination.

The microhardness test was at PSTA – BATAN using microhardness tester Vickers Matsuzawa MMT-X7. The hardness test was carried out on initial material and 5 implanted samples on various doses. The load used was 1 gf for 10 seconds for each sample.

The corrosion test was at Material Engineering Laboratory, UGM. The electrochemical method was performed using potentiostat Princeton Applied Research Versatat 4 instrument. The samples characterized were the initial material and the sample that has the highest hardness value. Each sample was exposed to the 0.5 mol/l NaCl solution then the corrosion rate was analyzed in mpy (mils per year) unit.

The crystal structure for initial material and implanted sample that has the highest value were analyzed by X-ray Diffraction meter (XRD) at Chemistry Laboratory, UNY. The operation was carried out at 40 kV and 15 mA. The source used was Cu-Kα with the wavelength was 1.54 Å. The 2-theta angle used was at 10° - 90°. This characterization was performed to see the existence of the AlN layer after the ion implantation process.

The roughness test was carried out using Atomic Force Microscopy (AFM) NEOS N8 at Energy Laboratory ITS. The AFM result showed the 2D and 3D surface morphology of the material. The sample characterized was the implanted sample which has the highest hardness value. The aim of this characterization was to know the effect of ion implantation on surface morphology.

3. Result and Discussion

3.1. Hardness Measurements

The load used was 1 gf with the indentation time was 10 seconds. Micro indentation measurement is needed on the hardness thin layer because the penetration depth is limited to 10% of film thickness. This is intended to avoid the influence of bulk material [15].

Figure 1 shows typical hardness profile measured on unimplanted and implanted samples. It shows that the hardness value on the unimplanted sample is 23.3 VHN. The hardness value for implanted samples from the lowest dose to the highest dose is 27.03 VHN, 28.06 VHN, 30.73 VHN, 44.46 VHN,
and 27.30 VHN. The maximum improvement occurs 90.81% from the initial material at $2.17 \times 10^{17}$ ion/cm$^2$ dose.

Figure 1 also shows that hardness value for implanted samples is increasing until it reaches the optimum dose. The increase of hardness value is due to the collision between nitrogen ion and material atoms during the ion implantation process which causes the detached of atoms from its orbit. Nitrogen ions will fill the emptiness so the new layer of AlN is formed. From several works related to ion implantation on aluminum alloy, it is known that the improvement of hardness value occurs due to the formation of the AlN layer which increases the hardness and reduces the wear rate of the material. Although the improvement factor is affected by the implantation process condition and the material itself [4], [9], [10].

After the optimum dose is reached, the hardness decreases to be 27.3 VHN. This can be caused by the emptiness after the collision is full already so the material is saturated. Adding more ions to this condition will cause a lot of defects on the material surface. This resulted in the hardness value is decreased [16].

![Hardness Value for Initial Material and Implanted Samples on Various Doses](image)

### Figure 1. Hardness Value for Initial Material and Implanted Samples on Various Doses

#### 3.2. Crystal Structure

Crystallography measurement was carried out at 10° - 90°. The result for the unimplanted sample and implanted sample at $2.17 \times 10^{17}$ ion/cm$^2$ dose is shown in Figure 2. In Figure 2 the black line shows the result for initial material while the blue line shows the result for the implanted sample.

At the initial material, it is known the experimental data is related to COD data entry number 96-900-8461 which is the aluminum database on Match! 2 programs. The 2-theta peaks are at 38.43°, 44.77°, 65.23°, 78.11°, 82.37°. The experimental result of the implanted sample is related to COD data entry number 96-152-3096 which is the AlN phase data base. The report shows that the 2-theta are at 39.53°, 45.84°, 66.90°, 80.54°. As can be seen from Figure 2 there is a difference between the XRD pattern for initial material and implanted sample. The pattern is shifted and the new peak is showed up after ion implantation. This phenomenon can be caused by the nitrogen ion shifted the atom of material so the angle incident was changed.

From previous works, Abdi and Savaloni said that the intensity of XRD peaks on implanted sample aluminum alloy 7049 was relatively decreased compare to the unimplanted sample. The AlN phase was formed at 2-theta 44.8°, 65.2°, 78.39°, 82.6°, 99.31° [17]. The result is almost similar to this work, so it can be said that the AlN phase is formed on this work. However, further analysis is needed to corroborate the result.
3.3. Corrosion Test

Figure 3 shows the result of the unimplanted sample and implanted sample at $2.17 \times 10^{17}$ ion/cm$^2$ dose. The curves are relatively similar but the implanted sample has a lower current density ($I_{corr}$) than the unimplanted sample. The implanted sample also has more positive corrosion potential ($E_{corr}$) value than the unimplanted sample. The lower of $I_{corr}$ and more positive of $E_{corr}$ make the implanted sample has a lower corrosion rate than the unimplanted sample.

The analysis using the VersaStudio program showed that the corrosion rate for the initial material is 4.49 mpy while the corrosion rate for the implanted sample is 1.43 mpy. The decrease of corrosion rate at implanted samples means that the resistance of corrosion is increased. This improvement is due to the new phase of the AlN layer formed on the sample after the implantation process. The resistance of corrosion is also caused by the native oxide layer contained on aluminum. Therefore, these two layers protect the material from the corrosion process so the corrosion resistance is increased [18].

Previous work related to the characterization on corrosion properties after ion implantation showed that the change of corrosion potential ($E_{corr}$) value to be more positive and lower current density ($I_{corr}$) value indicated improvement of corrosion resistance after implantation process [19]. Another work showed the same result. The potentiodynamic curve for implanted aluminum 7075-T6 and aluminum 7075-T73 has a lower current density ($I_{corr}$) value which means the corrosion resistance increased due to obstruction of redox process [20].
3.4. Roughness Measurement

The roughness measurement was carried out at $2.17 \times 10^{17}$ ion/cm$^2$ implanted sample. Figure 4 shows the result of roughness measurement both 2D and 3D. Figure 4(a) shows the 2D graph for the surface morphology. It can be seen that the roughness means (Ra) value is 37.5 nm and the root mean square (RMS) is 47.6 nm. In Figure 4(b), there are hills cone-shaped. The distribution of these hills is almost evenly distributed. This structure can be caused by the penetration of high energy nitrogen ion into the sample.

In several study related roughness measurement after ion implantation, it is observed that the ion implantation modify the surface structure of the material. The change of surface structure can be caused by the penetration of N$^+$ ion to the material. The roughness value of the sample also depends on the energy used, the surface condition before implantation, the implanted element, and the implantation dose [8], [9], [11], [21].

![Figure 3. Potentiodynamic Polarization Curves for Implanted Sample on $2.17 \times 10^{17}$ ion/cm$^2$ and Raw Material](image)

![Figure 4. Surface Morphology for Implanted Sample on $2.17 \times 10^{17}$ ion/cm$^2$: (a) 2D; (b) 3D](image)
4. Conclusion

Analysis of the effect of nitrogen ion implantation on aluminum alloy 7075 was done. The highest hardness value obtained was 44.46 VHN or it increased 90.81% from raw material. The corrosion rate reduced from 4.49 mpy to 1.43 mpy. The improvement of hardness and the reduction of corrosion rate can be caused by the formation of AlN layer which shown by XRD result at 2-theta 39.53°, 45.84°, 66.90°, dan 80.54°. The atomic force microscopy (AFM) showed the arithmetical mean height (Sa) value is 37.5 nm and the root mean square (Sq) value is 47.6 nm. The ion implantation induced the change of material surface due to the penetration of nitrogen ion into the material.

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