

Effect of Nitrogen Ion Implantation on the Surface Hardness, Corrosion Rate, and Crystal Structure of Pure Aluminium

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Abstract: The weakness of aluminium and its alloys are relative low hardness and wear resistance. To improve this weakness a nitrogen ion implantation technique has been carried out. For the purpose, an ion implantation process was carried out for various of dose such as 0.578×10^{16} ion/cm², 0.706×10^{16} ion/cm², 0.842×10^{16} ion/cm², 0.970×10^{16} ion/cm², and 1.106×10^{16} ion/cm² at a certain energy and beam current, 60 keV and 75 μ A, respectively. Hardness test was performed using microhardness tester, the corrosion resistance was tested using the electrochemical method, and the crystal structure was analyzed using X-ray diffraction. From the hardness test result, it can be concluded that the optimum hardness in order of 37.5 VHN was achieved at an ion dose of 0.83×10^{17} ion/cm². While the hardness for the untreated sample was 18.70 VHN. It meant, there is an increasing hardness by a factor of 100,53%. At these conditions, the corrosion rate reduces from 0.012 mmpy to 0.011 mmpy or reduce by a factor of 8.3%. Based on the XRD analysis, it can be obtained the AlN phase is formed through the peaks at 2-theta was 39.37° (111), 45.76° (200), and 66.88° (202).

Keywords: Ion Implantation, Hardness Test, XRD, Corrosion Rate, Pure Aluminium

1. Introduction

Aluminium and its alloys have been widely used in the chemical, aerospace, food, automotive, electronics and marine industries due to their low price, high wear resistance, low density and great strength [1]. However, the application of Aluminium alloys is restricted by their high chemical activity and potentially poor corrosion resistance. Although the formation of an oxide layer increases the corrosion resistance of the alloy, this layer is easily eroded. This erosion can be attributed to defects in the oxide layers. Defects are more likely to be exposed to the atmosphere and suffer attacks from chloride ions, leading to more serious corrosion cracks [1, 2].

There is a growing interest in extending the use of aluminium alloys, especially in motor vehicles components, in order to achieve better energy efficiencies through weight reduction. But the relatively low hardness, and low wear resistance of Aluminium alloys make these alloys especially prone to wear in sliding and rolling contact situations, which is

a major constraint for their use. Although requirements for these applications can be met through the use of Aluminium matrix composites, the cost of manufacturing these components makes the application of surface engineering methods a more cost-effective approach [2, 3].

To improve the quality of the Aluminium surface, there are various types of surface coatings available to engineers, some technique can be applied such as Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD) or Ion Implantation (II). Several studies showed that nitrogen ion implantation could increase tribology properties such as hardness, wear resistance, fatigue life and corrosion resistance [4-7]. Some elements such as N, Ti, and Cr increase occurrence of new phase formation and microstructure alteration as well as the chemical and mechanical properties [8]. However, among those ions, the ion that is an interstitial solute which can contribute to the formation of Aluminium nitride phase on the surface [8]. The importance of Aluminium nitride (AlN) is due to its excellent strength-to weight ratio, reasonably good corrosion resistance [9], extreme hardness, its electrical

insulating properties (a band gap approximately 6.3 eV) and its high melting point (about 2400°C [10]). Its light weight, high shearing strength, and its high corrosion resistance [11].

Ion implantation is a surface modification technique by which atoms or molecules are ionized, accelerated in an electrostatic field, and implanted into the surface of a substrate. This technique produces a modification in the structure of targets (metal) surface by formation of new crystalline phases, metastable or amorphous, and those to improve the surface properties [3]. A great advantage is the negligible effect of ion implantation on the dimensions of the treated element; hence, the process can be applied in the final stage of manufacturing of products that already have their final dimensions [12]. Besides improvement of tribological properties, ion implantation contributes to an increase in mechanical strength. This is associated with an increase in the microhardness of the implanted samples. The implantation process is accompanied with appearance of compressive stresses and inclusions of nitrides. The implantation-induced hardening process depends on the type and dose of implanted ions and the temperature of the implanted material. The introduction of new atoms in the crystal lattice is not the only effect of ion implantation but also, the damage originated in the crystal structure of the target by the energetic collision cascades must also be taken into account [13].

As each ion penetrates the target, it undergoes a series of collisions displacing host atoms along the way. Both the ion and dislodged target atoms can continue and cause further damage, and so the energy is spread over many moving particles. Therefore, after implantation of high doses of ions an initially crystalline target will be so perturbed that it will have changed to a highly disordered state [14]. The amount of crystallographic damage can be enough to cause the partial amorphization of the metal surface, depending on the dose, energy, temperature (governing self-annealing that can occur to repair some or all of the damage as it is generated) and ion species (heavy ions displace a greater volume of target atoms per ion [15]). Finally, the implantation of high dose of ions induces significant compressive stress that can contribute to the blocking of the fissures and close the channels of corrosion [2].

A great advantage of ion implantation technique compare to

others method is the negligible effect of ion implantation on the dimensions of the treated element; hence, the process can be applied in the final stage of manufacturing of products that already have their final dimensions [16, 17].

2. Methodology

In this experiments rectangular AA 5086 Aluminium plate was cut into specimens 4 mm×14 mm in size in a disc shape using *wather jet cutting*. The specimens were grounded with SiC papers from # 80 up to 5000 mesh and polished mechanically with 1 μm diamond paste. The polished specimens were washed with acetone in an ultrasonic cleaner and dried at room temperature. The samples were implanted by using 150 keV/2 mA ion implanter that's performed at dose 3.107×10^{16} ion/cm², 3.148×10^{16} ion/cm², 3.728×10^{16} ion/cm², 4.039×10^{16} ion/cm² and 4.35×10^{16} ion/cm² and at 60 keV of ions energy. The increase of the sample temperature was ensured solely by incoming ion beam without any additional heating. The chemical compositions of AA5086-is 0.4% Si, 0.5% Fe, 0.1% Cu, 0.35% Mn, 4.0% Mg, 0.15% Cr, 0.25% Zn, 0.15% Ti, balance Al.

3. Result and Discussion

3.1. Analysis of the Hardness

The effect of nitrogen ion implantation in micro hardness properties of samples was tested by using Vickers Tester Microhardness Tester type MTX7 type (see Figure 1). It can be concluded that the hardness of samples improves after nitrogen ion implantation and extend of improvement increases with dose. The maximum hardness appears at a nitrogen ion dose of 0.706×10^{16} ion/cm². In this condition, the hardness increases from 18.7 VHN (raw material) to optimum 37.50 VHN or increase by factor 100.53%, while the corrosion rate reduces from dose 0,012 mmpy to 0,011 mmpy or reduces by factor 8.3%. Over this dose the hardness decreases, this decrease is may be caused by defect due to the excess ion irradiation. Effect of nitrogen ions doses on the surface hardness of implanted samples is presented in Figure 1.

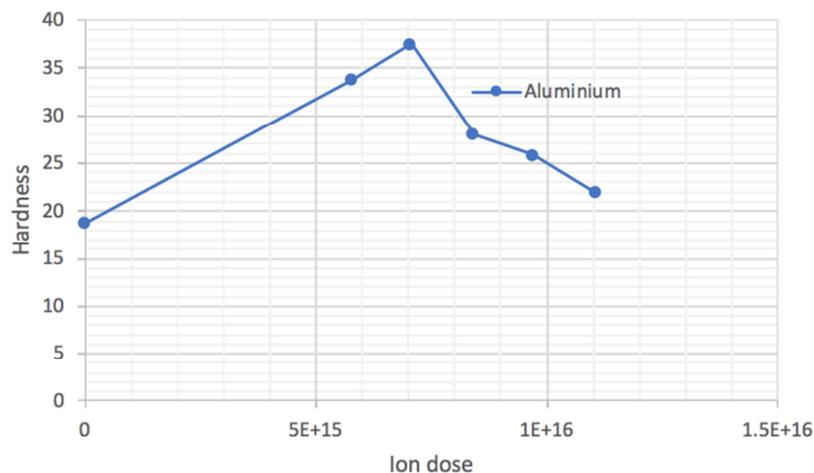


Figure 1. Effect nitrogen ions doses on the surface hardness of pure aluminium.

3.2. Corrosion Measurement

Electrochemical measurement were carried by using three electrode Potensio Galvanostat VersStat 4 type in 3.5% NaCl solution. Tafel plot measurement were carried out using conventional three electrode Pyrex glass cell with platinum counter electrode and Ag/AgCl electrode as reference electrode. Finally, un-implanted and implanted specimens (at optimum conditions) of 1 cm², surface area were exposed to corrosion medium of 3.5% NaCl solution. The potensidynamic current potential curves were recorded by polarizing the specimen to -250 mV cathodically and 250 mV anodically with respect to open circuit potential at scan rate of 5 mVs⁻¹. The

potensidynamic polarization parameters like corrosion potential (E_{corr}), corrosion current (i_{corr}), polarization resistance (R_p), anodic and cathodic slopes (b_a and b_c), and corrosion rate are calculated from Tafel plots. Potentio dynamic polarization curves for un-implanted and implanted specimens at optimum conditions is presented in Figure 2. It's observed that there is shifting in the corrosion potential E_{corr} from - 0, 410,378 mV to - 399,951 mV, and there is a reducing in corrosion rate from 0.012 mmpy, to 0,011 mmpy, or there is an increasing corrosion rate by factor 8.3%. The positive shift in the corrosion potential E_{corr} , indicates that anodic process is much more affected than the cathodic.

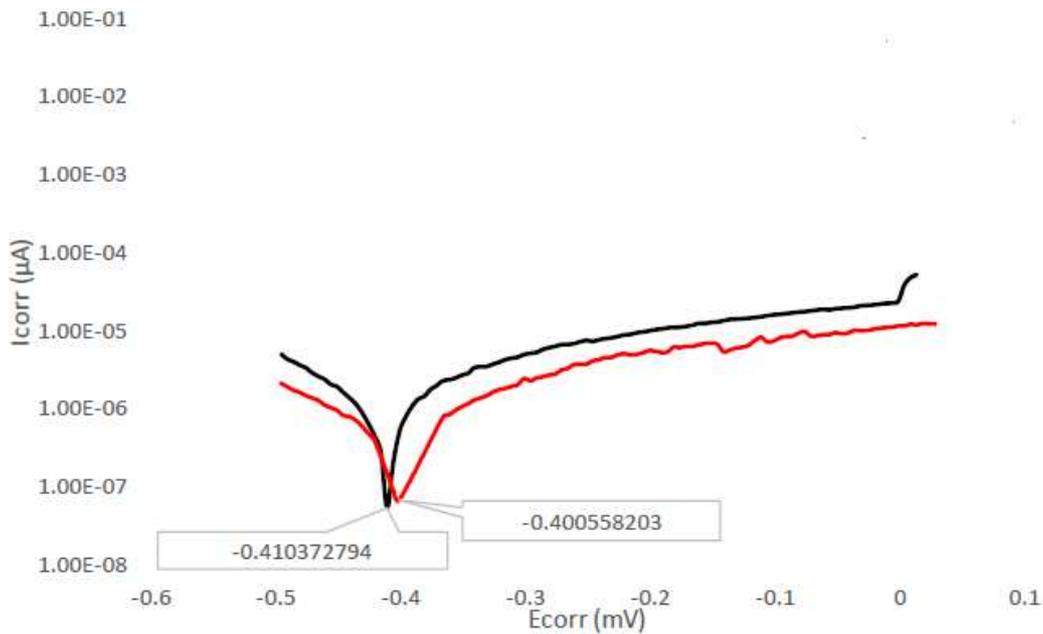


Figure 2. Potentio dynamic polarization curves for un implanted and implanted samples of pure aluminium in 3.5% NaCl solution.

3.3. XRD Analysis of Implanted and Un-implanted Samples

The phase composition of un-implanted and implanted samples was analyzed using X-rays in the θ - 2θ mode and $\lambda = 1.548 \text{ \AA}$ of Cu K_{α} radiation. Figure 3 or Table 1 shows the XRD patterns of un-implanted samples materials. From the patterns shown that four peaks (111), (200), (202) and (301) with cubic structures at $2\theta = 38.71^{\circ}$, 45.07° , 65.14° , and 78.48° respectively which were related to the aluminium alloys

substrate with the main elements is Aluminium (Al) and after being analyzed using *Crystallography Open Database (COD)*, entry number 96-901-2003 code, it's observed that the phase is 100% of Al. For implanted samples at optimum conditions which is presented in Table 2 or Figure 4 and after being analyzed using *Crystallography Open Database (COD)*, entry number 96-152-096 code, it's observed that the phase is 100% of AlN.

Table 1. Peaks positions of un-implanted materials of AA 5086.

$2\theta_{meas.}$	$2\theta_{cat.}$	Intensity	hkl
38.71	38.538	100	111
45.07	44.798	469	200
65.14	65.215	263	202
78.48	78.3866	278	301

Table 2. Peaks positions of implanted materials of AA 5086.

$2\theta_{meas.}$	$2\theta_{cat.}$	Intensity	hkl
39.7	39.4	275	111
45.76	45.81	1000	200
66.88	66.80	497	202

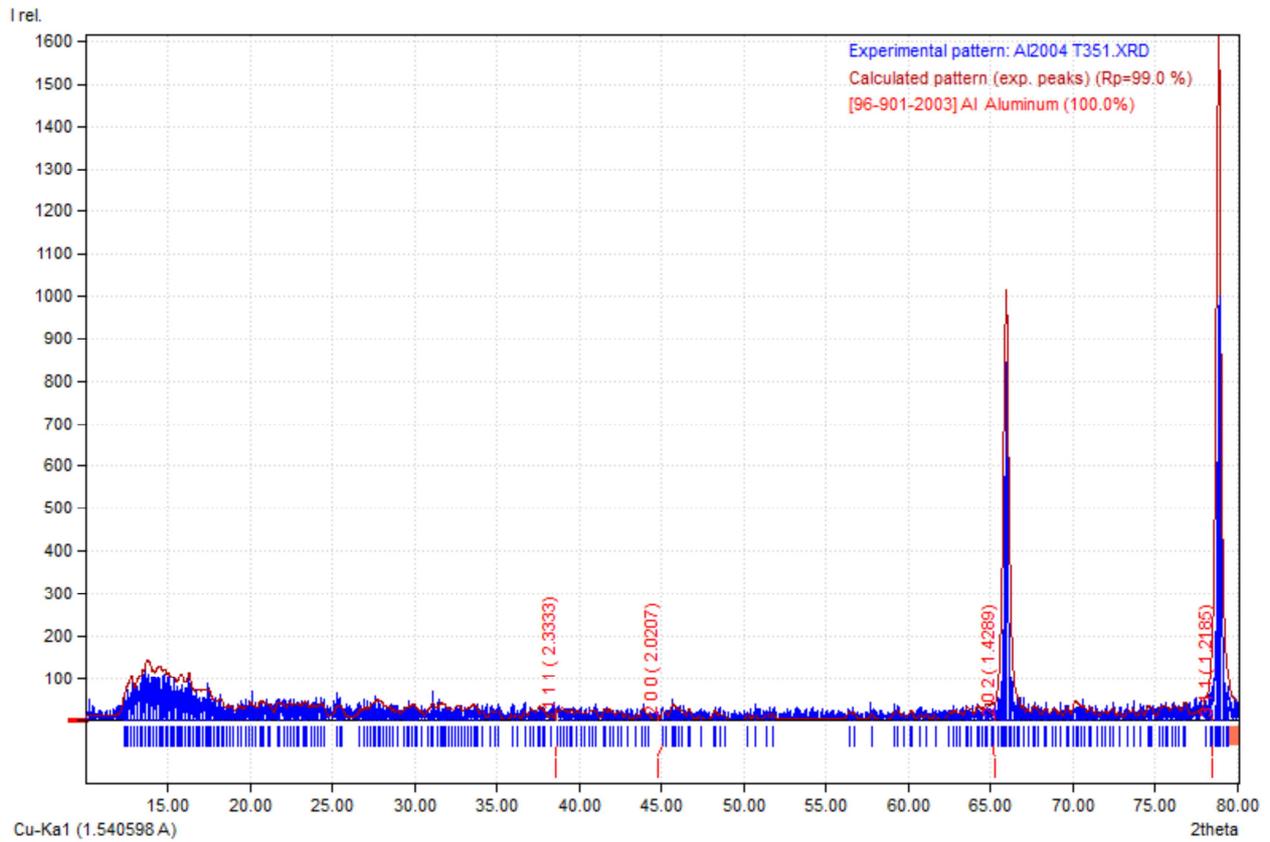


Figure 3. Diffractogram of the un-implanted samples materials of Aluminium.

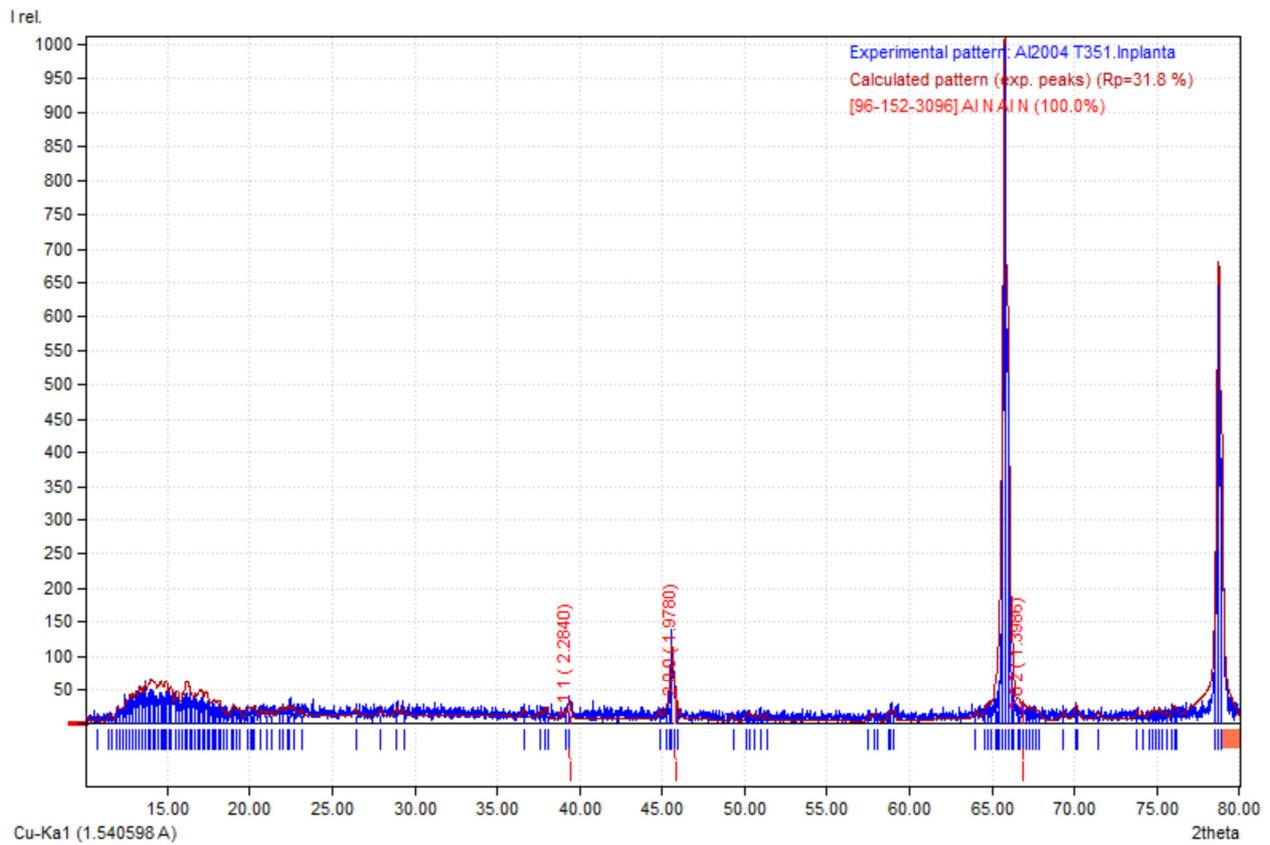


Figure 4. Diffractogram of implanted samples with nitrogen ions at energy of 60 keV for 54 minutes of implantation time or 0.706×10^{16} ion/cm² of ions dose (100% of AlN phase).

4. Conclusion

Based on the experiments carried out, it can be concluded as follow:

The hardness of un-implanted materials is 18.70 VHN. The optimum hardness order of 37.50 VHN or increases by factor 100.53%, appears at a nitrogen ion dose of 0.706×10^{16} ion/cm². Over this dose, the hardness decreases, this may be caused by defects due to the excess ion irradiation. Increasing in hardness is mainly caused by the formation of Aluminium Nitride (AlN) new phase, this phase is indicated by XRD analysis shown by Figure 2 and Figure 3.

In the corrosion test, it's observed that there is shifting in the corrosion potential E_{corr} from $-0,410,378$ mV to $-399,951$ mV, and there is a reducing in corrosion rate from 0.012 mmpy to 0,011 mmpy, or there an increasing in corrosion rate by factor 8.3%. The positive shift in the corrosion potential E_{corr} , indicates that anodic process is much more affected than the cathodic.

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