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Increase in Hardness and Chloride Corrosion Resistance of 6061 Aluminum Alloy by Pulsed Plasma Nitriding

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***Abstract*— Enhancement of hardness and corrosion resistance of aluminum alloys persist as an important challenge in order to increase the lifetime of industrial parts and accessories. This improvement of surface properties must be accomplished by low cost and minimum environmental impact processes. On these considerations, in the present work DC pulsed plasma nitriding at rough vacuum (1.9 torr) was carried out on 6061 aluminum alloy using different N_2/Ar mixtures (100/0, 50/50 and 75/50) to sustain the DC glow discharge. Influence of gas mixture on surface morphology, hardness, phases composition and corrosion performance was evaluated through scanning electron microscopy, Vickers micro indentation, X-ray diffraction and potentiodynamic polarization curves (3.5% NaCl), respectively. For the better evaluated case ($50N_2$/50Ar mixture), results show the increase in surface hardness from 113 to 148 $HV_{0.025}$, and the decrease in the corrosion current value to an a half respect untreated sample. The increasing in hardness and corrosion performance of evaluated aluminum alloy was attributed to the chemical surface modification by formation of a thin layer constituted by cubic and hexagonal aluminum nitrides.**

***Keywords*— Aluminum 6061, corrosion resistance, hardness, plasma nitriding.**

I. INTRODUCTION

The tribological problems, as well as the corrosion phenomena taking place on metallic materials, continue being important challenges facing in order to streamline several industrial processes and to reduce the costs of them. These challenges are clearly evident for the case of aluminum and its alloys, which are characterized by interesting properties such as light weight, high specific strength, good machinability and corrosion performance. Although these alloys are used in many industrial applications such as automotive, aeronautics, food and chemical, their main limitation to expand its range of applications is related to the lack of surface hardness and other tribological qualities.

Based on the expressed requests for the increase of surface properties of aluminum alloys, different surface modification processes have been conducted on aluminum and its alloys. Technologies such as physical and chemical vapor deposition [1], anodizing [2] and plasma enhanced thermochemical treatments [3,4,5] have been used for these purposes. In the last years it has been reported the considerable increase in tribological properties of this materials, as a result of nitrogen surface incorporation by plasma assisted thermochemical treatments. Through this processes, which can be identified as DC plasma nitriding, Inductively plasma nitriding and plasma immersion ion implantation, it is possible to produce AlN thin layers characterized by its high hardness and thermal conductivity as well as high wear and corrosion resistance properties.

Plasma assisted process using surface nitrogen introduction have become the focus of several researchers, mainly because these techniques allow the high control of the several process parameters. Additionally, it is widely reported that the use of this kind of processes promotes the increase in life time products with a minimized environment impact. Although the advantage related to this processes, the technological variants as plasma immersion ion implantation (PIII) and inductively plasma nitriding does not find jet, any large-scale industrial application mainly because to its high cost and complicated equipment [6].

In contrast, direct current (DC) pulsed plasma nitriding, a rough vacuum variant of plasma enhanced processes for nitrogen introduction, has proved its industrial functionality. In this sense, it is considered as promising method to obtaining AlN in the surface of aluminum and its alloys. This technique is characterized by the use of simpler equipment with lower energy consume than previously enounced techniques. On these bases, exists considerable interest for development of a practical methodology which promotes the effectiveness of this plasma nitriding aluminum process.

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In order to contribute to the last enounced, DC pulsed plasma nitriding process on aluminum 6061 was carried out and evaluated in the present work. There is analyzed the effect of the use of three different processing atmospheres during pulsed plasma nitriding of aluminum 6061 on surface hardness, corrosion resistance and surface morphology. Process was carried out keeping constant variables such as temperature, frequency, duty cycle, processing time and discharge current density.

II. Experimental Procedure

Samples of 6061 commercial aluminum square bar of 2.54 X 2.54 X 0.5 cm were mechanically ground using SiC emery paper (120, 240,360, 400, 600,800,1200 grit) and polished to mirror-like surface using 2 µm diamond and 0.5 µm alumina abrasives. Previous plasma processing, polished samples were cleaned in an ultrasonic bath with acetone. The nominal chemical composition of the alloy 6061, determinate by optical emission spectroscopy, is (all in weight percentage): Mn 0.02, Si 0.66, Cr 0.10, Sn 0.01, Mg 0.85, Pb <0.01, Zn 0.02, Ni 0.01, Cu 0.21, Fe 0.21, Ti 0.02, Al Balance.

Polished and cleaned samples were placed in an own design laboratory reactor with 42 liters of useful volume. The vacuum reactor is a cylindrical chamber which was pumped down to a base pressure of 10^{-3} Torr. A central cathode (samples holder) is negatively biased respect to the vessel wall by means a specifically designed high voltage pulsed power supply; an auxiliary heating system affords full control over the sample temperature. The gas inlet system allows a precise control on pressure and gas mixture ratio due to the use of mass flow controllers. The described surface modification system has the capability to manipulate all the process variables: work piece temperature, atmosphere composition and pressure, discharge current and voltage, pulse duration and frequency.

In order to remove the naturally formed oxide layer from the samples surface, prior to the nitriding process, a cleaning stage by sputtering was performed. This sputtering (cleaning) stage was conducted during 30 minutes in a 100% Ar DC pulsed discharge under the following parameters: temperature 350°C, vacuum pressure 1 Torr, duty cycle 50%, frequency of 1000 Hz and discharge current density of 2 mA/cm^2.

Immediately after sputtering stage, samples temperature was increased to 400°C to start the plasma nitriding stage.

Nitriding was carried out during 4 h using a pulsed discharge sustained at a pressure of 1.9 Torr in three different atmospheres, 50%N_2/50%Ar, 75%N_2/25%Ar and 100%N_2. Frequency, duty cycle and discharge current density were kept constant at values of 1000Hz, 50% and 1mA/cm^2, respectively. Once that plasma processing was concluded, samples were cooling down to room temperature inside the processing chamber in an argon atmosphere to avoid oxidation.

Surface analysis through Scanning Electron Microscopy (SEM) was accomplished to do evident surface morphological changes on the samples as a consequence of plasma nitriding process. Influence of gas mixture on surface hardness of nitrided samples was evaluated through Vickers micro-hardness measurements. Ten surface random measurements were conducted using a load of 25 g and load time application of 10 s, the average values are reported.

In order to evaluate the evolution of crystalline phases as a consequence of pulsed plasma nitriding process, the phases near the surface of nitrided samples were identified by X-ray diffraction technique (XRD; PANalytical model Empyrean) with CuKα radiation (λ=1.5406 Å) operated at 45 kV, 40 mA and an X'Celerator detector in a Bragg–Brentano geometry. The scans were performed in the 2θ range from 35° to 85° with a step scan of 0.016° and 20 s per step in a continuous mode. The phases were identified using X'Pert HighScore Plus software, version 3.0d and the ICDD PDF-4 plus database (ICDD International Centre for Diffraction Data, Newtown Square,PA).

Finally, electrochemical corrosion performance of untreated and plasma nitrided samples was evaluated through polarization electrochemical technique using a 3.5 % NaCl solution at scanning rate of 60 mV/min in a potential range from -1500 mV to -600 mV. Corrosion current density was determinate through Tafel extrapolation methodology.

III. Results And Analysis

Figure 1 shows SEM surface views of plasma nitrided sample using 100% N_2 (No chemical etched). It can be appreciated the phenomenon of grains boundaries reveal on the surface of samples as a consequence of plasma processing (Figure 1a). This effect has been attributed to the intensification of sputtering phenomenon in the grains boundaries [7]. Additionally, it was evident the presence of surface cracks trough the majority of grains boundaries.

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Cracking phenomenon promotes misplace of coherence between grains resulting inclusive in the removal of grains from its original position losing contact with the substrate. Figure 1b shows clearly a nitrided grain which has been lost the contact with the substrate.

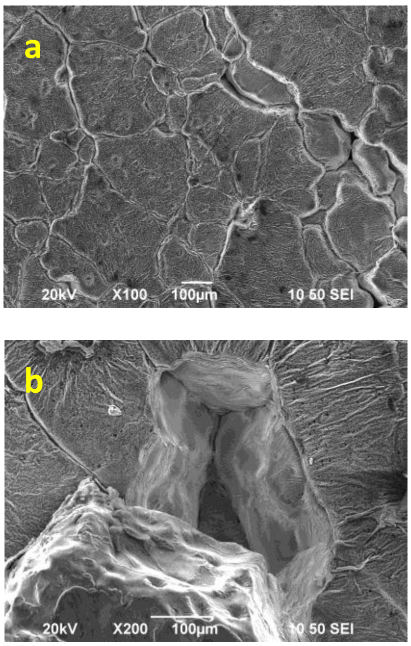


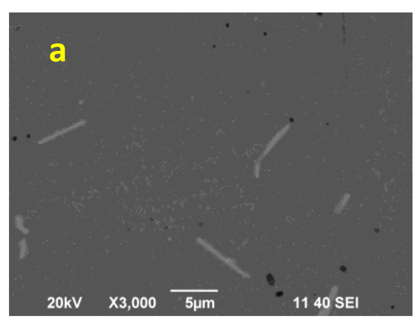
Figure 1. SEM surface views of sample plasma nitrided using an atmosphere containing 100%N_2

The cracking phenomenon on the surface of aluminum nitrided samples has been previously reported, and it has been related to the generation of high stresses as a result of the nitrogen incorporation on the surfaces and the corresponding formation of hard AlN [8,9]. Reports in the literature [10] suggest that the difference of the thermal expansion coefficient between the nitride layer and the substrate promotes thermal stresses. The stress in such AlN/Al systems has been estimated as high as 2-3 GPa. Therefore, the delamination effect has also been attributed to internal stresses built up during nitrided layer formation [9]. Looking for the development of a practical methodology to aluminum plasma nitriding, in this point it is possible to dismiss plasma processing using 100% N_2 atmospheres as alternative, so this sample will not be subjected to additional characterization.

Figure 2 show surface views of a) untreated and plasma nitrided samples using gas mixtures with b) 50% N_2 and c) 75% N_2. Untreated sample shows a characteristic view of polished 6061 aluminum alloy. For the case of nitrided samples it is clear the drastic morphological changes as a result of plasma processing. It can be appreciated the rough surfaces with roughness variation for the different evaluated conditions. Plasma nitrided samples using a gas mixture containing 50% N_2 show an irregular morphology which includes a serial of porous. For the case of sample processed using 75% Nitrogen (Figure 2c), it shows that roughness of surface decreased as well as the level of surface porosity, getting a more smoothed surface.

Results obtained from hardness tests show that the hardness value of untreated 6061 aluminum alloy is about 113 $HV_{0.025,}$ exhibing that plasma nitriding promotes the increasing in hardess values to 148 $HV_{0.025}$ for samples processed using gas mixtures containing 50 % of N_2. The increase in nitrogen content in gas mixture to 75 % resuls in a slightly reduction of the average hardness, respect samples processed with 50% N_2, getting hardness values of 142 $HV_{0.025.}$

Hardness and roughness similar results have been reported previously by R. López-Callejas and Cols. [11] for samples of Al-6061 nitrided through plasma immersion ion implantation. Besides, reported that 88 $HV_{0.001}$ nitrided rough-surfaced samples were generated on aluminum substrate nitrogen plasma implanted using a gas mixture containing 50% of nitrogen at 400°C (4h periods at 2kV bias). Furthermore, the increase to 70% the nitrogen content in the gas mixture, results in surfaces characterized by lower hardness and low roughness which they have been related to both: presence of polymorphic AlN into cubic and hexagonal phases and the sputtering phenomena.



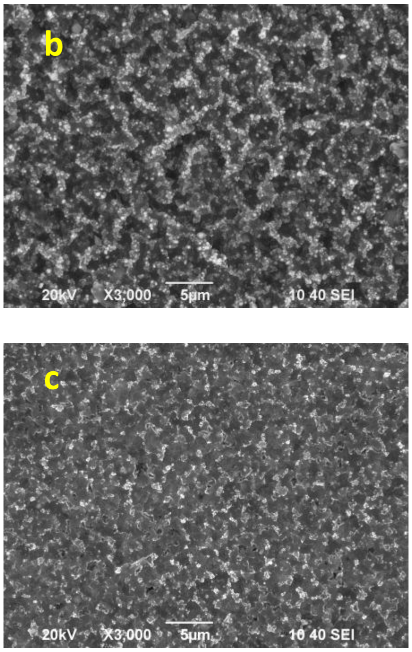


Figure 2. SEM images of surface views of a) untreated and plasma nitrided using gas mixtures containing b) 50% N_2 and c) 75% N_2.

Figure 3 shows XRD patterns for untreated and plasma nitrided samples using mixtures containing 50 and 75% of N_2. Plasma nitriding promotes chemical modification of samples surface through formation of hexagonal (h) and cubic (c) aluminum nitrides. An additional phenomenon promoted by plasma nitriding is the broadening of the aluminum reflections, which can be clearly observed for reflection at 78.2°. This phenomenon has been reported previously and was attributed to the formation of metastable interstitial solid solution of N into Al, which phase is commonly identified as cubic aluminum nitride [5]. Unfortunately, because the proximity of aluminum and cubic aluminum nitride XRD reflections is not possible identify it clearly on the diffraction spectrum. In the same way, it can be appreciated from XRD analysis, the decreasing of the reflection intensity located at 38.4°. In agreement with E. Hug and Cols, this behavior can be attributed to an initial crystallographic texture generated by plasma surface modification [5]. Additional to aluminum nitrides, it is possible to identify presence of aluminum oxide type Al_2O_3 which presence is common in plasma processing technologies [6,12].

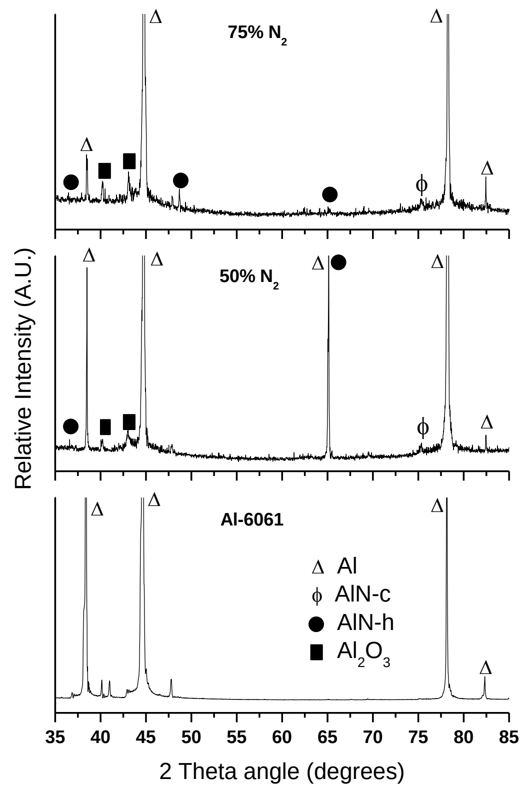


Figure 3. XRD patterns for untreated and plasma nitrided samples.

Figure 4 shows potentiodynamic polarization curves for untreated and plasma nitrided samples using mixtures with 50 and 75% N_2. As a first indicative of increasing in corrosion resistance of nitrided samples it can be appreciated the shift to lower polarization current values of curve corresponding to 50% N_2 sample. Corrosion current (Icorr) values were determinate through Tafel extrapolation method. The corresponding obtained values for nitrided samples with 50 and 75 % of N_2 as well as obtained for the untreated sample were 0.0013, 0.0030 and 0.0028 mA/cm^2 respectively. The decreasing in Icorr value of sample processed with 50% N_2 is clear evidence of the increasing in corrosion resistance, however sample nitrided using 75% N_2 showed practically the same Icorr value than the untreated sample. The reduction to Icorr value from 0.0028 mA/cm^2 for untreated aluminum to 0.0013 mA/cm^2 for one of the nitrided samples can be paraphrase as a reduction to around a half of the corrosion susceptibility respect untreated sample.

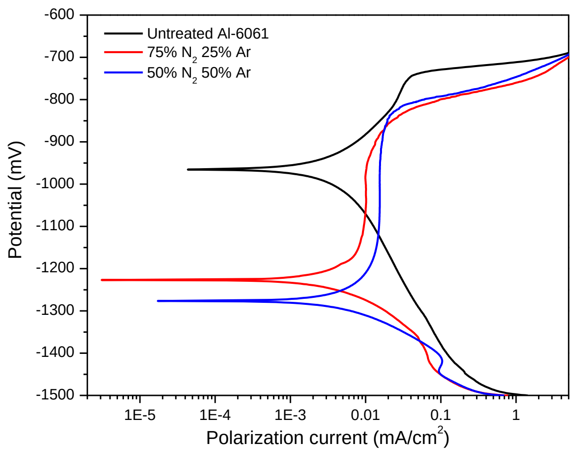


Figure 4. Potentiodynamic polarization curves for untreated and plasma nitrided samples.

In agreement with XRD results, it can be inferred that the reduction of Icorr value computed for sample processed with 50% N_2 is a consequence of presence of new crystalline phases (cubic and hexagonal aluminum nitrides) developed on the surface of Al-6061 as a result of plasma nitriding process. In agreement to morphological characterization, it would be expected that sample nitrided using gas mixture containing 75% N_2 would be exhibit the best corrosion performance (Based on more regular and less porous surface morphology) but, the results indicate that the corrosion control is dominated mainly by chemical factors. Although plasma nitriding using 75%N_2 has not any improving on the corrosion performance of Al-6061, its effect, as well as the chemical surface modification, is evident through the considerable increase of its surface hardness.

The sowed results, let us to evidence the increase in hardness and corrosion resistance properties of aluminum 6061 alloy through rough vacuum pressure DC pulsed plasma nitriding, an environmental friendly process characterized by lower energy consumption and minor instrumentation requirements than similar processes as PIII and Inductively plasma nitriding.

IV. Conclusions

Aluminum 6061 alloy was subjected to a plasma nitriding process at 400°C using a pulsed DC discharge sustained in an atmosphere of three different N_2/Ar gas mixtures. Analysis of surface properties and morphology let us to conclude the following:

Plasma nitriding using 100% N_2 atmosphere promotes the formation of a modified surface characterized by presence of cracks and the detachment of material sections from the substrate. This performance can be related, in agreement with previous works, to high stress concentration as a result of microstructural transformation because nitrogen incorporation.

Samples processed using glow discharge containing 50% of nitrogen showed the highest hardness values reaching values around 148 $HV_{0.025.}$ This performance represents the increase in harness around 1.3 times respect untreated sample. The increase in the nitrogen content in gas mixture to 75% results in a slight phenomenon of decrease in the hardness values.

Plasma nitriding under evaluated conditions produce a surface characterized by presence of cubic and hexagonal aluminum nitrides and aluminum oxide type Al_2O_3. These phases provide to the aluminum alloy a considerable increase in its corrosion performance specifically when they are generated with 50%N_2 gas mixtures

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