STUDY ON CORROSION PROPERTIES OF PLASMA NITRIDED PURE ALUMINIUM

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Abstract: In this research plasma nitriding of pure aluminium and effect of iron elemental alloy on the formation and growth of aluminium nitride was investigated. Also corrosion properties of formed AlN were investigated. After preparation, the samples were plasma nitrided at 550°C, for 6, 9 and 12 h and a gas mixture of 25%H₂-75%N₂. The microstructure and phases analysis were investigated using scanning electron microscopy and X-ray diffraction analysis. Moreover corrosion resistance of samples was investigated using polarization techniques. The results showed that only a compound layer was formed on the surface of samples and no diffusion zone was detected. Dominant phase in compound layer was AlN. Scanning electron microscopy results showed that nitride layer has particulate structure. These nitried particles have grown columnar and perpendicular to the surface. It was also observed that the existence of iron in the samples increases the nitrogen diffusion, thus growth rate of iron containing nitrides are higher than the others. Corrosion tests results showed that formation of an aluminium nitride layer on the surface of aluminium decreases the corrosion resistance of aluminium significantly. This is due to elimination of surface oxide layer and propagation of cracks in the formed nitride layer.

Keywords: Aluminium, Aluminium nitride, Plasma nitriding, Corrosion.

1. INTRODUCTION

Aluminium and its alloys are widely utilized due to their light weight, high specific strength and corrosion resistance but they do not have good wear resistance [1]. Therefore, many researchers have tried to improve the surface properties of Al alloys by the formation of an AlN layer on Al alloys because AlN has a relatively high hardness (~HV1400) with a melting point of 2490°C and good thermal conductivity (320 W/mK) [2, 3]. Aluminium nitride (AlN) is attractive as a protective coating film for automotive and electrical aluminium alloy parts [4]. In recent years many different technologies such as plasma source ion implantation (PSII), plasma nitriding (PN), conventional ion implantation, reactive ion sputtering deposition, and plasma deposition including ECR CVD process have been reported for the formation of AlN [5-8]. Among these technologies, plasma nitriding and PSII are relatively effective techniques for the various applications due to their advantages for the surface treatment of three-dimensional objects [6-8]. In the process of AlN formation on Al alloys in a nitriding process, aluminium oxide (Al₂O₃) phase can be easily formed on Al substrate because the reaction enthalpy of Al with oxygen is approximately 10 times higher than that of Al with nitrogen. This is one of the critical problems in such processes because formation of Al₂O₃ prevents nitrogen atoms from reaching the surface of the Al substrate. So the use of high purity gases and pre-sputtering are important issues [10]. In this research formation of AlN on the surface of aluminium by the use of pulsed D.C. plasma nitriding method and corrosion resistance of the resulted coating was investigated.

2. EXPERIMENTAL PROCEDURE

In this research, commercial pure aluminium (~99.6 wt% Al) was used as substrate material. Chemical composition of the alloy is shown in Table 1.
Specimens were prepared in the shape of disks with 20 mm diameter and 10 mm height. Then they were cut into two equal parts. Upper and lateral sides of disks were ground and mirror polished with SiC papers from 120 to 1200 grit and 0.5 μm alumina powder, respectively. For nitriding, the polished specimens were tightly fastened together and placed in a pulsed DC plasma reactor, where they were plasma nitrided. Firstly, plasma nitriding chamber was evacuated up to 10⁻⁴ Pa by a rotary vacuum pump. Pre-sputtering treatment was performed to eliminate the oxide layer at the surface followed immediately by the nitriding. Nitriding process was carried out with 60% duty cycle, 10 kHz frequency, 500 ± 100 Pa pressure, an atmosphere of 75%N₂, 25%H₂ and at 550 ±5oC. Samples code and treatment specifications are summarized in Table 2.

After nitriding the samples surface was characterized using X-ray diffraction (XRD: Seifert, 3003TT). The morphology of surface was investigated by scanning electron microscope (VEGA ² TESCAN, Czechoslovakia).

### 3. RESULTS AND DISCUSSIONS

As it is shown in Fig. 1, AlN phase is formed on the Al substrate. Peaks of AlN with f.c.c structure (JCPDS file No. 46-1200) with aluminium could be seen in X-ray diffraction patterns of samples.

It is obviously seen that with increasing the processing time up to 9 h, aluminium phase peaks intensity gradually decreases, on the other hand peaks intensity of f.c.c-AlN phase grows. The results are compatible with the previous results obtained by Y.K. Shim et al. [11]. After that, decrease in the intensity of AlN peeks and also increase in that of substrate peak is due to sputtering effect. It is well known that sputtering could decrease the surface layer thickness and thus, nitride layer peaks intensity will decrease. On the other hand the intensity of substrate peaks increase. Previously, several experimental results have reported that the AlN layer has two different crystal structures such as hexagonal close packed structure (h.c.p) of Wurtzite-type and face centered cubic structure (f.c.c.) of NaCl-type [12,13]. Setoyama et al. [14] explained that f.c.c.-AlN had a higher hardness and higher strength than h.c.p.-AlN due to the higher volume density. Generally h.c.p.-AlN crystal structure has been observed in plasma source ion implantation (PSII) and plasma nitriding (PN) techniques. But under applied conditions in this research, only f.c.c.-AlN was formed and detected.

Surface morphologies of samples were investigated using SEM. In Fig (2-a), a typical surface image of sample AC12 is shown. Generally, it could be seen that surface has a particulate structure. EDS analysis proved that these deposited particles are aluminium nitrides (Fig (2-b)).

Cross section SEM image of sample AC12 is shown in Fig. 3.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Plasma nitriding time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC0</td>
<td>Un-treated</td>
</tr>
<tr>
<td>AC6</td>
<td>6</td>
</tr>
<tr>
<td>AC9</td>
<td>9</td>
</tr>
<tr>
<td>AC12</td>
<td>12</td>
</tr>
</tbody>
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Table 1. Chemical composition of used aluminium alloy (wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>99.635</td>
</tr>
<tr>
<td>Fe</td>
<td>0.226</td>
</tr>
<tr>
<td>Ni</td>
<td>0.016</td>
</tr>
<tr>
<td>Pb</td>
<td>0.006</td>
</tr>
<tr>
<td>Ca</td>
<td>0.002</td>
</tr>
<tr>
<td>Mg</td>
<td>0.003</td>
</tr>
<tr>
<td>Mn</td>
<td>0.004</td>
</tr>
<tr>
<td>Na</td>
<td>0.002</td>
</tr>
<tr>
<td>Sb</td>
<td>0.004</td>
</tr>
<tr>
<td>Si</td>
<td>0.094</td>
</tr>
<tr>
<td>Sn</td>
<td>0.007</td>
</tr>
<tr>
<td>Sr</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 2. Nitriding process conditions.

![Fig. 1. XRD patterns of plasma nitrided samples.](image-url)
In Fig. 3 it can be seen that from the surface to the core of the sample, there are only two distinct regions corresponding to AlN layer and substrate. So it could be said that there is only compound layer on the surface of plasma nitrided aluminium and no diffusion zone could be seen.

Thermodynamic studies have also proved that the tendency of nitrogen to form AlN is much greater than that of nitrogen to diffuse into the substrate.

In Fig. 4 the cross section of sample A12 is shown at higher magnification.

In this figure it could be seen that nitrides have columnar growth and are perpendicular to the surface. Also there are distinct differences between these columns height and diameter. In order to gain more information, EDS analysis was applied to determine their chemical compositions. So, two regions were selected. Selected areas are name by A and B in Fig. 4. The EDS results are shown in Fig. 5.

It is seen that chemical composition of these columns are completely different, especially in the amount of Fe element. Fe exists in Al as
impurity, thus forms some intermetalics. By nitriding these intermetalics seems to be decomposed and resulted nitrides grows more than aluminium nitride. Because of higher diffusion of nitrogen in Fe, this higher growth rate could be explained. According to higher diffusion coefficient of nitrogen in Fe than that of nitrogen in aluminium, it is expected that larger columns with higher Fe contents, have more amount of nitrogen and oxygen and higher growth rate.

Corrosion tests were carried out in distilled water solution containing 3.5% NaCl and 0.001mV/sec scan rate. Polarization curves obtained from corrosion tests are shown in Fig. 6. It can be seen that the corrosion potential of untreated sample is higher than that of treated sample. So it can be concluded that the formation of aluminium nitride layer on the aluminium substrate, reduces its corrosion resistance in chloride solution. SEM images obtained from the samples surface after corrosion tests are shown in Fig. 7.

Results show severe local corrosion, while in all samples aluminium nitrid layer is completely detached from the surface and substrate is corroded. In fact, it could be said that low adhesion of coating to the substrate causes the detachment of it and corrosion will be intensified in the detached areas of the surface. Thus, corrosion occurs in the form of pitting. Because of low thickness of AlN layer, sample AC6 has poor corrosion resistance. In other studies [7], it has been proved that during the formation of aluminium nitride, layer cracking is inevitable. Stock et al. [7] also observed some cracks in the AlN film above a thickness of 3 μm because of the large difference of thermal expansion coefficients between Al and the AlN layer [7]. So in the case of nitrided samples, surface cracking, causes severe corrosion. By increasing the nitriding time up to 12h, this phenomenon causes more cracks and thus corrosion resistance of the sample AC12 becomes lower than sample AC9. But before 9 hours nitriding, the layer thickness increases and it causes more corrosion resistance. This is in agreement with polarization curves (Fig. 6).

SEM image obtained from un-treated sample is shown in Fig. 8.

It is also seen that pitting is the main mechanism of corrosion in reference sample. This confirms that detachment of surface layer has caused lower corrosion resistance of coated
samples. Also in the reference sample, existence of a thin un-cracked Al₂O₃ layer improves the corrosion resistance.

4. CONCLUSIONS

1. Aluminium nitride formed on the surface of plasma nitrided aluminium samples has particulate and f.c.c structure.
2. Corrosion resistance of plasma nitrided aluminium sample in 3.5% NaCl solution is lower than that of untreated aluminium sample.
3. Due to the formation of a cracked aluminium nitride layer, severe local corrosion in the form of pitting occurs.

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