# Corrosion protection of aluminum alloys by magnetron sputtering and ion implantation

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Corrosion protection of aluminum alloys for aerospace applications is mostly ensured by an environmentally hazardous chromate conversion treatment. As possible clean alternatives, we investigated magnetron sputtering of  $AlN_X$  coatings and ion implantation with passivating metals. The elemental composition of the treated surfaces was determined. Corrosion behavior was tested by carrying out potentiodynamic polarization scans. Sputtering and implantation possess a potential to promote the corrosion resistance of aluminum alloys.

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## **1** Introduction

Aluminum alloys are widely used in aerospace industry due to their low weight combined with relatively high strength. Among the most prominent of these alloys are AA 2024 and 6061 where precipitates are formed after quenching leading to a higher strength. But especially for copper containing alloy 2024 the precipitates like A½CuMg differ in electrochemical potential from the matrix and behave as local elements so that this alloy is more susceptible to corrosion. Careful surface treatments for corrosion protection have to be carried out consisting today mainly of a conversion treatment with chromate containing baths. But  $Cr^{6+}$  ions are known to be dangerous to health and environment so that cost intensive recycling procedures are enforced by law. Therefore, environmentally clean alternatives are highly desirable. Such processes are predominantly solvent based, galvanic treatments like phosphating with fluor and metals like Ti, Zr, Ce, Mn, and Ni<sup>1-2</sup>. Recent developments include protection with self-assembling organic molecules or silicon containing liquids<sup>3</sup>. But all of these processes are solvent based so that production and disposal of liquids may also turn out to be environmentally harmful.

For this reason we propose a gas phase deposition process for surface protection of aluminum alloys. This process produces no liquid waste and benefits from low material consumption so that there are no environmental concerns<sup>4-5</sup>. Ion implantation is a promising process because only the surfaces are treated at low temperatures preventing the bulk properties from being changed. As the implanted species are introduced into the material, there are no adherence problems as may be in the case of coatings. Implantation of transition metal ions into aluminum alloys has been shown to promote the corrosion resistance of aluminum alloys. There are reports on corrosion behavior enhancement by implanting ions of Mo<sup>6</sup>, Cr<sup>7</sup>, and W<sup>8</sup>, where Mo ion implantation is especially used for aerospace aluminum structures<sup>9</sup>. McCafferty showed that the implanted metals change the electrochemical state of the surface and alter the corrosion mechanisms<sup>10</sup>.

PVD coatings can be used to protect surfaces from corrosion attack<sup>5, 11-12</sup>. A prominent example in aerospace industry is replacement of galvanic cadmium coatings by ion vapor deposited aluminum on steel fasteners<sup>13</sup>. Layers of sputtered AlN<sub>X</sub> should provide a corrosion protection due to their chemical inertness. Aita and Tait found out that sputtered AlN<sub>X</sub> layers can have a passivating effect on carbon steel<sup>14</sup>. McCafferty et al. observed a higher pitting potential in nitrogen containing aluminum surfaces<sup>15</sup>. Booske et al. showed that nitrogen containing surfaces of alloy 6061-T4 show a more noble pitting potential and very little corrosion attack in salt spray testing<sup>16</sup>.

On the basis of these results, we want to show that corrosion protection of standard aluminum alloys 2024 and 6061 is possible by coating with  $AlN_X$  and implantation with transition metal ions.

# 2 Experiment

Samples of AA 2024-T3 and 6061-T4 were ground with grade 600 und 1000 sand paper and cleaned with water and ethanol in an ultrasonic bath before processing.  $AlN_X$  coatings were deposited in a Leybold Z700 magnetron sputtering device. After pumping down to a base pressure of  $10^{-4}$  Pa the process consisted of 10 min plasma etching of target and substrates followed by 10 min coating deposition. Sample temperature was approx. 190°C implying only little growth of precipitates which can even enhance strength of the material. The structure of the coatings was visualized by scanning electron microscopy (SEM) of cross sections.

Ion implantation was carried out in a Danfysik 1090 unit at approx. 150°C achieved by sample cooling. Ti<sup>+</sup> and Cr<sup>+</sup> ions were extracted from a sputter ion source and accelerated to 160 keV. The applied dose was  $1 \times 10^{17}$  ions cm<sup>-2</sup> for both species. Depth profiles of the chemical composition of the treated surfaces were obtained by glow discharge optical emission spectroscopy (GDOES).

The corrosion properties of the modified surfaces were investigated with potentiodynamic polarization scans (anodic polarization curves). The electrolyte consisted of 3% NaCl aerated deionized water and the potential was measured against a saturated calomel electrode (SCE). The measurements were carried out by an Ibendorf ECMC device. In this method the sample is not immersed into the electrolyte, instead the electrolyte contacts the probe just in an area of approx. 2 mm<sup>2</sup>. Before scanning the voltage was kept constant at -1 V for 10 s. The voltage scanning speed was 0.2 Vmin<sup>-1</sup>. The scans were repeated two times at different sites for statistical purposes. The corrosive attack was checked by salt spray testing according to ASTM B117. Testing was chosen to be 12 h until some change in surface appearance occured. The exposed surfaces were investigated afterwards by scanning electron microscopy.

## **3 Results**

Magnetron sputtering of AlN<sub>X</sub> coatings and implantation with  $Ti^+$  and  $Cr^+$  ions were applied to samples of 2024-T3 and 6061-T4. Table 1 gives an overview of the applied treatments.

Table 1   Summary of the applied treatments.			
Aluminum alloy	Magnetron sputtering of AlN <sub>X</sub> (fraction x )	implantation of Ti <sup>+</sup> 160 keV, 1 <sup>-</sup> 10 <sup>17</sup> cm <sup>-2</sup> (max. concentration, at.%)	implantation of Cr <sup>+</sup> 160 keV, 1 <sup>-</sup> 10 <sup>17</sup> cm <sup>-2</sup> (max. concentration, at.%)
2024-T3	0.25, 0.67	10	10
6061-T4	0.25, 0.67	10	10

 $AIN_X$  coatings were deposited with two different nitrogen contents by adjusting the nitrogen flow during the sputtering process. GDOES analyses of the coated samples yielded values of x = 0.25 and

0.67 which correspond to nitrogen contents of 20 and 40 at.%, respectively. Coating thicknesses was estimated from SEM images to be approx.  $1 \mu m$ .

As a second treatment,  $Ti^+$  and  $Cr^+$  ions with a dose of  $1 \times 10^{17} \text{ cm}^{-2}$  were implanted in samples of alloys 2024 and 6061. The elemental composition of these treated surfaces was quantified by high resolution GDOES and showed a gaussian like distribution of the implanted species with a maximum at a depth of 0.2 µm. Maximum concentrations of approx. 10 at.% were determined.

The altered electrochemical behavior of the treated surfaces was checked with potentiodynamic polarization scans. Fig.1 shows the polarization curves of the AlN<sub>X</sub> coated samples, together with a reference scan of the uncoated surface (sample back). For AlN<sub>0.25</sub> coated alloy 2024 (fig.1a) the pitting potential of  $U_P = -0.75$  V<sub>SCE</sub> is not shifted but the current increase for  $U > U_P$  is somewhat less pronounced. For the coating with higher nitrogen content (AlN<sub>0.67</sub>) U<sub>P</sub> is shifted to -0.5 V<sub>SCE</sub> and the anodic current rises more slowly. In the case of coated alloy 6061 a similar tendency can be observed in fig.1b. As this alloy is electrochemically less noble pitting occurs at a lower voltage of -0.9 V<sub>SCE</sub>. The AlN<sub>0.25</sub> coating already leads to a clear shift of the corrosion potential to -0.5 V<sub>SCE</sub>. The increase of the corrosion current is less steep and noisy indicating that some passivation occurs. For the AlN<sub>0.67</sub> coated alloy 6061 an even more shifted pitting potential (-0.27 V<sub>SCE</sub>) is measured coupled with a very slow current increase.



Fig.1 - Potentiodynamic polarization scans of AlN<sub>X</sub> coated alloys 2024 and 6061.

In fig.2 the polarization curves of  $Ti^+$  and  $Cr^+$  implanted alloys 2024 and 6061 are shown. For 2024 alloy (fig.2a) both implantations lead to a shift in pitting potential from -0.75 V<sub>SCE</sub> to about -0.6 V<sub>SCE</sub>. Ion implantation into alloy 6061 yields an even more pronounced shift from U<sub>P</sub> = -0.9 V<sub>SCE</sub> to -0.6

 $V_{SCE}$  (fig.2b) The current rise is not straight upward indicating again some passivation during the pitting process.



Fig. 2 - Potentiodynamic polarization scans of  $Ti^+$  and  $Cr^+$  implanted alloys 2024 and 6061.

The protective effect of the applied methods as revealed in salt spray testing is shown in fig.3 with some examples for alloy 2024. SEM images were taken of the uncoated reference surface (fig.3a), AlN<sub>0.67</sub> coated surface (fig.3b), and Ti<sup>+</sup> implanted surface (fig.3c). As is obvious from fig.3a the unprotected sample shows a pitted surface whereas this is not the case for the coated and implanted sample.  $Cr^+$  implanted alloy 2024 which is not shown here reveals some pitted areas. The AlN<sub>0.25</sub> coated alloy 2024 exhibits only very few pits. For alloy 6061 there was no pitting detectable for any applied treatment.



Fig.3 - SEM images of alloy 2024 surface with different treatments after salt spray testing: untreated surface (a),  $AlN_{0.67}$  coated (b),  $Ti^+$  implanted (c).

# **4** Discussion

From the polarization curves it can be concluded that magnetron sputter coating with  $AlN_X$  (fig.1) and ion implantation with titanium and chromium (fig.2) lead to a higher pitting potential of the two aluminum alloys investigated. It also turns out that sputter coating of  $AlN_X$  layers with high nitrogen contents provides a more effective protection than implantation. AlN is a ceramic material so that  $AlN_X$  coatings with sufficient nitrogen content should be chemically stable. Due to dominant covalent bonding nitrogen rich  $AlN_X$  coatings are electrically insulating so that they are not able to form an electrode which would promote the corrosion process. The  $AlN_{0.25}$  coatings are less effective in protecting the underlying material especially for alloy 2024 (fig.1a). This may be due to the stronger metallic bonding in this coating which favors corrosion. Additionally, SEM cross section images reveal that  $AlN_{0.25}$  coatings show a more columnar structure (fig.4a) whereas the nearly stoichiometric  $AlN_{0.67}$  layers exhibit no preferred orientation or grain boundaries (fig.4b). Thus migration of CI ions to the substrate is easier through  $AlN_{0.25}$  coatings. In contrast,  $AlN_{0.67}$  layers provide a very effective barrier for migrating ions suppressing corrosion reactions at the coating/substrate interface.



Fig.4 - SEM cross section images of  $AlN_{0.25}$  (a) and  $AlN_{0.67}$  coating structure (b).

As Aita and Tait showed AlN<sub>X</sub> coatings are able to form Al(OH)<sub>3</sub> in aqueous solutions providing some passivation mechanism<sup>14</sup>. McCafferty and co-workers found NH<sub>3</sub> and NO<sub>X</sub> on corroded AlN<sub>X</sub> surfaces and also concluded an inhibition and repassivation mechanism<sup>15</sup>. This could explain the unsteady increase of the corrosion current in fig.1. As is obvious from fig.1 the copper containing 2024 alloy is more difficult to protect than alloy 6061 presumably due to the strong local elements (precipitates).

As can be seen in fig.2 implantation with Ti<sup>+</sup> and Cr<sup>+</sup> ions leads to a shift in pitting potential to the more noble direction but there is no significant difference between the two implanted species. The shift can be explained by the fact that titanium and especially chromium are passivating metals with a higher electrochemical potential than aluminum. The potential shift is consistent with the results of other groups who studied transition metal implanted aluminum<sup>6-8</sup>. In all cases where transition metals of group IV to VII were introduced into the aluminum matrix a reduced tendency towards pitting in corrosive environments is observed. This was explained by McCafferty who showed that the

electrochemical behavior of implanted surfaces is modified leading to a change in reactivity with OH<sup>-</sup> and CI ions<sup>10</sup>.

The potential shift is less pronounced for the copper rich alloy 2024 which may again be an effect of the copper containing precipitates. These local elements hinder passivation reactions so that the current increase is relatively constant for  $U > U_P$  (fig.2a). Implantation into alloy 6061 leads to a more pronounced passivation (fig.2b). In this case silicon containing precipitates may even enhance the passivation reactions.

The SEM images of salt spray tested samples confirm the protective effect of the applied methods although the differences between coated samples do not become as obvious as with polarization measurements. Further investigations and longer test periods will be done in future works. In general, pitting of larger areas which occurs for the unprotected sample (fig.3a) is suppressed by both applied methods. Salt spray tests also confirm that alloy 6061 can be easier protected than alloy 2024.

Although polarization curves show the same pitting potentials for  $Ti^+$  and  $Cr^+$  doped 2024 samples (fig.2) the salt spray test shows that in case of  $Cr^+$  implantation pitting occurs. This may be due to chromium rich precipitates which may have formed in the implanted zone. This result makes clear that electrochemical and long term testing are complementary procedures which are both necessary to evaluate the corrosion resistance of treated surfaces.

#### **5** Conclusion

In the search for environmentally clean corrosion protection treatments, magnetron sputtering of AlN<sub>x</sub> coatings and implantation with  $Ti^+$  and  $Cr^+$  ions were applied to the common aluminum alloys 2024-T3 and 6061-T4. The corrosion behavior was tested by potentiodynamic polarization and salt spray testing. The results show that higher pitting potentials can be achieved by both methods. Alloy 2024 is more difficult to protect due to copper precipitates disturbing passivation reactions. AlN<sub>0.67</sub> layers provide a better protection than AlN<sub>0.25</sub> coatings. Implanted titanium leads to a slightly better protection than chromium although pitting potential is equal. The applied treatments generally promote passivating processes on the treated surfaces so that a reduced corrosive attack in salt spray testing is achieved. Therefore, magnetron sputtering and implantation of suitable materials are able to provide a corrosion protection of aluminum alloys.

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