

ENHANCING PASSIVITY OF ALUMINIUM BY SUPERFICIAL ALLOYING WITH CHROMIUM

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ABSTRACT

An study of the chemistry of chromium in the passive film on Aluminium substrates after ion implantation, electrochemically grown in aqueous solutions of carbonate/bicarbonate with added chloride ions, was done by X-Ray Photoelectron Spectroscopy (XPS).

The results confirmed that Cr^{3+} is responsible for passivation and also that pitting of Al-Cr alloys occurs when the concentration of Cr^{3+} in the film is reduced due to oxidization to the a more soluble species, Cr^{6+} . Clearly, enrichment of the passive film in the solute element of the alloy is beneficial, but the piting potential is chromium concentration dependent, exhibiting a maximum.

Results will be discussed in terms of the ability of Cr to produce a more effective hydrolysis when compare to Aluminium ions.

INTRODUCTION

Pitting corrosion resistance and mechanism for aluminium alloys produced by non-equilibrium methods have been the subject of numerous studies in the last few years [1-8]. Electrostatic repulsion of Cl^- by oxidized solute atoms; formation of an oxidized solute barrier layer; blockage of Cl^- transport through the passive film; stabilization of the passive film oxide structure; replacement of oxidized Al in the passive film by oxidized solute to form a more stable oxide; reduction of the acidification and dissolution within occluded cells, have been proposed to explain the passivity of the refered alloys [1, 5, 8].

In this work Al-Cr alloys produced by ion implantation with very low surface concentrations and peak concentrations between 8 and 16% are studied regarding pitting susceptibility and chages in the chemistry of the passive film at the pitting potential.

EXPERIMENTAL

Discs of aluminium of 0.55 cm^2 of diameter were implanted with chromium and were used as working electrodes in contact with a $0.05\text{M Na}_2\text{CO}_3 + 0.5\text{M NaHCO}_3 + 0.5\text{M NaCl}$ solution. A conventional electrochemical cell was used with a Luggin Harber capillary as a bridge to an external saturated calomel electrode (SCE). A Data Logger from Solarton Schlumberger Model 3531D was used for the open circuit

measurements. Voltammetric curves were obtained using an electrochemical interface from Solartron Model 1286 and a scan rates from 5 to 80 mV/s. The step by step method was also used (0.08 mV/s) to assess pitting potential. Morphology of exposed surfaces was examined using a JEOL JFM35CF Scanning Electron Microscope. XPS data were obtained on a Microlab 310F.

RESULTS AND DISCUSSION

Al-Cr alloys were obtained by Cr ion implantation of 5×10^{16} , 1×10^{17} and 2×10^{17} ions/cm² at 150 KeV.

Exposure to a normally aerated carbonated solution with added chloride ions (0.5 M NaCl) during 500 hours produced pitting for the samples containing Cr in excess of 8%. Using the same solution as for the open circuit tests, samples were polarized from -2V (SCE) to potentials just before breakdown in the range of sweep rate from 5 to 80 mV/s, and the passivation currents measured. Results agree with those obtained at the open circuit.

Current densities, for the sample that did not exhibit pitting at the open circuit are shown to be an order of magnitude lower than those corresponding to Al without treatment, in the same experimental conditions. Etched pits were produced in both implanted and non-implanted alloys after allowing the current to increase after polarizing at the break breakdown potential.

The susceptibility to pitting in chloride containing solution was evaluated by means of potentiostatic polarization by the step by step method with steps of 25 mV every 300 seconds. Typical current density-time profiles evidencing breakdown potentials together with the polarization program used are shown in Figure 1.

Ennoblement of the pitting potential as a function of the implanted dose, is not continuous, a maximum at $\sim +250$ mV (SCE). This is thought to be related to a threshold concentration of $\sim 8\%$; higher Cr concentration make difficult for pits to repassivate. A more effective hydrolysis of Cr ions when compared with Al ions is thought to be responsible for this behaviour in agreement with the suggested by Frankel et al [6]. In this way, the critical pit environment may be maintained at a lower potential and current density when more Cr is available for hydrolysis. This, however does not explain the remarkable improvement obtained with low Cr concentration where pitting potentials were ennobled in ~ 800 mV regarding the base metal.

Changes in the chemistry of the passive film were studied by XPS measurements performed ex-situ. Samples were polarized potentiostatically to breakdown and surface spectra were taken in non-pitted areas. Binding energies and oxidation states for the Cr containing constituents of the passive film on chromium implanted aluminium are presented in Table 1.

Cr⁺³ state corresponding to Cr oxyhydroxide phase is the predominant oxidation compound even though, non stable species in aqueous solutions such as Cr(VI) and Cr(IV) were, as expected, present. CrOOH restricts oxidation of Al since no other oxidation states are normally detected in the film below Epit [1]. Cr₂O₃ was detected for the sample that exhibit more resistance to pitting. CrO₃ is formed in all cases.

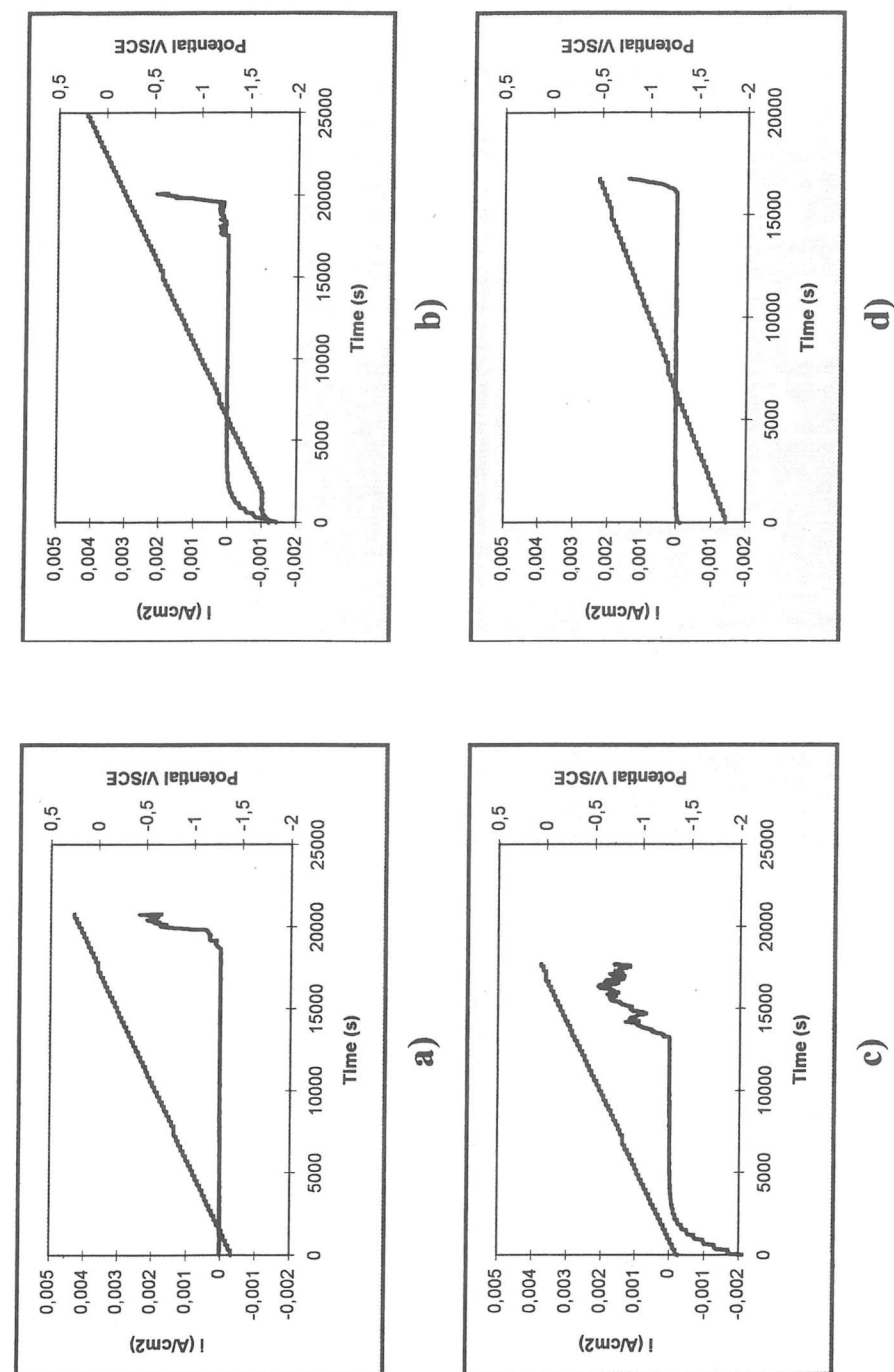


Fig.1 -Current density-time profile showing breakdown potential for
a) 5×10^{16} ions Cr/cm², b) 1×10^{17} ions Cr/cm², c) 2×10^{17} ions Cr/cm², d) Al 99.999%.

Table I- XPS binding energies and oxidation states for passive film on chromium implanted aluminium.

Oxidation state	Compound	Binding energy (eV)	Literature binding energy (eV)	Al with 5×10^{16} ions Cr/cm^2	Al with 2×10^{17} ions Cr/cm^2
+6	CrO_3	578.9	578.1	Yes	Yes
+4	CrO_2	576.3	576.1	No	Yes
+3	$\text{Cr}(\text{OH})_3/\text{CrOOH}$	577.3	577.0	Yes	Yes
+3	Cr_2O_3	575.9	576.0	Yes	No
0	Cr metal	573.8	574.0	Yes	Yes

Changes in the film were found to be consistent with a more noble pitting potentials, suggesting that the solute has an effect on the characteristics of the passive film with enrichment in the oxidized solute. It is to be noticed that after a certain %Cr, higher than 8 at %, pitting potentials seem to remain practically independent of alloy concentration. This is associated to XPS results regarding the concentration of Cr in the film at breakdown, which does not appear to be related to Cr bulk concentration. So, the obtained results do not support the idea that improvement in the pitting resistance of the studied alloys is mainly due to enrichment of the passive film in the solute element.

CONCLUSIONS

- Ennoblement of the pitting potencial was obtained for all concentrations of implanted Cr used. This ennoblement is not continuous, a maximum being evident at +250 mV(SCE) for a peak concentration of ~8 at%.
- Chromium concentration in excess of ~8 at % made pit repassivation difficult. This might be due to a more effective hydrolysis of Cr ions regarding Al ions that maintains the critical pit environment at lower potential and current density.

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Passivation of Al-W-Ta Alloys Produced by Ion Implantation.

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Abstract

It is proposed that the passivation region for Aluminium could be extended, outside the 4 to 9 pH range, by surface alloying with W and Ta, using ion implantation as a non-equilibrium alloying method. Extension into the acid region was achieved by surface alloying with W. This is justified in virtue of the thermodynamic stability of the solute oxide. As Tantalum exhibits passivation all across the pH range, it is reasonable to believe that passivity of Aluminium could be induced or at least greatly improved by alloying with W and Ta [1]. A fluence of $1.3 \times 10^{16} (\text{W}^+ + \text{Ta}^+) \cdot \text{cm}^{-2}$ at different ion beam energies, (40 KeV and 150 KeV was used for surface alloying 99.999% purity Aluminium from Good Fellows Metals.

The passivation of the produced implanted alloys was studied by voltammetry and impedance spectroscopy. Pre-passivated samples, in acid sulphate solutions were used in neutral 0.1M NaCl solutions. The pitting potential values are more active when polarizing without pre-exposure to acid solutionst his seems to support the idea that some Ta is lost in acid media by dissolution through the film, which is probably a mixture of Ta_2O_5 and Al_2O_3 in proportions that would depend on potential amongst other factors. A comparison with the values obtained using the same experimental conditions, but without pre-passivation of the sample, is made. According to the dc and ac electrochemical data the protective character of the Al implanted alloys is presumably due to the formation of a passive film containing probably a mixed oxide of Ta_2O_5 and Al_2O_3 . The passivation model seems to agree with the solute rich interphase model [2-3], which requires that the solute forms a more protective passivating species than the Aluminium under occluded cells conditions.

Experimental

Al 99.999% purity was chosen as the base metal and used as disc with a diameter of 10 mm. After mechanically polished by abrasive SiC paper with 320 to 1000 mesh, samples were given a final polish on cloth pads impregnated with diamond particles down to 0.25 μm . After washing with distilled water, degreasing with ethanol and drying with cool air, the samples were implanted with W and Ta. The fluence and the energies of the ion beam were $1.3 \times 10^{16} (\text{W}^+ + \text{Ta}^+) \cdot \text{cm}^{-2}$, 40 KeV and $1.3 \times 10^{16} (\text{W}^+ + \text{Ta}^+) \cdot \text{cm}^{-2}$, 150 KeV. The samples were implanted at INETI/Portugal. RBS (Rutherford Backscattering Spectroscopy - with a