

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	$\text{Cr(OH)}_3/\text{CrOOH}$	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 1.3×10^{16} ($\text{W}^+ + \text{Ta}^+$). 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 μ m. 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 1.3×10^{16} ($\text{W}^+ + \text{Ta}^+$). cm^{-2} , 40 KeV and 1.3×10^{16} ($\text{W}^+ + \text{Ta}^+$). cm^{-2} , 150 KeV. The samples were implanted at INETI/Portugal. RBS (Rutherford Backscattering Spectroscopy - with a

2 MeV Van der Graff) was used to determine the implanted ions concentration profile in the surface alloyed layers. The concentration ratio W/Ta is 70/30.

The solutions are prepared with double distilled water and Analar reagents. The solutions used were a mixture of H₂SO₄ and Na₂SO₄ with pH3 and 0.25M H₂SO₄, pH≈0.5. The pH was measured with a Chemtrix model 45AR.

A conventional electrochemical cell was used, with a Luggin capillary to minimise errors in the potential due to the uncompensated solution resistance. For polarization studies an auxiliary electrode, Pt, was also used.

The potentiodynamic polarization was supplied by an Electrochemical Interface (model 1286, Solartron) and the range of potential covers a scale of values going from a cathodic potential -2.0V to a anodic potential +3.5V, with a scan sweep rate, v , of 12.5 mVs⁻¹.

A Frequency Response Analyser (model 1250, Solartron) connected with Electrochemical Interface (model 1286, Solartron), was used to obtain the impedance data covering a range of frequencies from 65x10³Hz to 1x10⁻² Hz.

The amplitude of the ac sinusoidal wave was kept low, 10mV, peak to peak and the integration time is 5 seconds the frequency scan was made from high to low values.

All measurements were carried out at room temperature and in normally aerated solutions and the potential is always referred to a saturated calomel electrode (SCE).

Results

Polarization curves for aluminium and the implanted alloys were run at scanning rate of 12.5 mVs⁻¹ within a potential range from -2.0 V to +2.0 V. A passive region, extending from -0.5V to +1.7V is evident. A current density reduction of 25 to 50 times at + 1.0 V is found regarding the Al behaviour, see Table 1.

Table 1 - Current density taken from polarization curves run at a scan rate of 12.5 mVs⁻¹ for pure metals, Al, W and Ta, and Al implanted with W and Ta at different beam energies.

Sample	$i / \mu A.cm^{-2}$
Al	490.0
W	700.0
Ta	54.5
Al-W-Ta (40 KeV)	11.4
Al-W-Ta (150 KeV)	17.6

Although the passivation currents for the implanted samples were rather similar, successive sweeps in acid media revealed that the sample with lower concentration of (W + Ta) breaks down at +0.654 V (SCE), after the second successive sweep, whilst the implanted alloy

with higher concentration, lost its passivity only after the sixth sweep, and at a more anodic potential. Data are summarised in Table 2.

Table 2 - The breakdown potential, E_p , for Al and Al-W-Ta implanted alloys in sulphate solution (pH3), after successive sweeps. Scan rate used: 12.5 mVs⁻¹.

Sample	$E_p/V(SCE)$	n° of sweeps
Al-W-Ta (40 KeV)	+1.140	6
Al-W-Ta (150 KeV)	+0.654	2

When narrowing down the potential range outside the domain of the film breakdown, further reduction in current densities were produced. Indication of film formation is given by impedance data.

As evident from the presented results, film formation is favoured in acid environment. It was thought to be interesting in association with pH values encountered in pit enclaves to study the behaviour of the implanted alloy in a solution with a pH even lower than 3.

Tests in a sulphate solution of pH 0.5 were performed. In this case at the open circuit, for the implanted samples, impedance data were collected. If the sample suffered further polarization in the anodic direction, between -1.0V and -0.5V, in acid medium (pH 0.5), the impedance data indicated degradation of the film, only after ten successive sweeps . In the case of the sample implanted at 150 KeV, the slope from Bode plot suggest a diffusional component associated to the film degradation, see Table 3.

Table 3 - Parameters related to impedance spectra obtained for Al-W-Ta alloys in a H₂SO₄ solution, pH 0.5, after ten successive sweeps.

Material	$R_1/\Omega cm^2$	$C_1/\mu Fcm^{-2}$	f_{max}/Hz	$\frac{\partial \log Z }{\partial \log f}$
Al-W-Ta (40 KeV)	24483.0	11.2	0.6	0.9
Al-W-Ta (150 KeV)	3750.0	28.0	1.5	0.4

Polarization of the system in 0.1M NaCl solution was done with and without pre-exposure to a sulphate solution of pH 0.5. Results show that the pitting potential values are more active when polarizing without pre-exposure to acid solutions. Data are shown in Table 4.

Table 4 - The pitting potentials, E_p , for Al-W-Ta implanted alloys in 0.1M NaCl solution, without (A) and with (B) pre-exposure to an acid sulphate solution of pH 0.5.

Material	E_p / V (SCE) (A)	E_p / V (SCE) (B)
Al-W-Ta (40 KeV)	-0.101	+1.025
Al-W-Ta (150 KeV)	-0.325	-0.225

This 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.

Conclusions

- i) - In acid media, passivation of Al-W-Ta alloys produced by ion implantation yields a film containing presumably a mixture of Ta_2O_5 and Al_2O_3 . The alloy behaviour depends on the solution pH: For pH 0.5, the sample reveals a stronger passivating tendency than for pH 3.
- ii) - Passivation in Al-W-Ta alloys seems to agree with the solute rich interphase model which requires that the solute forms a more protective passivating species than Al under conditions within occluded cells. It is thought that the role of Tantalum is two fold:
 - contributes to the enrichment of the film in Ta_2O_5 ;
 - acts as a reservoir of solute to be oxidized under occluded cell conditions, role thought also to be played by W.

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LOCALIZED CORROSION OF COPPER IN NEAR-NEUTRAL SODIUM PERCHLORATE SOLUTIONS

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ABSTRACT

The effect of perchlorate ions on the electrochemical behaviour of copper in near neutral solutions was studied using cyclic voltammetry. Results showed that perchlorate ions do not interfere with the formation of the duplex oxide film on copper in the potential range before breakdown. In fact, results seem to be in agreement with the passivation model for Cu in mild alkaline solutions. There is a solubilization of the film that gives place to Cu (I) soluble species, that are collected at $-0.875 V$ (SCE). Solubilization of the film acidifies the interface and precedes breakdown with nucleation and growth of pits. Soluble species of Cu (I) and Cu (II), related to breakdown, were detected in the cathodic cycle.

INTRODUCTION

The anodic oxidation of copper has been the subject of numerous investigations, particularly in alkaline solution [1-23]. Oxidizing states have been identified by in-situ techniques such as rotating split ring-disc technique, ellipsometry, electron reflectance, photoacoustic spectroscopy, photocurrent, as well as by ex-situ spectroscopic methods such as XPS, ESCA, ion-scattering spectroscopy, etc. [10-13]. The oxidation cycle is been amply studied with the second oxidation stage involving the electroformation of a mixtures of copper oxides in the +1 and +2 oxidation states. Regarding the reduction cycle, the kinetics and mechanism is complex and still a matter of discussion. Some authors consider that the mechanism of the reaction involves the electroreduction of Cu (II) oxide to Cu (I) oxide prior to the electroreduction of Cu (I) to Cu^0 , whereas others claim that the electroreduction of Cu (II) oxide to Cu^0 occurs at more negative potentials that those where the former takes place. The participation of ageing of Cu (I) oxide and chemical reactions yielding new phase formation have been also suggested [10].

The potentials at which copper (I) and (II) are reduced depend on the thickness of the oxide and on the conditions of formation, nevertheless it is generally possible to identify the different species on copper surface by analyzing the characteristics of reduction.

Works in near neutral media are somewhat scarce. In this work an analysis of the cathodic cycle is used.

EXPERIMENTAL

The working electrode was made of high purity copper from Good Fellow Metals with an exposed area of $0.5 cm^2$. After mounting with epoxy resin the electrode and prior to every experiment the electrode was polished with emery paper up to 1000 grit, rinsed with water, cleaned with ethanol and finally dried with cold air.