

## Improving Corrosion Resistance of Aluminium in Acid and Near Neutral Media. Surface Alloying by Ion Implantation.

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### Abstract

New surfaces more resistant to corrosion were produced by ion implantation of W and Ta into aluminium targets. The thermodynamic limitations associated with the low solubility of the solutes were overcome thus increasing the alloying element concentrations to levels necessary to achieve improved corrosion performance. Studies were conducted in solutions of varying acidity, suggested by the E-pH diagrams of the substrate and the alloying elements.

The electrochemical results in acid environments (pH 0.5 to 3.0) revealed that passivation of the implanted alloys is pH dependent. The film suffers degradation with Ta dissolution after several polarization cycles. There is no apparent indication of W dissolution according to the polarization characteristics shown by pure W at the same pH. In near neutral chloride solutions, the implanted alloy with higher concentration of the alloying elements showed a marked protective character. A displacement of the pitting potential,  $E_p$ , related to aluminium greater than 1.5 V (SCE), was observed.

The role of Ta seems to be twofold, contributing to the enrichment of the film in  $Ta_2O_5$  and acting as a reservoir of solute to be oxidized under occluded cell conditions whilst the role of W seems to be in agreement with the solute rich interphase model, that implies local passivation of a pit due to the stability of oxidized solute in localized low pH conditions.

### Introduction

In the last several years a series of works in the field of non-equilibrium aluminium alloys has been produced, amongst other techniques by sputtering deposition and ion implantation, with encouraging results regarding the corrosion resistance of surface alloyed layers to pitting corrosion [1-14].

Identification of the most suitable candidate ions for implantation is based on the fact that, many alloying elements (Mo, Cr, Ta or W) even when present in relatively low concentrations, increase the metal resistance to corrosion, either because they are inherently noble or because they readily form highly protective passive films [1]. With the introduction of these passive film formers into aluminium, in which they are scarcely soluble, the formation of new alloys, more corrosion resistant, might be achieved. It should be noticed that when implanted elements form precipitates and second phases, protection could be impaired by a galvanic cell mechanism.

The passive film that form on Al alloys containing the above named alloying elements, is a function of solute concentration and applied potential. The mechanism by which the solute protects the Al alloy, differs in conformity with the type of implanted ion [2-11].

Ta implanted into an Al matrix [2,3] improves passivity since the formation of a Ta<sub>2</sub>O<sub>5</sub> film is efficient at blocking oxygen and thus prevents the substrate subsequent oxidation. The oxidized solute protects the substrate by restricting the ingress of chloride and oxygen - preventing or reducing localized attack, and also by film formation. The passive film on Al-Ta alloys, possibly a combination of aluminium and tantalum oxide [3], remains thin and protective at noble potentials. Breakdown occurs only as the potential drop across the film becomes sufficiently large to allow the transport of chloride ions.

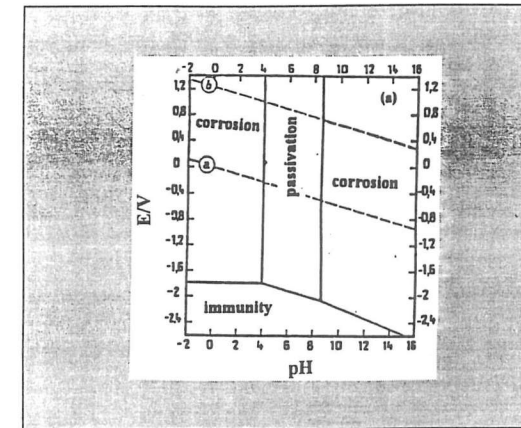
Film solute enrichment is observed for passive films on Al-Ta alloys as well as on Al-Cr. In contrast, very little oxide solute was found for Al-W alloys. The oxidized W is present as WO<sub>3</sub> or WO<sub>2</sub> and the film is thin. Two metallic states are detectable, elemental W and a lower binding energy state identified as alloyed W [3]. The improved properties of Al-W alloys [4-14] are due to a synergetic interaction between W and hydrated Al<sub>2</sub>O<sub>3</sub> resulting in the formation of a more stable oxide layer at the metal-oxide interface. The modification of the passive film structure assures a more protective barrier to oxygen and chloride transport.

In this work, tungsten and tantalum have been chosen as alloying elements. The reason for this, is based on the information from Pourbaix diagrams. Figure 1, shows the E-pH diagrams for Al, and alloying elements, W and Ta.

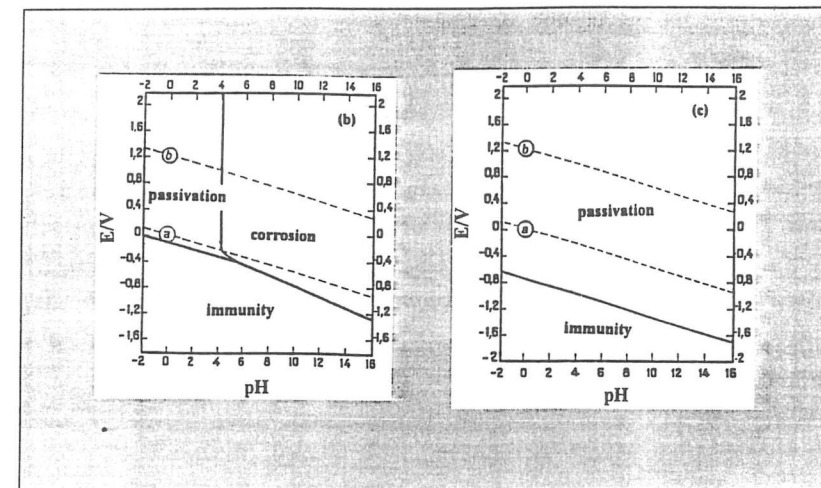
The stability of tungsten in acid media suggests that the passivation region of the aluminium/water system could be extended outside the 4 to 9 pH range and into the acid region by surface alloying with W. As tantalum exhibits passivation all

across the pH range, it is reasonable to believe that passivity of aluminium could be achieved or at least greatly improved by alloying with W and Ta.

In the present work a study of the behaviour of Al-W-Ta alloys produced by ion implantation in acid and near-neutral environment, is conducted.



(a)



(b)

(c)

Fig. 1 - Pourbaix diagrams for Al (a), W (b) and Ta (c).

### Experimental

Al 99.999% purity was chosen as the base metal and used in the shape of discs with a diameter of 10 mm. After mechanically polished with abrasive SiC paper up to 1000 mesh, samples were given a final polish on cloth pads impregnated with diamond particles down to 0.25 $\mu$ 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  $1.3 \times 10^{16}$  (W<sup>+</sup>+Ta<sup>+</sup>)-cm<sup>-2</sup>, 40 KeV and  $1.3 \times 10^{16}$  (W<sup>+</sup>+Ta<sup>+</sup>)-cm<sup>-2</sup>, 150 KeV. The samples were implanted at INETI, using a Danfysik implanter. 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 of W/Ta was of 70/30.

For the electrochemical studies, apart from the implanted alloys, pure aluminium, tungsten and tantalum were also used in this work, with exposed areas of 0.67, 0.67, 0.13, 0.20 cm<sup>2</sup>, respectively.

The solutions are prepared with double distilled water and Analar reagents. The acid solutions used were a mixture of H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> with pH 3 and 0.25M H<sub>2</sub>SO<sub>4</sub>, pH  $\approx$ 0.5, while the near-neutral solution of pH $\approx$ 6, was a 0.1M NaCl solution.

The electrochemical techniques used included a Data Acquisition System (353 ID from Solartron), to follow the potential with time.

The potentiodynamic polarization was supplied by an Electrochemical Interface (model 1286, from Solartron) and the range of potential covered values from a cathodic potential of -2.0V to an anodic potential of +3.5V at scan sweep rates,  $v$ , from 1 to 20 mV.s<sup>-1</sup>. A Frequency Response Analyser (model 1250, from Solartron) connected with Electrochemical Interface (model 1286, from Solartron), was used to obtain the impedance data covering a range of frequencies from  $65 \times 10^3$  Hz to  $1 \times 10^{-2}$  Hz.

The morphology of exposed surfaces was examined using a JEOL Scanning Electron Microscope (SEM), model JFM 35 CF.

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

The concentration profile of (W+Ta) in the alloyed layers obtained after implantation into Al was obtained by RBS. Fluences were of  $1.3 \times 10^{16}$  ions.cm<sup>-2</sup> at 40 and 150 KeV. The sample implanted with a higher energy ion beam (150 KeV), has the smallest peak concentration (4 at%), with the ions profile extending up to a depth of  $\approx$ 1300 Å. The depth profile showed a penetration of  $\approx$  550 Å for samples implanted with low beam energy (40 KeV), and the peak concentration, as expected, was larger (12 at%). See fig.2.

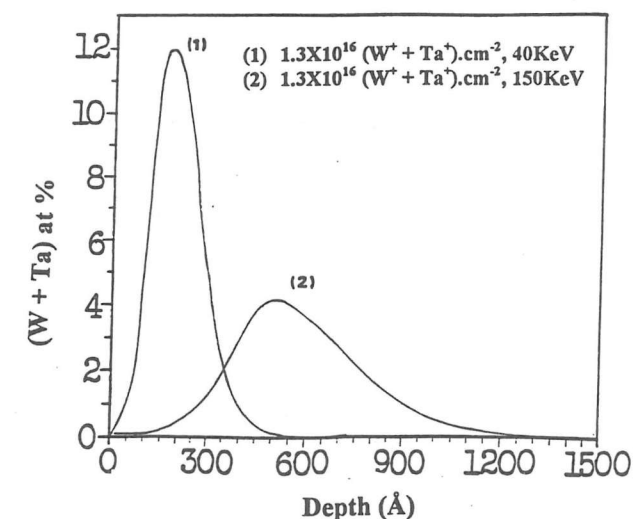


Fig. 2 - RBS concentration profile for (W+Ta) aluminium implanted samples.

### Acid Behaviour

The open circuit behaviour of the implanted samples, when immersed in a sulphate solution (H<sub>2</sub>SO<sub>4</sub> + Na<sub>2</sub>SO<sub>4</sub>) of pH 3, was followed for 240 hours. Figure 3 shows the E-t profile, with curves exhibiting a maximum at  $\sim$  -550 mV (SCE). The ennoblement of the open circuit potential is significant, 500 mV during the first 10 hours of exposure, when compared to values obtained for aluminium in the same experimental conditions. Potential versus time curves follow the shape of the ions depth profile. The potential passes through a maximum and then decreases to values (-0.9, -1.0V (SCE)) close to those exhibited by aluminium, (-1.1V (SCE)). These suggest that in the absence of an external polarization at least part of the implanted layer is dissolved.

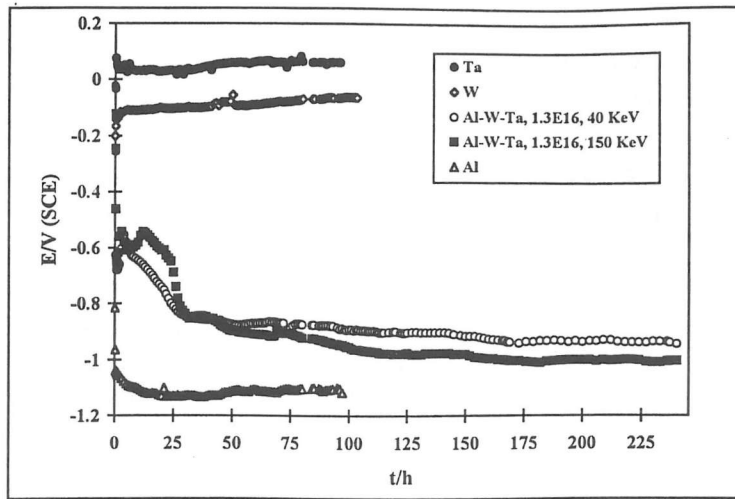


Fig. 3- E-t profile for the system Al-W-Ta / H<sub>2</sub>SO<sub>4</sub> + Na<sub>2</sub>SO<sub>4</sub> (pH3) for an exposure time, at the open circuit, of 150 hours. The profile obtained when using pure metals (Al, W, Ta) in the same experimental conditions is also shown.

The implanted samples, at short immersion testing times, revealed a capacitive behaviour. In fact, when examining ac data, the corresponding Bode plots showed a linear region with a slope of about -1.0 at high frequencies. This is taken as indicative of film formation.

After 120 hours exposure, the impedance spectrum for Al implanted with,  $1.3 \times 10^{16}$  (W<sup>+</sup>+Ta<sup>+</sup>).cm<sup>-2</sup> at (40 KeV), shows a semicircle followed by a low frequency tail, the latter considered typical of resistive behaviour, figure 4. For the implanted sample with higher energy, the tail is not present and the semicircle associated resistance is larger, exhibiting the same capacitance value. This situation is in qualitative agreement with the E vs t profiles that show a slightly more active behaviour for the lower concentration alloy.

Polarization curves for aluminium and implanted alloys were run in a sulphate solution of pH 3, at a scanning rate of 12.5 mV.s<sup>-1</sup> within a potential range from -2.0 V to +2.0 V. A passive region, extending from -0.5V to +1.7V was evident. A current density reduction of 25 to 50 times, when comparing to pure aluminium, was found at + 1.0 V, see Table 1.

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. The implanted alloy with higher concentration, lost its passivity only after the sixth sweep, and at a more anodic potential, figure 5. Data are summarized in Table 2.

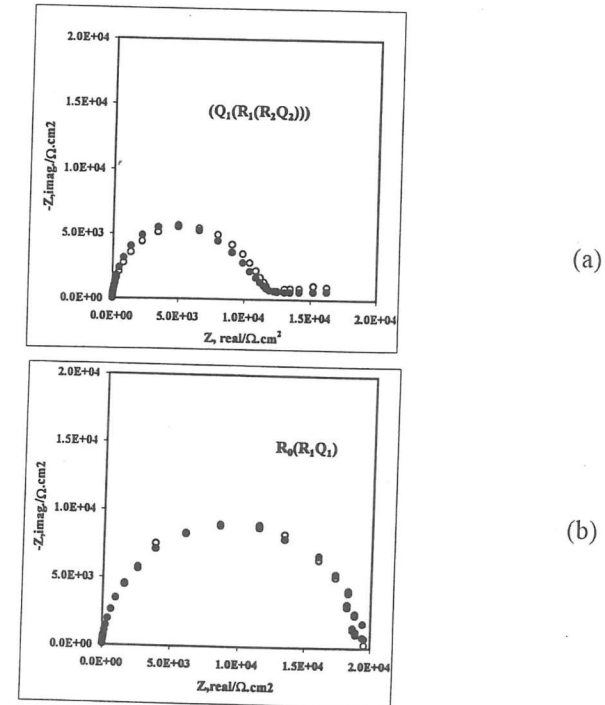


Fig. 4 - Nyquist diagrams for the implanted samples, after 120h at the open circuit, in a sulphate solution (pH3):  $1.3 \times 10^{16}$  (W<sup>++</sup>Ta<sup>+</sup>).cm<sup>-2</sup>, 40KeV(a),  $1.3 \times 10^{16}$  (W<sup>++</sup>Ta<sup>+</sup>).cm<sup>-2</sup>, 150 KeV(b). ° Experimentals data, • simulations data.

Table 1 - Current density taken from polarization curves at +1.0V(SCE) run at a scan rate of 12.5 mV.s<sup>-1</sup> for pure metals, Al, W and Ta, and Al implanted with W and Ta at different beam energies in a sulphate solution of pH 3.

Sample	i / μA.cm <sup>-2</sup>
Al	490.0
W	700.0
Ta	54.5
Al-W-Ta ( 40 KeV )	11.4
Al-W-Ta ( 150 KeV )	17.6

Table 2 - The breakdown potential,  $E_p$ , for Al-W-Ta alloys implanted in a sulphate solution ( pH3 ), after successive sweeps. Scan rate used:  $12.5 \text{ mVs}^{-1}$ .

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

It is assumed that the increased in current density shown after successive sweeps, represented in figure 5 (c), is due to film breakdown and/or dissolution, since the isolating characteristics of the oxide do not allow solvent breakdown with oxygen evolution, figure 5 (a), (b).

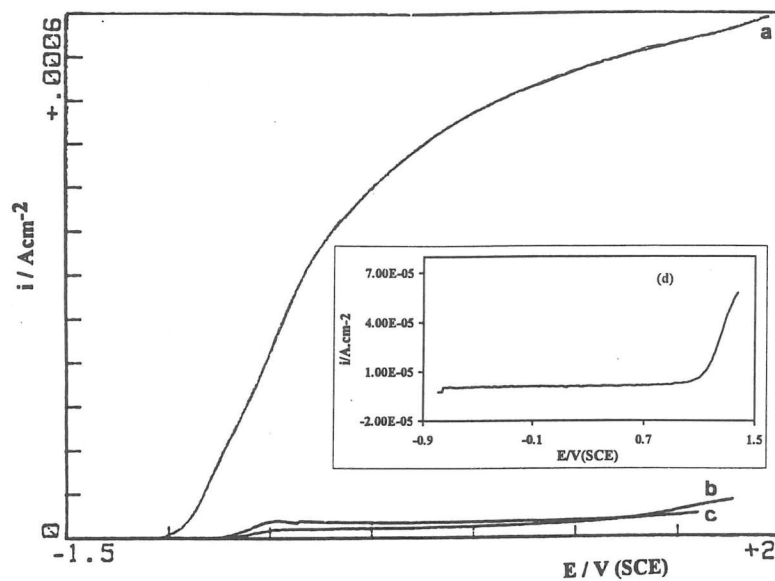


Fig. 5 - Polarization curves at sweep scan rates  $v=12.5\text{mV.s}^{-1}$  in a sulphate solution of pH 3 for: (a) Al, (b)  $\text{Al-}1.3 \times 10^{16} (\text{W}^+ + \text{Ta}^+).\text{cm}^2$ , 40 KeV, (c)  $\text{Al-}1.3 \times 10^{16} (\text{W}^+ + \text{Ta}^+).\text{cm}^2$ , 150 KeV, (d)  $\text{Al-}1.3 \times 10^{16} (\text{W}^+ + \text{Ta}^+).\text{cm}^2$ , 40 KeV, after six successive sweeps.

When narrowing down the potential range to (-0.8V - +0.6V), in the running of the successive sweeps, i.e., outside the domain of the film breakdown, further reduction in current densities were produced. Indication of film formation is

given by impedance data obtained after successive sweeps. Associated parameters are present in Table 3.

Table 3 - Impedance parameters for Al-W-Ta alloys, in a  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  solution ( pH 3 ) after seven successive polarization curves run at  $12.5 \text{ mV.s}^{-1}$ . Proposed equivalent circuit is also shown.

Sample	$R_1 (\Omega.\text{cm}^2)$	$C_1 (\mu\text{F}.\text{cm}^{-2})$	$f_{\text{máx.}} (\text{Hz})$	$\frac{\partial \log  Z }{\partial \log f}$	Proposed equivalent circuit
Al-W-Ta (40KeV)	70 000.0	1.5	1.5	0.9	$R_0(R_1C_1)$
Al-W-Ta (150KeV)	40 000.0	4.2	0.9	0.9	

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. Calculated parameters were in agreement with passive film formation, Table 4.

Table 4 - Impedance parameters for Al-W-Ta in a  $\text{H}_2\text{SO}_4$  solution, pH 0.5, after 0.5 h at the open circuit. Proposed equivalent circuit is also shown.

Sample	$R_1 (\Omega.\text{cm}^2)$	$C_1 (\mu\text{F}.\text{cm}^{-2})$	$f_{\text{max}} (\text{Hz})$	$\frac{\partial \log  Z }{\partial \log f}$	Proposed equivalent circuit
Al-W-Ta (40 KeV)	130 600.0	0.4	2.9	1.0	$R_0(R_1C_1)$
Al-W-Ta (150 KeV)	280 000.0	2.8	0.4	0.9	

If the sample suffered further polarization in the anodic direction, between -1.0V and -0.5V (SCE), in acid medium (pH 0.5), the impedance data indicated degradation of the film, only after ten successive sweeps. Corresponding

polarization curve is shown in figure 6, with evident current fluctuations as well as an increase in current density at around -0.5V (SCE).

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 5.

Table 5 - Parameters related to impedance spectra obtained for Al-W-Ta alloys in a H<sub>2</sub>SO<sub>4</sub> solution, pH 0.5, after ten successive sweeps. Proposed equivalent circuits are also shown.

Sample	R <sub>1</sub> (Ω.cm <sup>2</sup> )	C <sub>1</sub> (μF.cm <sup>-2</sup> )	F <sub>max1</sub> (Hz)	∂log Z / ∂logf(1)	Proposed equivalent circuit
Al-W-Ta (40 KeV)	24 483.0	11.2	0.6	0.9	R <sub>0</sub> (R <sub>1</sub> C <sub>1</sub> )
Sample	R <sub>1</sub> / R <sub>2</sub> (Ω.cm <sup>2</sup> )	Q <sub>1</sub> / C <sub>2</sub> (μF.cm <sup>-2</sup> )	F <sub>max1</sub> F <sub>max2</sub> (Hz)	∂log Z / ∂logf(1/2)	Proposed equivalent circuit
Al-W-Ta (150 KeV)	472.4/ 3750.0	1.3/28.0	268/1.5	0.7/0.9	R <sub>0</sub> (R <sub>1</sub> Q <sub>1</sub> )(R <sub>2</sub> C <sub>2</sub> )

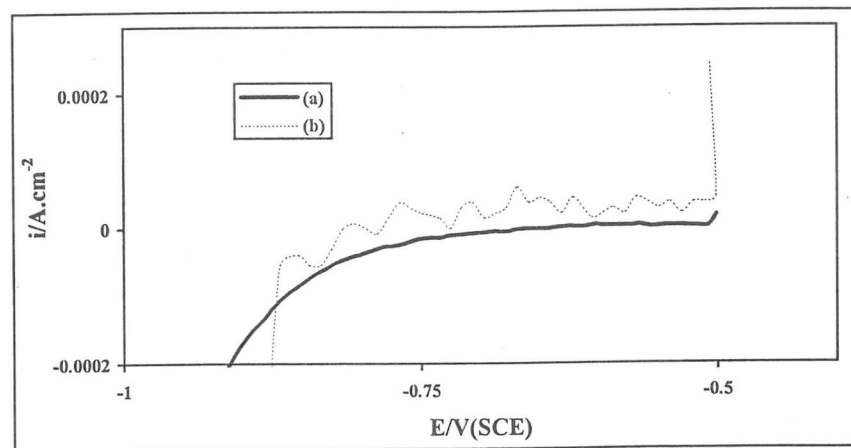


Fig. 6 - Polarization curves for Al-W-Ta alloy,  $1.3 \times 10^{16}$  (W<sup>+</sup>+Ta<sup>+</sup>).cm<sup>-2</sup>, 150 KeV in a sulphate solution, pH 0.5;  $v=12.5$  mV.s<sup>-1</sup>. (a) first sweep running, (b) after ten successive sweeps, with current fluctuations.

### Near-neutral Behaviour

The electrochemical behaviour of implanted samples was studied in a near-neutral solution. The pitting potentials were estimated from polarization curves run at a sweep rate,  $v$ , of  $12.5$  mV.s<sup>-1</sup>, in 0.1M NaCl solution, see figure 7(a).

Pitting potentials were estimated from polarization curves at a sweep rate of  $12$  mV.s<sup>-1</sup>. This choice was made in view of the thickness of the implanted layer being between  $500$  and  $1000$  Å and justified by the fact that in the same experimental conditions, aluminium showed no significant variation of the pitting potential with scan rate for values between  $1$  mV.s<sup>-1</sup> and  $20$  mV.s<sup>-1</sup>, figure 7(b).

The pitting potentials found for the implanted alloys are more noble than the pitting potential of Al, however without reaching the stability of pure Ta and W which films do not break up to  $+3.5$  V. The values are indicated in Table 6.

Table 6 - The pitting potentials, E<sub>p</sub>, for the pure metals ( Al, W, Ta) and Al-W-Ta implanted alloys in 0.1M NaCl solution.

Sample	E <sub>p</sub> / V (SCE )
Al	-0.675
Al-W-Ta (150KeV)	-0.225
Al-W-Ta (40KeV)	+1.025
W	≥+2.000
Ta	≥+3.500

The more noble pitting potential value is observed for the sample with highest concentration of W and Ta at the surface ( $1.3 \times 10^{16}$  (W<sup>+</sup>+Ta<sup>+</sup>).cm<sup>-2</sup>, 40KeV). The displacement of the pitting potential related to that of Al is greater than 1.5V at the used scan rate.

The obtained SEM images for the implanted alloys revealed crystallographic pitting, typical of pure aluminium, although, in the former case, pits were found to be smaller. See figure 8.



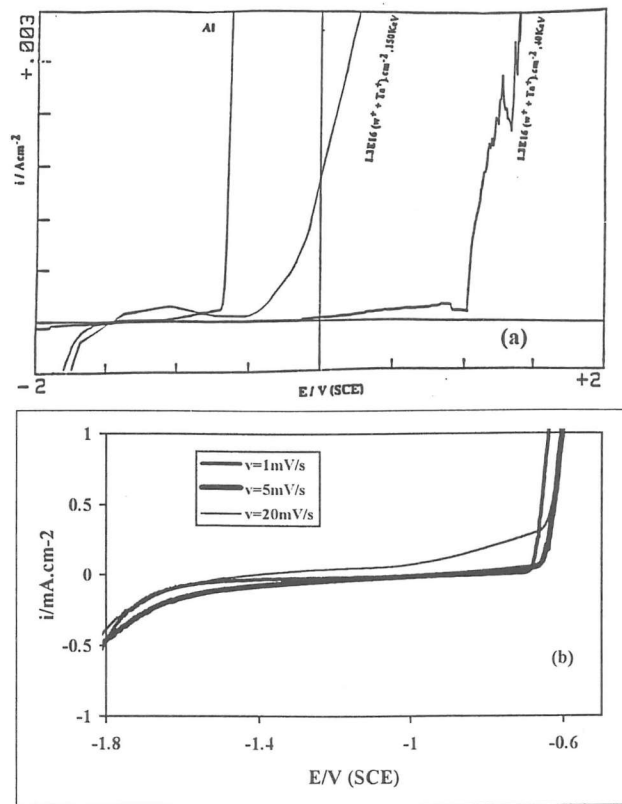


Fig. 7 - The effect of the chloride ions (0.1M NaCl solution) on the polarization behaviour of Al and Al-W-Ta implanted alloys;  $v=12.5\text{mV}\cdot\text{s}^{-1}$  (a), the effect of scan rate (1-20  $\text{mV}\cdot\text{s}^{-1}$ ) on the breakdown potential of pure aluminium (b).

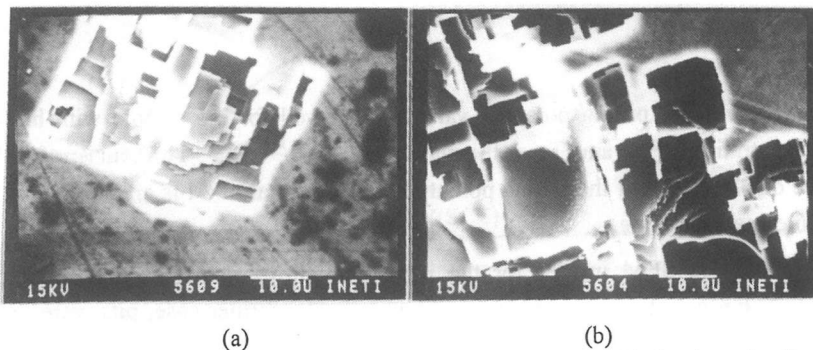


Fig. 8- SEM images after  $\text{Cl}^-$  ion attack for: Al (a); Al implanted alloy,  $1.3 \times 10^{16} (\text{W}^+ + \text{Ta}^+) \text{cm}^{-2}$ , 150KeV (b).

The behaviour of the implanted samples are compared with that of pure metals (Al, W and Ta) in the same experimental conditions. The anodic polarization curves for tungsten and tantalum in 0.1M NaCl are shown in figure 9, indicating that W dissolves probably to  $\text{WO}_4^{2-}$  from -0.400V (SCE). The formation of protective oxides such as  $\text{WO}_3$  is only possible for lower solution pH values which is the case inside pits. In the case of Ta, a passivation region in the potential range from -1.0 to +1.0V(SCE) is observed followed by two well defined peaks (I and II), located at +1.630V and +2.030V (SCE) and observed together with a shoulder at +1.720V(SCE), indicating dissolution of the oxide film.

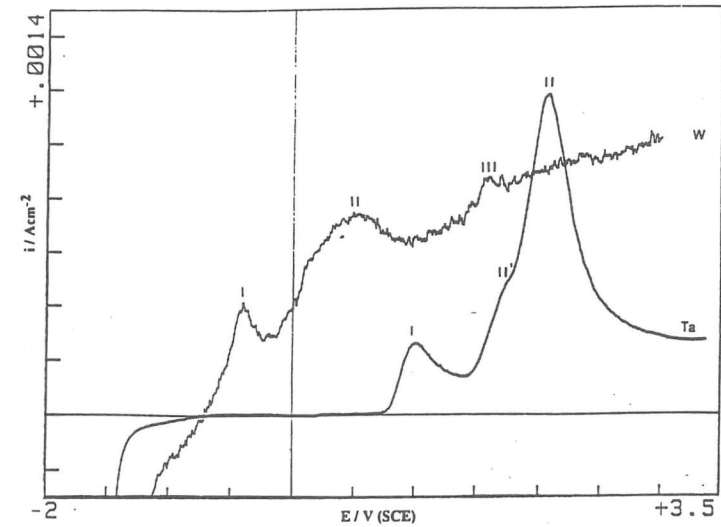


Fig.9 - The effect of chloride ions ( 0.1M NaCl ) on the polarization behaviour of W and Ta;  $v=12.5 \text{mV}\cdot\text{s}^{-1}$ .

Polarization of Al-W-Ta alloys in 0.1M NaCl solution was also done with 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 7. 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  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  in proportions that would depend on potential amongst other factors. Figure 10 shows pitting morphology for implanted samples that suffered pre-exposure to acid environment (pH 0.5) followed by polarization to breakdown in 0.1M NaCl.

Pitting morphology is apparently hemispherical, probably due to the dependence of pit morphology with growth potential which is remarkably anodic [14]. It is noticed that when the pit grows in depth, crystallographic features are shown.

Table 7 - 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

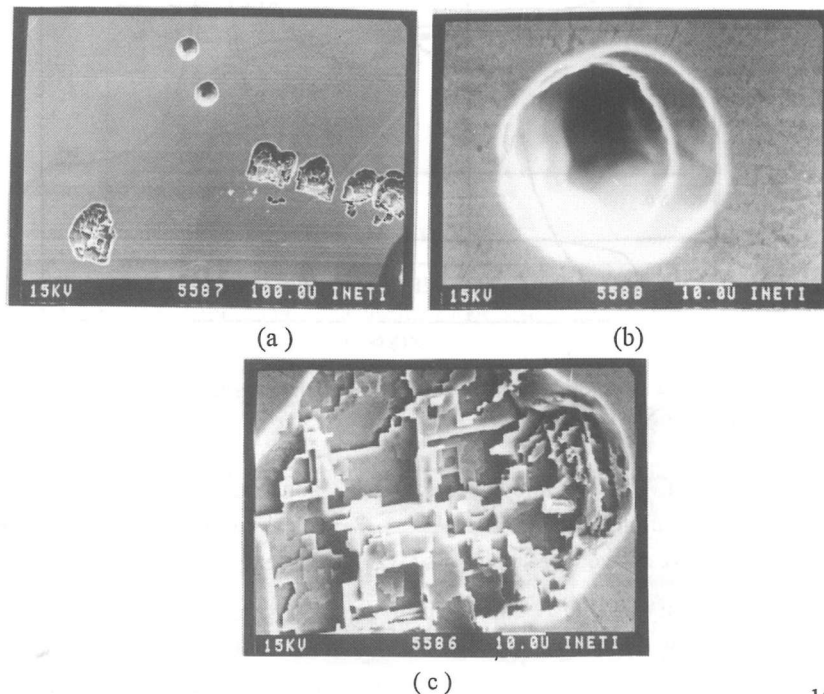


Fig.10 - SEM images, after chloride ions attack, for implanted Al alloys  $1.3 \times 10^{16}$   $(W^{+}+Ta^{+})cm^{-2}$ , 40KeV, after pre-exposure to an acid solution of pH 0.5 (a), Close-up view of hemispherical pitting (b), Close-up view of crystallographic feature at the bottom of the pit (c).

### Discussion

Several different mechanisms [4-12,16], have been proposed to explain the passivity of aluminium alloys produced by non-equilibrium methods including: 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 acidification and dissolution within occluded cells.

The favourable effect of Ta on passivation is reached by solute oxidation and the film enrichment in, for example,  $Ta_2O_5$ , [8], acting by electrostatic repulsion to chloride ions or modifying the oxide structure. The oxide of the alloying element is less soluble than the base metal oxide.

W, alloy element used in this work along with Ta, seems to exhibit a different passivation mechanism. The addition of W to iron base alloys has given good results, and was suggested to be due to a synergetic effect with Cr and Ni present in the alloy. With low alloy steels, this behaviour was not verified [17-19]. For aluminium, the passivation obtained with W additions indicates that in this case, the interaction is not necessary [4, 9-12]. The role of the W in the pitting resistance of Al-W could also result, from inhibition and repassivation of pits due to the stability of oxidized W in low pH environment as described by the solute-rich interphase model [12]. However, it is possible that more than one mechanism controls the passivity of the various Al alloys under different conditions. The fact that low concentrations of W form a film resistant to chloride ions attack [20], indicates that the mechanism in this case is not similar to the referred for Cr, Mo and Ta, since there is not enough oxidized solute in the film to form a barrier layer or to promote electrostatic repulsion to the chloride ion action.

Improved properties in the case of Al-W alloys were interpreted as being the result of the formation of a more stable oxide layer containing very little oxidised solute. Passivation currents were the same, irrespective of dose and concentration and in fact, the more noble value of  $E_p$  was obtained for the lowest concentration of W that corresponded to the sample with the extended depth profile of the implanted layer [20]. Here, the solubility of the oxidised solute species in acid and neutral solutions was correlated to the high pitting potentials found. Data collected by Smialowska [4] indicate that in the case of W even at high anodic potentials and as pH in the occluded cell decreases, W oxide remains stable



accounting for superior pitting resistance. For Al-W alloys the solubility of the oxide in the pit solution might determine the pitting potential value. The solute rich interphase model [12], that implies local passivation of a pit due to stability of oxidized solute in localized low pH conditions, seems more in agreement with the results regarding implantation of W alone [14,21].

W and Ta when implanted separately seem to comply with the solute rich interphase model, which requires that the solute forms a more protective passivating species than Al under conditions within occluded cells [12,20,21].

When W and Ta are implanted together the stability of W oxide in acid media and the ability of Ta to promote passivation all across the pH range, justifies the pitting potentials obtained especially for the alloy implanted with a higher concentration of W + Ta.

Since the ratio W / Ta in the alloys is of 70 / 30, it is thought that for the sample implanted with the higher energy, which amounts to a concentration of 4 at % of implanted elements, the operating passivation mechanism is similar to the observed in Al-W samples [21] with a diminished role for Ta, i.e, the oxide is predominantly constituted by aluminium oxide with W acting as a reservoir to produced W oxide in conditions of occluded cells.

For the sample with a 12 at % ( W + Ta ), it is anticipated that the concentration of Ta in the implanted layer contributes to the enrichment of the film in Ta<sub>2</sub>O<sub>5</sub> and also acts as a reservoir of solute to be oxidized under occluded cell conditions. At high anodic potentials some Ta might be dissolved through the film, as indicated by the higher currents displayed in the pure Ta polarization curves in low pH solutions.

In fact, samples that have been polarized previously in acid environment, with the objective of forming a passive film - in a medium that partially simulates an occluded cell solution - showed, after several cycles in acid and posterior polarization in 0.1 M NaCl solution, more active pitting potentials. The film degradation is supported by the obtained impedance data. This seems to support the idea that some Ta is lost in acid media by dissolution through the film, that is presumably a mixture of Ta<sub>2</sub>O<sub>5</sub> and Al<sub>2</sub>O<sub>3</sub> in proportions that would depend on potential amongst other factors.

When the implanted samples were polarized in sulphate solutions of pH 3, low currents indicated passivation. This suggest an evolution in the film chemistry as the specimen is polarized, with the magnitude of the current more consistent with

the currents shown for Ta and with no apparent indication of W dissolution according to the polarization characteristic shown by pure W at the same pH and also by XPS results [20,21].

## Conclusions

•In acid media, passivation of Al-W-Ta alloys produced by ion implantation yields a film containing presumably a mixture of Ta<sub>2</sub>O<sub>5</sub> and Al<sub>2</sub>O<sub>3</sub>.

The alloy behaviour depends on the solution pH. For pH 0.5 the sample reveals a stronger passivating tendency when compared to pH 3.

Passivation on 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<sub>2</sub>O<sub>5</sub>;
- acts as a reservoir of solute to be oxidized under occluded cell conditions.

The role of W was in agreement with the solute rich interphase model, that implies local passivation of a pit due to the stability of oxidized solute in localized low pH conditions.

•In near -neutral media ennoblement of the pitting potentials was found in the presence of chloride ions for Al implanted with (W+Ta).

The protective character depends on the concentration of the implanted elements. The alloy with higher concentration of the alloyed elements presents a remarkable displacement of the pitting potential (+1.5 V (SCE)) related to Al and also to Al implanted alloys that use W alone as alloying element.

The pitting potential value (+1.025V(SCE)) is only exceeded by samples produced by sputtering deposition of higher average atomic concentration (≥ 9 %), that in some cases are reported as amorphous.

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## REDUCTION OF FAMOTIDINE AT A MERCURY ELECTRODE USING SQUARE-WAVE VOLTAMMETRY

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### Abstract

Famotidine is an electroactive and a surface-active compound which can be irreversibly reduced at a mercury electrode in moderate acidic media at the potential of about -1.20 V vs Ag/AgCl (KCl sat.). Square-wave voltammetry of this reaction can be utilised for a quantitative determination of the drug.