

Corrosion behaviour of tungsten-implanted aluminium in carbonate and sulphate solutions

J. C. S. Fernandes and M. G. S. Ferreira

Department of Chemical Engineering, Instituto Superior Técnico, 1096 Lisboa Codex (Portugal)

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Abstract

Ion implantation is a technique that can improve the corrosion behaviour of metals and alloys and is used both in industry and in laboratory for fundamental research. The present study involves the behaviour of tungsten-implanted aluminium in solutions of carbonate and sulphate/chloride. The role of tungsten depends on the solutions used and, whereas it is deleterious for aluminium in carbonate solutions, it seems to be beneficial in passivating media such as sulphate solutions. This fact is due to the stabilization of the oxide films by WO_3 . Subsequent nitrogen implantation of tungsten-implanted aluminium does not improve its behaviour, at least in carbonate solutions.

1. Introduction

Light alloys, such as those of aluminium, are of particular interest in the transport industry, especially in aeronautics. Apart from adequate mechanical characteristics, the alloys must show a good corrosion resistance. In order to improve this property the use of techniques that modify the surface seem to be of special interest.

Ion implantation is one of these surface modification techniques, since it allows the insertion of various elements in the surface part of the materials. Moreover, there is the possibility of forming solutions beyond the limits of solubility imposed by the thermodynamic relationships, which is of particular interest when the low solubility of the alloys does not allow the right level of a certain element to be achieved in order to improve a certain property.

The present study looks at the effect of tungsten implanted in aluminium, from the point of view of improving corrosion resistance. Previous studies of tungsten are scarce [1, 2], whereas the addition of molybdenum to, for example, stainless steels and aluminium alloys has been widely studied and the effect usually reported as beneficial. Since molybdenum and tungsten have similar metallurgical and chemical behaviours, similar results might also be expected.

The present study was carried out in carbonate- and sulphate-containing solutions. Different results were obtained in the two solutions and in a latter stage the implantation of nitrogen in tungsten-implanted aluminium was also tried with the aim of improving

the corrosion behaviour of the tungsten-implanted specimens.

2. Experimental details

Pure aluminium specimens were implanted at Harwell (UK) with tungsten to fluences of $10^{16} \text{ W}^+ \text{ cm}^{-2}$ at an energy of 40 keV, and in some cases 150 keV. In a few cases, the tungsten-implanted specimens (implantation energy of 40 keV) were again implanted at LNETI (Portugal) with N_2^+ to fluences of $2 \times 10^{17} \text{ N}_2^+ \text{ cm}^{-2}$ at an energy of 40 keV.

Anodic polarization plots were carried out in deaerated 0.01 M Na_2CO_3 and 0.1 M Na_2SO_4 solutions, without and with addition of NaCl. The sweeping rate was 0.1 mV s^{-1} , since at this rate there is a sharper differentiation between the various processes occurring in the range of potentials covered.

The potential vs. time was also measured in relation to a saturated calomel electrode using a high impedance voltmeter. Data acquisition was in all cases made through an HP-85 microcomputer.

3. Results and discussion

3.1. Carbonate solutions

Cyclic anodic polarization plots relative to pure aluminium and tungsten-implanted aluminium (40 keV) in 0.01 M Na_2CO_3 are shown in Fig. 1. The polarization plot obtained for the implanted specimens (Fig. 1(B)) is

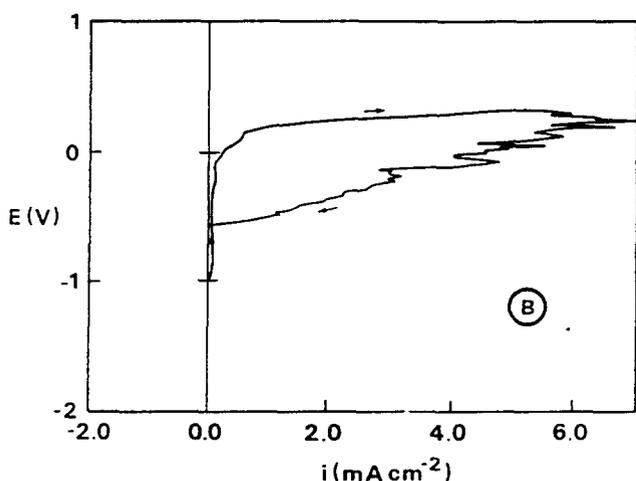
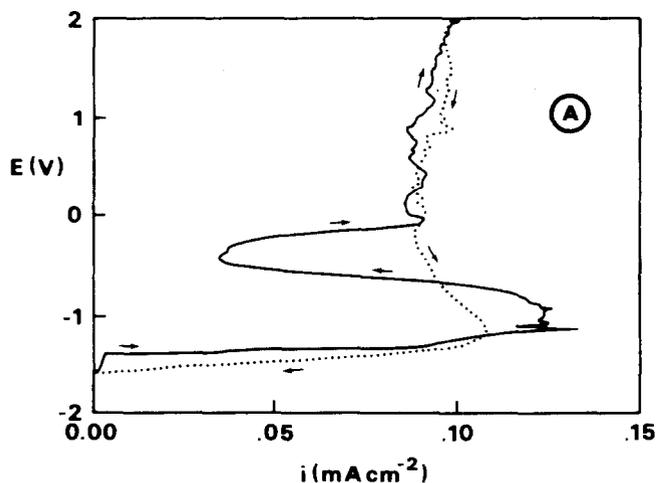


Fig. 1. Cyclic anodic polarization plots in 0.01 M Na_2CO_3 for (A) pure aluminium and (B) tungsten-implanted aluminium.

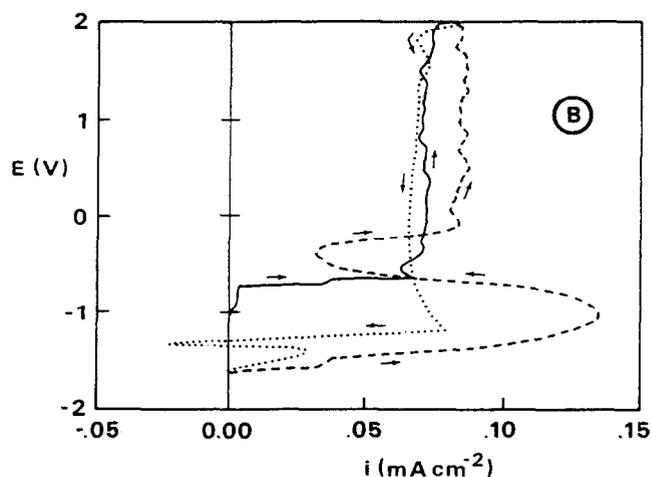
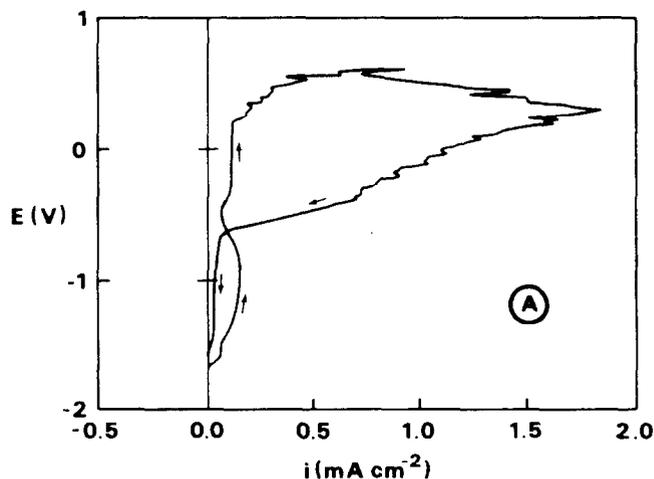


Fig. 2. Cyclic anodic polarization plots in 0.01 M $\text{Na}_2\text{CO}_3 + 0.01$ M NaCl for (A) pure aluminium and (B) tungsten implanted aluminium.

initially (lower anodic potentials) different from that obtained for specimens without implantation (Fig. 1(A)). Furthermore, the free corrosion potential is approximately 500 mV higher than that observed for pure aluminium. However, for applied potentials higher than 0 V, no difference between the two plots can be noticed. The same happens with the descending polarization plot. If a second ascending anodic plot is obtained, a similarity between this plot and that obtained without implantation is observed.

Cyclic polarization plots in chloride-containing solutions (0.01 M $\text{Na}_2\text{CO}_3 + 0.01$ M NaCl) show a breakdown of the film for both the pure aluminium and the tungsten-implanted specimens. However, the breakdown potential (pitting potential) is lower for the tungsten-implanted specimens (Fig. 2), which can be attributed to easy pitting nucleation in sites made available by previous tungsten dissolution.

A potential vs. time plot for the implanted specimens is shown in Fig. 3. Initially the potential is -1175 mV

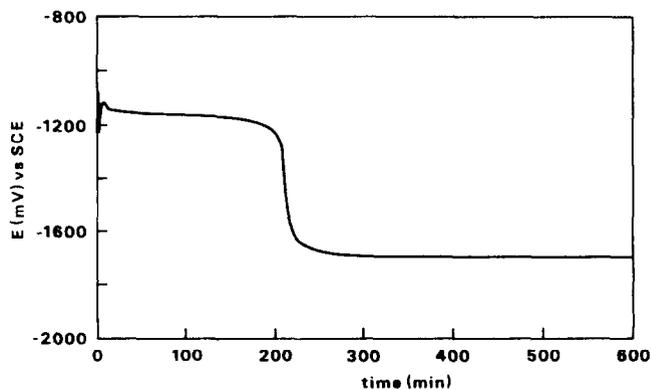


Fig. 3. Potential vs. time for tungsten-implanted aluminium in 0.01 M Na_2CO_3 .

but after a short time it becomes -1700 mV, i.e. the value of the free corrosion potential of pure aluminium.

The analysis of the above results can be done on the basis of the potential vs. pH diagrams [3] of aluminium and tungsten (Fig. 4). Fig. 4(A) shows that aluminium

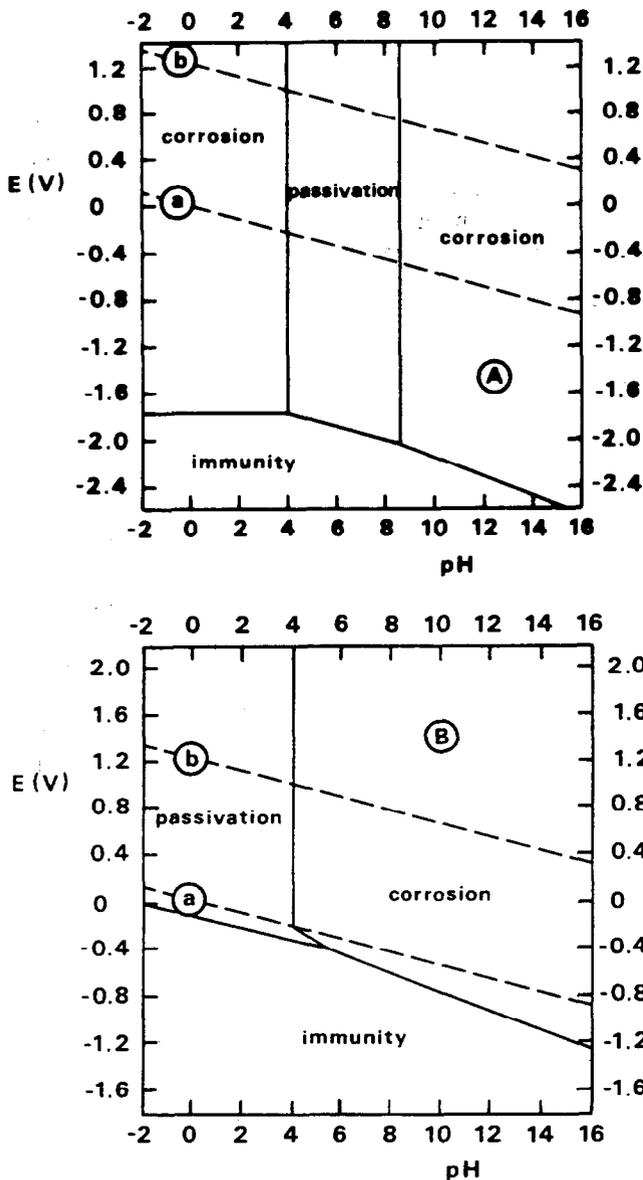


Fig. 4. Potential vs. pH diagrams for (A) aluminium and (B) tungsten in aqueous solutions.

corrodes in aqueous solutions for pH less than 4 and over 8.5; in our case (pH 11), the domain will be of general corrosion. According to Fig. 4(B), tungsten suffers dissolution for pH values over pH 4, thus being also in a corrosion domain in the solution used.

The role of tungsten has been mainly attributed to the presence of W (VI) in the passive layer, as a result of the adsorption of the dissolved tungsten in solution or of the oxidation of metallic tungsten in the alloy [4]. However, the mechanism by which tungsten enters the passive film is not clear. There is no experimental evidence of a direct reaction occurring in the solid state or of previous dissolution of tungsten leading to the formation of tungstate that, in a second stage, adsorbs

onto the passive film. This latter hypothesis has been put forward in some works [5, 6] to justify the beneficial effect of the presence of molybdenum in stainless steels under certain experimental conditions. However, this explanation has been refuted on different grounds [7] and, for tungsten, the fact that WO_4^{2-} would form, at least in acid solutions, tungstic acid without any inhibiting effect on the pitting corrosion [4] would impair this explanation for the positive effect of tungsten in aluminium. Thus the increase in corrosion resistance could be explained as a result of the presence of WO_3 on the passive film, which is particularly stable in water and acids. In contrast, WO_3 is soluble in alkaline hydroxides and carbonate solutions, and forms tungstate. The stability of the film in the case where WO_3 is stable would be improved by the formation of a more efficient barrier that would slow down the electronic and ionic transport through it. Moreover, the limit of the stability of the insoluble oxides when in the presence of other elements is spread beyond what is thermodynamically expected.

The above facts could explain the electrochemical behaviour of the tungsten-implanted alloys without contradicting the explanation put forward by other authors [1] who attributed the deleterious effect of tungsten implantation to the formation of an Al_8W metastable phase, which forms galvanic cells with the aluminium, so accelerating the corrosion.

3.2. Implantation with N_2^+

After the ion implantation with tungsten, a few specimens were implanted with N_2^+ . The polarization plot in 0.01 M Na_2CO_3 does not show any difference relative to that obtained without nitrogen implantation, i.e. Fig. 1(B).

In the same way as for the case of the tungsten-implanted specimens, the potential vs. time was recorded (Fig. 5). This showed that, although initially the free corrosion potential was higher than those of both pure aluminium and tungsten-implanted aluminium, after 1 h

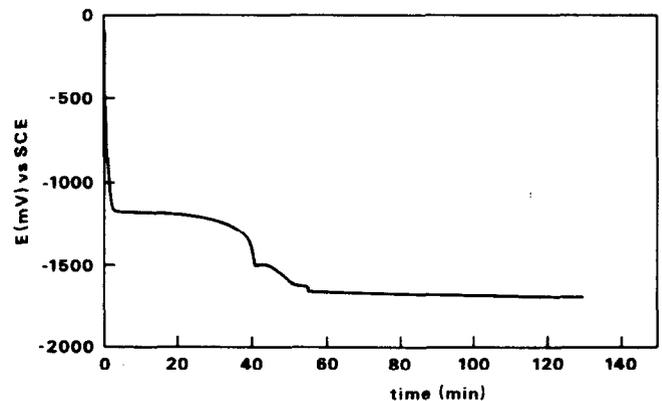


Fig. 5. Potential vs. time for tungsten- and N_2^+ -implanted aluminium in 0.01 M Na_2CO_3 .

the free potential dropped to values similar to those of pure aluminium. This behaviour indicates that the subsequent N_2^+ implantation of tungsten-implanted aluminium does not improve its corrosion resistance, contrary to the beneficial role which has been attributed to nitrogen in steels [8].

3.3. Sulphate solutions

The studies concerning the addition of molybdenum and tungsten to alloys, showing their beneficial effects, have been usually carried out in passivating environments where localized corrosion takes place. To establish the parallel between these studies and the present one, sulphate solutions were used, since the passivation of aluminium is there more stable.

Anodic polarization plots were obtained for pure aluminium and tungsten-implanted aluminium in 0.1 M $Na_2SO_4 + 0.6$ M NaCl (Fig. 6). For the non-implanted aluminium (Fig. 6(A)), a passive behaviour can be observed with residual passive currents of magnitude

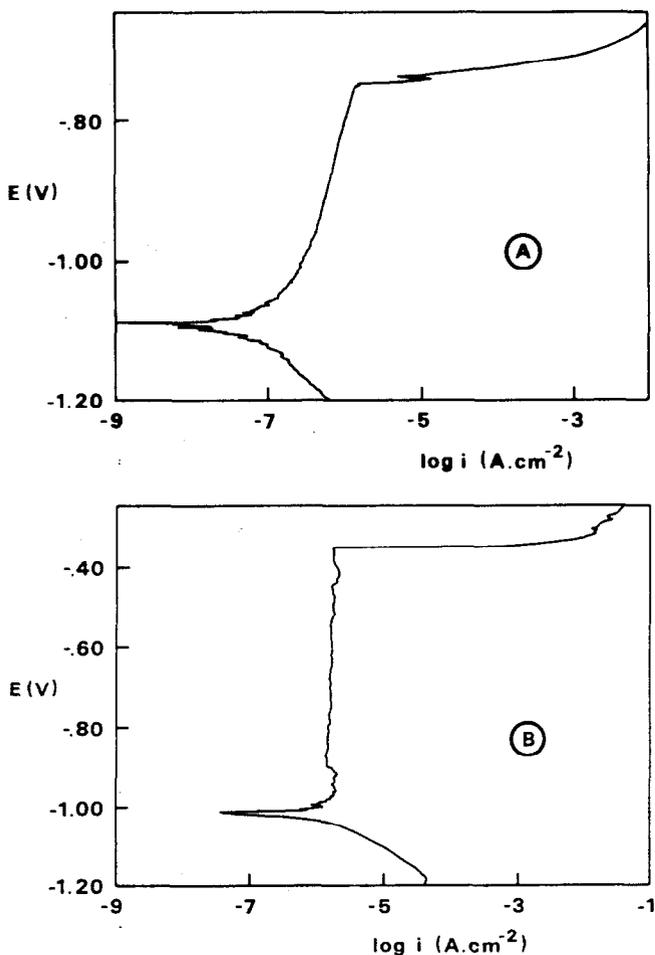


Fig. 6. Polarization plot in 0.1 M $Na_2SO_4 + 0.6$ M NaCl for (A) pure aluminium and (B) tungsten-implanted aluminium (implantation energy 150 KeV).

10^{-7} – 10^{-6} A cm⁻² followed by breakdown at -740 mV. For the implanted specimens a significant increase in the free corrosion potential was observed, simultaneously with an increase in the pitting potential (Fig. 6(B)). The residual passive currents are of the same order of magnitude as those found for pure aluminium. The tungsten implantation was carried out at energies of 40 and 150 keV, the results indicating a better pitting corrosion performance in the latter tests.

The above facts can be explained according to the previous explanation, *i.e.* the incorporation in the present experimental conditions of stable WO_3 into the passive film, interacting with the aluminium oxides and forming a more efficient barrier to metallic dissolution. Moreover, in the present solution (pH 7) and according to the thermodynamic data [3], aluminium is already in a passivation domain. The fact that higher implantation energies lead to better results from the point of view of corrosion, as found by Ives *et al.* [9] for the implantation of molybdenum for stainless steels, might be owing to a deeper penetration of the aluminium as shown by the implantation profiles determined by Rutherford back-scattering for the two energies. The formation of a thicker implanted layer makes the progression of nucleated pits more difficult, owing to a larger depth of WO_3 -stabilized aluminium oxides.

4. Conclusions

(1) The presence of implanted tungsten in aluminium in carbonate solutions does not have a beneficial effect on the corrosion resistance of the aluminium. In contrast, the behaviour becomes even worse. This is due to the fact that WO_3 is not stable in these solutions and also to the eventual formation of Al_3W which might accelerate aluminium dissolutions.

(2) The subsequent implantation of N_2^+ of tungsten-implanted aluminium does not improve the corrosion resistance of the material in carbonate solutions.

(3) In sulphate environments with chlorides the tungsten-implanted aluminium shows a higher pitting potential than that for the pure aluminium, this behaviour being attributed to the stabilization of the oxide film by WO_3 .

Acknowledgments

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