

Final Comments

- DC data pointed out to that the film grown on niobium, by cycling under potentiodynamic conditions in a borate buffer, has a duplex film structure corresponding probably to NbO_x ($x=1,2$) / Nb_2O_5
- Impedance data confirm dc data with an extra time constant exhibited for the oxide obtained by extension of cycling to +500 mV(SCE).
- Film formation is suggested to be controlled by a surface process mechanism.

Acknowledgements

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THE FORMATION OF AN ALTERNATIVE CONVERSION COATING FOR ALUMINIUM IN BUFFERED MOLYBDATE SOLUTIONS

¹C.M.Rangel*, ¹A.Simões, ²R.C.Newman

¹Instituto Nacional de Engenharia e Tecnologia Industrial
Electroquímica de Materias-DM/IMP
Paço do Lumiar, 22 - 1699 Lisboa Codex-PORTUGAL
²UMIST, Corrosion and Protection Centre
P.O.Box 88, Manchester M60 1QD, U.K.

Abstract

A uniformly rich molybdenum film was deposit on aluminium, without the use of external polarisation, using a buffer and a complexant. Potential - time curves showed that the coating is fully-grown within 60 seconds of immersion. Protective films formed within a narrow range of pH, from 4 to 6. Lower pH values, near those used for Cr treatment, gave rise to hydrous blue Mo(V) compounds with little or no protecting ability whilst higher pH values did not allow the coating to be formed probably due to insufficient thinning of the air formed alumina film. Stability of the produced coatings was assessed by polarising the samples to breakdown in a 0.5 M NaCl solution with added carbonate/bicarbonate. Optimisation of the coating produced a pitting resistance comparable to that of chromate conversion coatings. The mechanism of film formation is briefly discussed.

Keywords: conversion coatings, aluminium, molybdate, chromate replacements

Introduction

The search for the development of "stainless" aluminium is at the present based on a concept of corrosion protection that minimises environmentally hazardous processes.

Conversion coatings using a chromate-based solution are well established as a pre-treatment mainly due to its corrosion resistance, low surface resistivity and enhanced adherence to organic coatings. While these characteristics have been difficult to match by other inorganic conversion coatings, the use of such coatings is becoming increasingly restrictive due to the toxicity of hexavalent chromium[1-14].

Molybdates are obvious replacements candidates to chromates for the pre-treatment of aluminium with a participation by electroreduction, rendering compounds that are less soluble in acid than normal alumina or by blocking the cathodic reaction[1-4, 10, 14]. Several authors have tested Molybdates but most methods described require the use of an electrochemical step in the treatment[1-4]. Proposed treatments might include one or more heavy metal ions in addition to Mo [6,10,13,14].

The present paper deals with the formation of a conversion coating on 99.999% Al based on Mo and its resistance to pitting corrosion. The solution pH range was chosen from the Pourbaix diagram for the Mo-H₂O system[15], to lie in the region of stability of MoO₂.

Experimental

Rotating disc electrodes made of Al 99.999% Al (Goodfellow Metals, Cambridge, U.K.) were polished to a 1 μm finish, rinse with de-ionised water and ethanol, and dried in warm air. The exposed area was 0.785 cm^2 . Molybdate conversion layers were produced in solutions containing 6.7 mM molybdate as Na_2MoO_4 with 0.05M acetic/sodium acetate as a buffer. Sodium fluoride was added to give various concentrations in the range from 0.1 to 1 M, usually after immersion of the specimen.

Control experiments were done in solutions containing no molybdate and in a standard chromate/fluoride mixture containing 4 g/L chromic acid, 3.5 g/L sodium dichromate and 0.8 g/L sodium fluoride, pH 2.0. All the solutions were open to the air. The work reported here was conducted at 20 ± 2 $^\circ\text{C}$.

Potential - time curves were registered in a Solartron 3531 D data acquisition system Vs a saturated calomel electrode used as reference (SCE). A rotating disc electrode system from EG&G, PARC was used at a rotating rate (w) of 740 rpm. Pitting tests were performed, using a Solartron unit, ECI Model 1286, by immersing the treated specimens in 0.5M NaCl / 0.5M $\text{NaHCO}_3 + 0.05\text{M Na}_2\text{CO}_3$ with pH 8.7. Scan rate used was 10 mVs^{-1} .

Results

Fig.1 shows selected potential - time curves for the molybdate treatment using a fluoride concentration of 0.1 M. It is evident that there is a range of pH values for successful formation of a protective layer, indicated by the rise in potential to about -800 mV, after the initial sharp fall due to the dissolution of the air formed film. The coating is fully-grown in 60 seconds.

Protective films formed within a narrow range of treatment solution pH range, 4 to 6. Lower pH values, near those normally used for Cr treatment, gave rise to hydrous blue Mo (V) compounds with little or no protecting ability while higher pH values did not allow the coating to be formed, probably due to insufficient thinning of the air formed film.

A control experiment was carried out using a conventional chromate/fluoride mixture of pH 2.0. The open circuit potential corresponding profile is presented in figure 2. Comparison is made with data presented in figure 1 for the samples treated with molybdate/fluoride/acetate solutions : apart from the steady potential, more active for the molybdate solutions, the molybdate and chromate results were very similar. Best pH values for the Mo based conversion coating formation, in terms of reproducing the chromate transient, were between 4-6 for the fluoride levels studied. The molybdate treated surfaces had a uniform, light brown-gold colour.

The mechanism of conversion coating in chromate/fluoride solutions is well understood [5,7,8-12]. Cathodic reduction of chromate to CrOOH occurs at impurity sites in the aluminium after thinning or removal of the air formed film by fluoride complexing. The resulting nuclei of CrOOH grow laterally, incorporating some alumina and eventually covering the surface. Pitting in chloride solutions is strongly inhibited in this layer.

The idea in this work is that a molybdate treatment could, in principle achieve a similar effect if the pH was controlled in the region of stability of MoO_2 , roughly 4-6[15]. Some deposition of metallic Mo would probably occur and might be acceptable as a by-product of MoO_2 formation. In

a molybdate treatment it is important to use an additional buffer to control the surface pH, in chromate/fluoride treatment fluoride itself is an effective buffer at the solution pH 2-3.

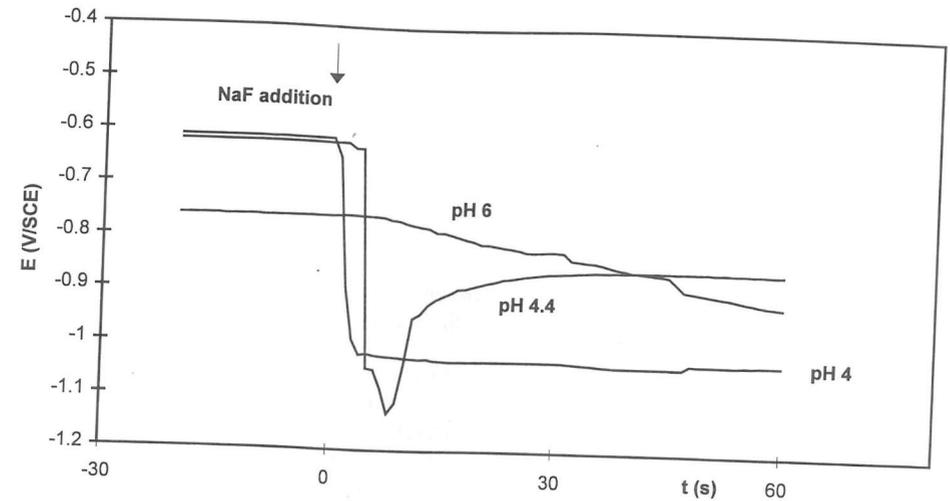


Fig.1 Potential time curves for immersion of pure aluminium rotating disc electrode in molybdate/ fluoride (0.1M)/ acetate solutions at different solution pH values. $w = 740$ rpm

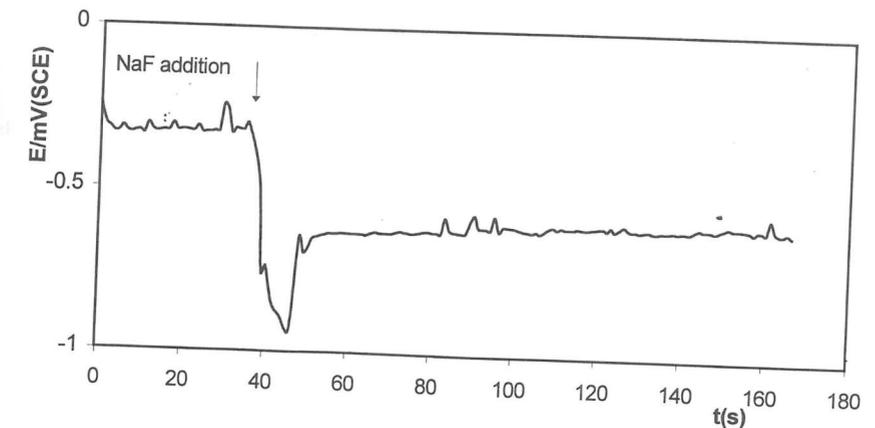
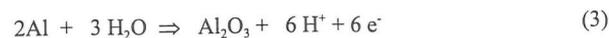
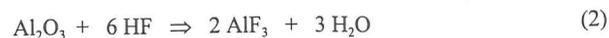


Fig. 2 Potential time curves for immersion of pure aluminium rotating disc electrode in chromate/ fluoride solutions at pH 2.0. $w = 740$ rpm

The role of fluoride additions is the thinning of the air formed film thickness. This results in a dynamic equilibrium between alumina film growth and its dissolution. Associated reactions are:



The pitting corrosion susceptibility of the coated material was assessed by polarising to breakdown in a solution containing 0.5 M NaCl with added carbonate/bicarbonate, pH 8.7.

Figure 3 shows the pitting potentials obtained as a function of the pH of the treatment solution. It is to be noticed that values equivalent to those shown for the chromate conversion coating were obtained for a pH of the treatment solution of 4.1. The absence of Mo in treatment buffer solution used in this work yielded expected pitting potentials of ~ -700 mV(SCE).

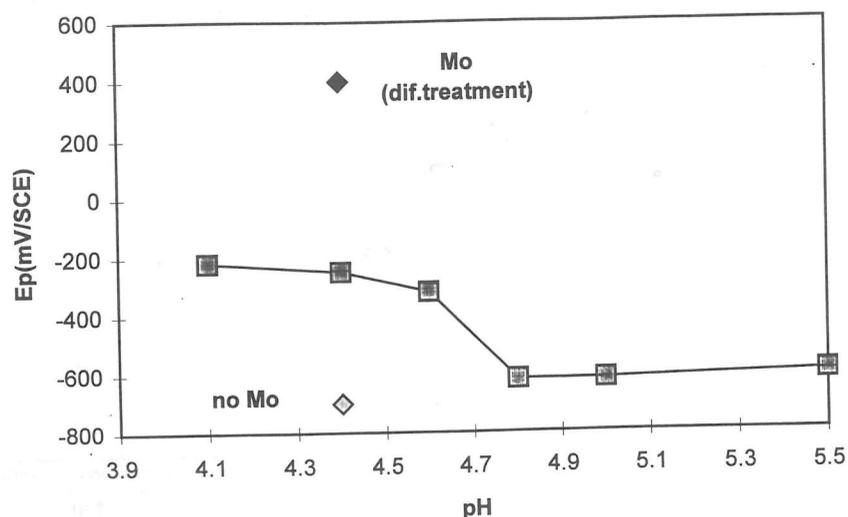


Fig.3 Pitting potentials for pure aluminium/ Mo based conversion coating as a function of treatment solution pH. Also shown are data corresponding to the control solution in the absence of molybdate and to sample with a different surface preparation.

Molybdate incorporation into the film was evident from RBS and XPS spectra. Results will be presented elsewhere. Main constituents of the conversion layers are MoO₂ and some form of alumina. Mo(VI) was also present.

Figure 3 also incorporates a remarkably noble pitting potential value found using the same solution treatment but with a different initial surface preparation. Research continues along these lines in order to optimise the incorporation of molybdenum in the film and make the surface more resistance to pitting corrosion.

Conclusions

- The production of a molybdate based conversion coating, without external polarisation, on aluminium has proven successful, using an immersion process that uses an acetate buffer and fluoride as a complexant.
- Protective coatings are produced within a narrow range of pH (4.6). At lower pH the desired Mo oxide did not form and at higher solution pH values fluoride was unable to attack the air formed film.
- Pitting potential values obtained with the produced coatings in chloride solutions as high as those achieved with conventional chromate/fluoride surface treatment.

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PITTING RESISTANCE OF TUNGSTEN IMPLANTED ALUMINIUM

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

Department of Chemical Engineering, Instituto Superior Técnico, 1096 Lisboa Codex, PORTUGAL
Tel. (351-1) 8417234, Fax. (351-1) 8404589, E-mail: pcjfern@alfa.ist.utl.pt

ABSTRACT

Tungsten can be successfully implanted on aluminium forming a solid solution. SIMS, XPS and AES analysis showed that almost no tungsten was found in the passive film formed on the alloy in 0.6M NaCl solution. The beneficial effect of tungsten in the increase of the pitting potential of the alloy is due to the ennobling of the pitting process caused by the presence of metallic tungsten. This element modifies the thermodynamics and kinetics of the dissolution and facilitates hydrogen evolution inside the incipient pits, diminishing the ability of the metal to maintain the critical pH associated to stable pitting.

Keywords: ion implantation, aluminium, tungsten, pitting

INTRODUCTION

Aluminium alloys are widely used in the transport industry, especially in aeronautics, because of their light weight, high strength and good resistance to uniform corrosion. However, they exhibit very poor resistance against localized attack and, in particular, to pitting in chloride-containing solutions.

It is known that the passivity of aluminium could be enhanced by using alloying elements such as Cr, Mo, Ta, Zr and W. However, improvements in the localized corrosion resistance of aluminium using conventional alloying techniques are difficult to achieve. In fact, to enhance passivation an alloying element should be retained in solid solution, without the formation of precipitates that normally act as microgalvanic cells, increasing the localized attack. Thus, the low solubility in aluminium of the transition metals (below 1% a/o) does not allow them to influence markedly the corrosion behaviour of the alloys.

In the past ten years, several authors [1-6] have investigated the metastable Al alloys obtained by nonequilibrium alloying additions of elements such as Mo, Cr, Ta, Zr and Si, using ion implantation or sputter deposition techniques that allow the amount of solute in solid solution to be increased by several orders of magnitude. From their results it seems that all the above elements lead to an improvement of the pitting resistance of the alloy, being Mo one of the most promising. Since molybdenum and tungsten have similar metallurgical and chemical behaviours, a few works devoted to supersaturated Al-W alloys have appeared recently [7-11]. These studies evidenced the beneficial effect of W on pitting corrosion resistance, but the mechanisms involved in this enhancement are not clear yet.

In the present work the role of implanted tungsten on the pitting corrosion of aluminium is studied and an explanation for the beneficial effect of tungsten is presented.