From absorvance vs. time plots, reactions can be monitored. This method offers a new way for the calculation of the kinetic and thermodynamic parameters for the reaction.

Final Comment

Active pyrrolic ester films can be easily prepared by electrochemical oxidation with reasonable efficiencies that are independent of film thickness. They can be characterised by electrochemical and spectroscopic techniques. They undergo facile, high yield reactions, this opens new prospects for their modification and insertion of new active functions, namely amides that can not undergo direct electropolymerisation.

Acknowledgements

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A DC/AC STUDY OF THE OXIDE FILM ON NIOBIUM IN BORATE SOLUTIONS

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Abstract

This paper reports on the electrochemical characterisation of the oxide film grown on niobium in a borate buffer solution of pH 8.8 at room temperature.

The formation of a duplex oxide, probably NbO_x (x= 1,2) / Nb_2O_5, is suggested by cyclic voltammetry results. Peak currents and scan rates showed a linear dependency when plotted in the log-log plane, exhibiting a unity slope indicating control by a surface process.

Electrochemical impedance spectroscopy confirmed the voltammetry results. Impedance spectra were conducted within the potential domains of both anodic peaks after 10 cycles at 200 mVs^{-1}. Bode plot analysis and simulation by the equivalent circuit approach suggested an extra time constant when cycling was extended to include the second peak.

The stability of the oxide film was tested in 0.5 M sodium chloride solutions at a low scan rate (0.2 mVs^{-1}) showing no breakdown up to 2500 mV (SCE).

Key words: niobium oxides, niobium, anodic oxidation, impedance spectroscopy.

Introduction

The motivation for this study lies on the excellent corrosion resistance of niobium and its oxides and also in the possibility of using it as a coating or as an element for superficial alloying. This is particularly attractive in the case of aluminium. In fact, in the last ten years, a variety of corrosion resistant aluminium alloys have been prepared by non-equilibrium alloying methods using Cr, Mo, Ta, W, Zr [1,2]. Results concerning Nb are somewhat scarce.

Most studies related to the formation of the anodic film on niobium use galvanostatic conditions for its growth [3,4]. Passivation behaviour is complex in nature. Films thicker than several nm are expected to behave as semiconductors with electronic states in the semiconductor participating in the electron-transfer reaction. The semiconducting properties of the film, which is an n-type semiconductor, have been studied by several authors [3-9].

This paper reports on preliminary results on the electrochemical characterisation of oxide film grown on niobium, under potentiodynamic control, in a borate solution of pH 8.8 at room temperature.

Experimental

The working electrode was a spectroscopically pure niobium rod with 3mm of diameter. The electrode was mounted in epoxy resin with a copper wire providing electrical contact. Experiments were run in a conventional three electrode cell (Greene cell). The secondary electrode was a helix of Pt wire and a saturated calomel electrode (SCE) was used as reference.

Solutions were prepared from Analar chemicals and distilled water. The electrolyte was a borate buffer solution of pH 8.8 with the following composition, 0.15M H_3BO_3+ 0.075M $Na_2B_4O_7.10H_2O$. The niobium rod was mechanically polished with abrasive SiC paper up to 1000 mesh. Afterwards, the electrode was washed with distilled water, degreased with ethanol and dried with cool air before immersion in the working solution.

Voltammograms were performed with a PAR potentiostat, mod. 273A at sweep rates (s) that varied between 550 and 5 mVs^{-1}. Electrochemical impedance spectra were obtained from a frequency response analyser (FRA), model 1250, couple to an electrochemical interface (ECI), model 1286, both from Solartron.

Results and Discussion

DC results

Figure 1a) shows a typical voltammogram of niobium in borate solution (pH 8.8) when sweeping from −1500 to 500 mV (SCE) at a sweep rate of 200 mVs^{-1}. In the first sweep two anodic peaks were identified. Peak (I) is thought to be associated with the formation of an oxide probably of the type NbO_x (x=1,2) and a second peak (II) with the formation of the more stable oxide specie, of Nb_2O_5 [10]. The absence of cathodic peaks was evident, indicating the absence of reduction of the niobium oxides in the studied potential domain.

A second sweep exhibited a remarkable decrease in the current density in the potential domain of peak II, reaching values of 0.2 $mAcm^{-2}$. Successive sweeps did not alter the voltammogram (see figure 1b).
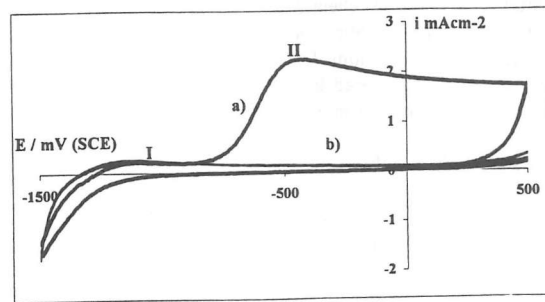

Fig. 1 Voltammograms for pure niobium in a borate buffer solution, v=200mVs^{-1},
first sweep (a)
second and successive sweeps (b).

The effect of sweep rate on the electrochemical characteristics of the system Nb/borate solution, figure 2, was studied over a wide range of values, 550 - 5 mVs^{-1}. Figure 3 shows a linear relationship between the peak current density (ip) and sweep rate (s) for peaks I and II. It is to be noticed that for the second peak the analysis was made for sweep rates above 100 mVs^{-1}, since for lower values the peak was not well defined. Near unity slopes values were estimated suggesting that film formation takes place controlled by a surface process [11].
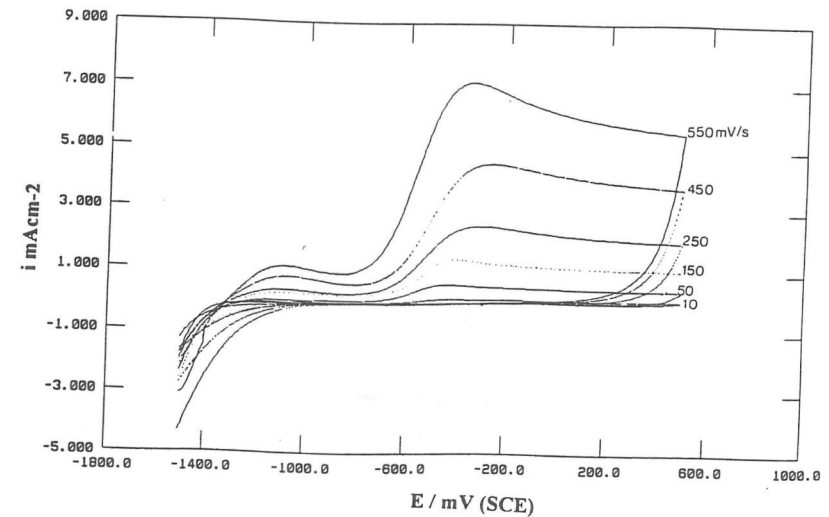
Fig. 2 The effect of sweep rate on the electrochemical characteristics of the system Nb/borate buffer solution, pH 8.8, s = 550-5 mVs^{-1}.
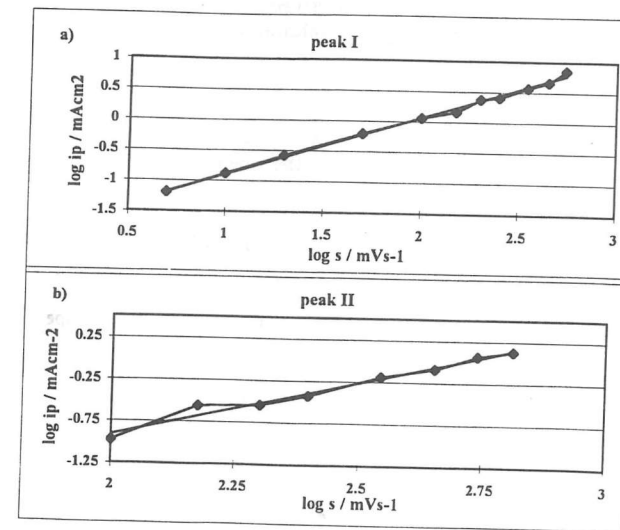

Fig.3 Peak current density vs. sweep rate for Nb/borate buffer solution, pH=8.8,
peak I (a)
peak II (b).

The stability of the oxide film was tested in 0.5 M sodium chloride solutions. Film growth conditions used included 30 cycles between -1500/500 mV (SCE) in the borate buffer solution, at a sweep rate of 200 mVs⁻¹, in order to form the respective oxides.

A unidirectional voltammogram was conducted from -1500 to + 2500 mV (SCE) at a slow sweep rate, 0.2 mVs⁻¹. Results are shown in figure 4 with no evidence of breakdown.
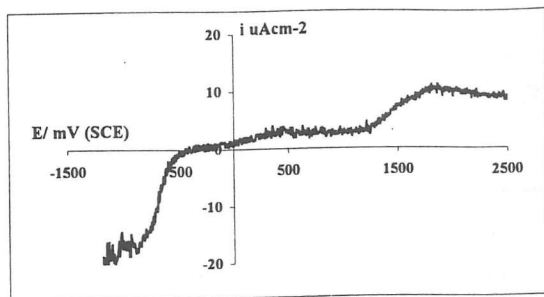

Fig. 4 Unidirectional voltammogram for Nb/NbOₓ (x= 1,2)/Nb₂O₅ in a 0.5 M NaCl solution at 0.2 mVs⁻¹. The oxide was grown after 30 cycles, -1500 → 500 → -1500 mV (SCE), in a borate buffer solution at 200mVs⁻¹.

AC results

The ac data were obtained for the systems Nb / NbOₓ (x= 1,2) and Nb / NbOₓ (x= 1,2) / Nb₂O₅ , just after the growth of the respective anodic film, at the open circuit potential. The experimental conditions for film growth are shown in table 1.

Results are presented as Bode plots in figure 5. Analysis and simulation of the experimental data with Boukamp's program [12] were conducted in both cases.

When cycling is extended to include the second peak, an extra time constant appears which might be associated to the presence of Nb₂O₅.

Table 1 Experimental conditions for film growth on niobium in a borate buffer solution, pH= 8.8.

Grown oxide	Voltammetric conditions
NbOₓ (peak I)	-1500 →-800 →-1500 mV, v=200mVs⁻¹, 10 cycles
NbOₓ (peak I) + Nb₂O₅ (peak II)	-1500 → +500 →-1500 mV, v=200mVs⁻¹, 10 cycles

Deviation from a perfect capacitor behaviour is evident judging by the values of the phase angle [8]. In spite of this difference an attempt was made to estimate the thickness of the film. Values were of the order of 0.70nm, equivalent to two monolayers [13], this seems to be in agreement with results found by D´Alkine et al. [5].
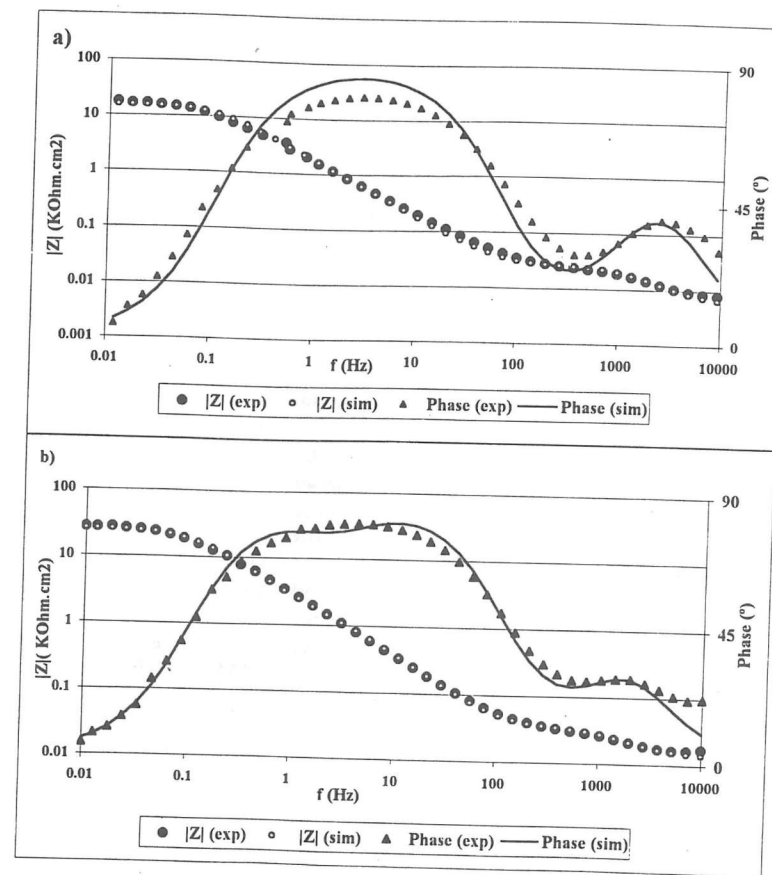

Fig. 5 Bode plots for Nb oxides grown according to conditions presented in Table 1. Experiments conducted in the borate buffer at the open circuit potential. Nb/NbOₓ (x= 1,2) (a) Nb/Boₓ (x= 1,2) /Nb₂O₅ (b).

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

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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-H_2O system[15], to lie in the region of stability of MoO_2.