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SHORT COMMUNICATION

OPEN-CIRCUIT BREAKDOWN OF ANODICALLY FORMED NICKEL OXIDE

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In previous papers[1-3], the authors have investigated the breakdown of anodically formed nickel oxide films on open circuit in pH 2.8 Na_2SO_4 solutions. In this note, experiments are described which support the mechanism of local breakdown at defect sites in the oxide and subsequent undermining of the remaining oxide film. These include an electron-optical examination of the surface for pits, measurement of the surface activity and both cathodic and anodic galvanostatic experiments.

The potential decay profiles for anodically formed oxide films display a series of distinct arrests, their number and duration depending on the conditions of film formation. For example, Fig. 1 shows the open-circuit potential decay profile obtained after a prior anodisation at 0.0 V for 1 h using the potential step technique. The recovered surface activity has been determined at various points on the decay curve by stepping the potential back to 0.0 V, measuring the anodic charge passed (q_a), and comparing this with the charge passed on an oxide-free specimen (q_a^0), *ie* % activity = $q_a/q_a^0 \times 100$ [1]. There are two distinct regions of potential decay in terms of the recovered surface activity, with a sharp potential spike being the transition point. In the region up to the potential spike, A, localized breakdown of the oxide occurs at the defect sites in the film, probably as a result of oxide chemical dissolution ($\text{NiO} + 2\text{H}^+ \rightarrow \text{Ni}^{2+} + \text{H}_2\text{O}$). The subsequent exposure of bare nickel metal sets up the corrosion couple:

which leads to the rapid potential shift to *ca* -0.75 V. Since the attack is localized at the defect sites, very little (<5%) activity is recovered in region A. The accelerated increase in surface activity in region B has been explained in terms of a general undermining of the oxide, nickel dissolution at the (oxide-free) defect sites serving to undercut the nickel oxide.

Figure 2 shows a series of electron micrographs of polycrystalline nickel surfaces after various electrochemical treatments. Both the electropolished surface and that obtained after anodising by the potential step technique to 0.0 V for 1 h are smooth (Fig. 2a). Also shown are photomicrographs taken before and after the potential spike, Fig. 2(b) and Fig. 2(c) respectively. Significant pitting attack at the surface is observed only after the potential has decayed through the region of the spike, in agreement with the model for breakdown previously proposed[3]. The pits are situated at those oxide defect sites which have broken down, *ie* in the area where nickel is dissolving. The remaining surface which is still covered with oxide can readily sustain the counter cathodic reaction of hydrogen evolution. However, if an electropolished nickel elec-

trode is immersed in the pH 2.8 solution with sufficient cathodic polarization to remove the prior 6-8 Å air-formed NiO film[4] and the system switched to open circuit, no pitting attack is observed. Instead, there is a uniform etch of the entire surface, the absence of an oxide film and its associated defect sites[5,6] explaining the absence of localized breakdown and pitting attack. A specimen with this general etch is shown in Fig. 2(d).

The undermining mechanism of oxide removal after the potential spike involves the reaction couple (i)-(ii), with the oxide being physically removed by undermining because of reaction (i). Ammar and Darwish[7], studying the breakdown of nickel oxide films in acid chloride solutions, also proposed that 'the first few pits lead to the destruction of passive oxide by local action'. However, their model essentially says that the nickel dissolution reaction, (i), provides electrons which participate directly in the cathodic reduction of the oxide:

To determine the role of nickel dissolution in the overall removal of nickel oxide, electrodes were anodised at 0.0 V for 1 h, the circuit was then opened and the potential permitted to decay to the sharp spike, *ie* through region A in Fig. 1. At this point, the electrode was galvanostatically polarized for 20 min with different anodic charging currents, after which the surface activity was determined (Fig. 3). The fact that anodic charging increases the recovered surface activity by more than 50% over that obtained on

Fig. 1. Open-circuit decay profile for a nickel electrode anodized at 0.0 V for 1 h using the potential step technique. The oxide film on electropolished nickel was cathodically removed before the anodisation. The surface activity at various times during the potential decay is also given. Solution pH is 2.8.

Fig. 2. Electron micrographs of a polycrystalline nickel surface after different electrochemical treatments: (a) electropolished in 53 vol % H_2SO_4 or anodically oxidized at 0.0 V for 1 h in pH 2.8 H_2SO_4 ; (b) anodization at 0.0 V for 1 h followed by open-circuit breakdown to point X in Fig. 1; (c) as in (b) but with open-circuit breakdown to point Y in Fig. 1; (d) exposed to the pH 2.8 solution for 30 min on open circuit after electropolishing and cathodic reduction, *ie* in the oxide-free state. Shadowed spheres are 900 Å polystyrene balls.

open circuit indicates that the nickel dissolution reaction removes oxide mainly through undermining.* With increasing anodic charging current, the recovered activity eventually begins to decrease, due to a repassivation of some of the breakdown sites with the higher anodic currents, *ie* some of the anodic current is used to reform the oxide as well as dissolve nickel and undermine oxide. At

a sufficiently high anodic current, the potential will shift very rapidly from the region of the spike (*ca* -0.75 V) towards that associated with oxygen evolution from a completely oxide covered surface.

A set of experiments were conducted to check the extent of oxide film breakdown in region A. Based on the small amount of recovered surface activity in this region, and the electron photomicrographs (Fig. 2), it has been proposed that chemical dissolution occurs only at the oxide defect sites, *ie* the (non-defective) oxide covering the rest of the surface is not attacked. However, it is already known[2] that even a monolayer coverage of chemisorbed oxygen can inhibit nickel dissolution and thereby diminish the amount of recovered surface activity. This means that

* The absence of a significant contribution from the reaction couple (i)-(iii) is also in agreement with the previous observation[1, 4] that the hydrogen evolution reaction is extremely facile on NiO (current efficiency ~100%) while cathodic reduction of NiO is extremely slow.

Fig. 3. Recovered surface activity as a function of the rate of anodic charging after the potential has decayed to the spike. The electrode was initially anodised at 0.0 V for 1 h. after which the potential was permitted to decay on open circuit to the spike. The various anodic currents were then applied for 20 min and the subsequent surface activity was determined.

the surface activity measurements may be insensitive to the thickness of the inhibiting oxide film and, therefore, the results do not rule out the possibility that substantial thinning of the non-defective oxide has occurred in region A. Under these circumstances, the rapid increase in surface activity after the spike could simply be due to the last bit of thinning, by chemical dissolution, of the remaining thin oxide film which covers most of the surface. To show that this is not the case, nickel electrodes were anodised for 1 h at 0.0 V and galvanostatic cathodic charging initiated either (i) immediately after the anodise, or (ii) after the potential had been permitted to decay on open circuit

up to the spike, ie after ca 30 min on open circuit. In both cases, the surface activity was determined after 20 min of cathodic charging at $20 \mu\text{A cm}^{-2}$. The surface activities recovered were 50% without and 55% with the intervening open-circuit decay. The almost identical results indicate that the intervening open-circuit decay to the potential spike has little effect on the amount of oxide present. If there had been substantially less oxide on the surface after the intervening open-circuit treatment, eg as would result from a general thinning of the film, the amount of recovered surface activity should be much higher after passage of the constant quantity of cathodic charge.

The results described above thus confirm that the open-circuit attack in region A is localized at the oxide defect sites, the oxide covering the rest of the surface being removed by undermining once bare nickel surface is exposed and nickel dissolution can occur.

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REFERENCES

1. B. MacDougall and M. Cohen, *J. electrochem. Soc.* **123**, 191 (1976).
2. B. MacDougall and M. Cohen, *J. electrochem. Soc.* **123**, 1783 (1976).
3. B. MacDougall and M. Cohen, *J. electrochem. Soc.*, in press.
4. B. MacDougall and M. Cohen, *J. electrochem. Soc.* **121**, 1152 (1974).
5. H. W. Pickering and R. P. Frankenthal, *J. electrochem. Soc.* **112**, 761 (1965).
6. J. Kruger, *J. electrochem. Soc.* **110**, 654 (1963).
7. I. A. Ammar and S. Darwish, *Electrochim. Acta* **13**, 781 (1968).