JOURNAL OF APPLIED ELECTROCHEMISTRY 21 (1991) · SHORT COMMUNICATION

SHORT COMMUNICATION

The passivation of nickel in 0.5 M sulphuric acid

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Received 14 December 1989; revised 19 March 1990

1. Introduction

It is well known that the results obtained for nickel by different authors using electrochemical measurements are in poor agreement [1]. In the case of potentiometry the existence of one [2] two [3–5] or even four peaks [6] has been reported. The relative heights of the current maxima are believed to depend on solution pH among other things. Real, Vilche and Arvia [7] gave a literature survey of relevant contributions published before 1980.

Droste and Feller [6] mentioned a shift of the corrosion potential in the positive direction as a function of time in a sulphuric acid medium. After relaxation at the corrosion potential for different periods of time, they performed linear potential sweep experiments, using a slow scan rate. They attributed a decrease in the first current maximum and a coherent increase in the second maximum to the formation of HS^- species from HSO_4^-. According to these authors total passivation could only take place when no sulphides remained present at the surface. The presence of a prepassive film has also been reported by Bockris *et al.* [8] who used steady state potentiometry together with ellipsometry and by Vilche *et al.*, among others [4], using voltammetry.

It has been shown that pretreatment such as electro-(chemical) polishing [9] and mechanical polishing [10] can give rise to different polarization curves. The change in the polarization curve as function of scan rate is also striking [11].

For a detailed interpretation of the experimental potentiostatic and potentiodynamic data it is therefore extremely important to understand the influence of the pretreatment procedures on the measured spectra.

The aim of the work presented here is to investigate the formation of the prepassive film on nickel at the corrosion potential in order to obtain more knowledge about the influence of the formation of such a film on the voltammograms from which conclusions are often drawn with respect to the mechanism of the initiation of film formation and of the growth mechanism of the passive film.

2. Experimental details

Nickel electrodes were made from spectrographically pure nickel rods (Materials Research Company). After machining the samples were annealed at 1050° C for 4.5 h and furnace cooled. After coating with an epoxy based paint the electrodes were embedded in an epoxy resin. Finally they were abraded with emery paper down to 800 grit, and dried in a jet stream of air. The 0.5 M H_2SO_4 electrolyte used was prepared from H_2SO_4 (Merck analytical grade) and deionized water (Millipore milliq quality) and deaerated with pure nitrogen for at least 3 h. An Autolab (ECO, PSTAT10) potentiostat was used. Potentials were measured with respect to the saturated sulphate electrode (Hg_2SO_4/K_2SO_4/saturated K_2SO_4 (SSE)). The potential scans were performed with a scan rate of $20\,mV\,s^{-1}$. The start potential of the potential scans was −0.65 V, which is anodic to the corrosion potential, and the end potential was +0.6 V, for all the experiments.

3. Results

The change in the corrosion potential as a function of time is shown in Fig. 1. The inset shows the change immediately after immersion in the electrolyte. Voltammograms recorded after various times at the corrosion potential are presented in Fig. 2. The voltammogram of an electrode immersed in the solution at an applied potential of −650 mV immediately after abrading, is also shown in Fig. 2. Figure 3 shows voltammograms recorded after 2.5 h at the corrosion potential, after 1 h at −675 mV and after 1 h at −650 mV. Experiments performed in aerated solutions gave the same results.

It is clear from Figs 2 and 3 that the first maximum in the active-passive transition region decreases when the electrode is exposed to the electrolyte for longer times and at more positive potentials. It also becomes clear that only two maxima are present (Fig. 3: I, II) when the first current maximum is high. However, three separate maxima are present in the case in which the first current maximum is low (Fig. 3: 1, 2, 3).

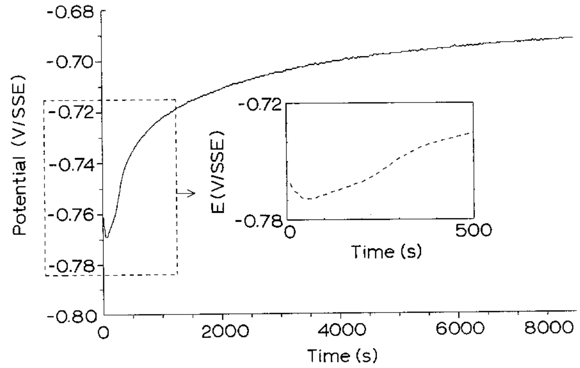

Fig. 1. Corrosion potential as a function of time after immersion.

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It is also apparent from Fig. 3 that for lower values of the first current maximum, a higher current density at positive potentials within the passive region can be observed.

4. Discussion and conclusions

The time between exposure of the nickel electrodes to the electrolyte, i.e. the time at the corrosion potential and the performance of a potential scan in a sulphuric acid medium obviously has a significant influence on the measured current-potential curves. A similar observation was reported by Droste and Feller [6]. When a measurement is made immediately after immersion of the electrode in the electrolyte the first maximum is almost completely absent. It can be seen from the inset of Fig. 1 that the potential initially shifts to lower value, indicating a change in surface properties. It is most likely that the initial shift of potential is due to dissolution of an air-formed oxide layer. Since the air-formed oxide film consists of NiO, the film formed initially in the electrolyte, the prepassive film, cannot be NiO. The real composition of the prepassive film, however, cannot be deduced from our measurements. Droste *et al.* [6] observed an increase in the second current maximum when the first current maximum decreases. They concluded that a prepassive film containing HS^- was present at the surface and impeded the formation of the final passive film. However in our experiments there is no coherent increase in the second maximum with a decrease of the first. Therefore such a film is not probable.

The corrosion potential rapidly reaches its lowest value and in the following linear sweep experiment the first current maximum then shows its highest current maximum. The electrode is believed to have a minimal surface coverage at the lowest corrosion potential. The shift to more positive corrosion potenials, which is accompanied by a decrease of the first current maximum in the potential sweep experiments, must therefore be ascribed to an increasing coverage by a surface film with a different composition.

The increase of the passive current density, when the value of the first current maximum decreases, shows that the film, which is initially formed, retards the formation of a good protecting passive film.

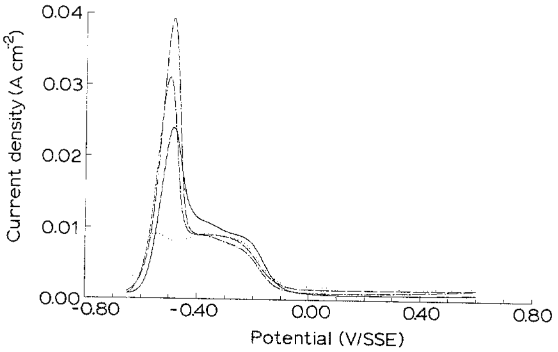

Fig. 2. Linear potential sweep experiments performed after various exposure times at the corrosion potential, except (- - -). (— —) after 120 s; (---) after 15 min; (——) after 2.5 h; (----) immediately after immersion under an applied potential of −0.65 V.

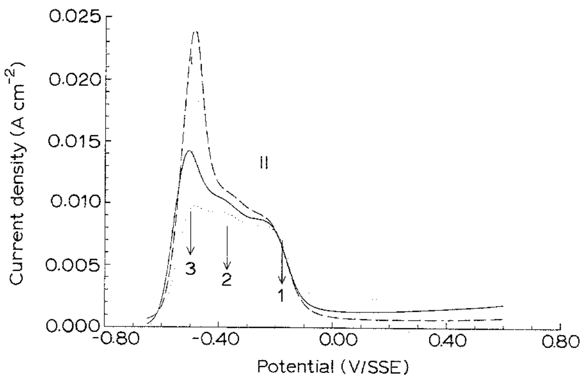

Fig. 3. Linear potential sweep experiments after various times at different potentials. (– – –) after 2.5 h at the corrosion potential; (——) after 1 h at −0.675 V; (----) after 1 h at −0.65 V.

The formation of a prepassive film at the corrosion potential and also at potentials between the corrosion potential and the potential where the first current maximum appears in a potential scan measured at $20\,mV\,s^{-1}$, indicates that during a (quasi) steady state polarization experiment a film has already been formed before the apparent active-passive transition region. Bockris *et al.* [8] observed the formation of a passive film at potentials anodic to −0.685 V, using steady state ellipsometry in a sulphuric acid medium with a pH of 3.15, where the current reached its maximum at about −0.5 V. In our experiments it is shown that although a medium with a lower pH was used, a prepassive film is formed at even more cathodic potentials, where the current maximum appears at about the same potential.

It can be seen from Figs 2 and 3 that during the active-passive transition at least three maxima are present, from which the second maximum is usually obscured by the first current maximum.

The results show that the use of voltammograms for the determination of the electrochemical mechanism of the active-passive transition of nickel is not straight forward. Comparison of literature data in order to propose an unambiguous mechanism for the passivation does not appear possible due to different pretreatment procedures.

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