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PITTING OF NICKEL DURING ANODIC GALVANOSTATIC CHARGING IN Na_2SO_4 SOLUTIONS

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Abstract—The anodic galvanostatic charging technique has been used to study the pitting of nickel in acid and neutral Na_2SO_4 solutions containing various concentrations of Cl^- . Pit initiation is indicated by a change in potential in the cathodic direction, this potential being substantially higher than that required to sustain pitting. The steady-state pitting potentials are in the passive, rather than the active, potential region, a result which can be explained by the highly localized nature of the pitting process. Increasing the $[\text{Cl}^-]$ lowers the potential for pit initiation as well as the steady-state pitting potentials. The influence of anodic charging rate (i_a°) on pit initiation depends on the $[\text{Cl}^-]$ in solution; at high $[\text{Cl}^-]$ the charging curves are similar except for the potential shift with i_a° , while at low $[\text{Cl}^-]$ pit initiation is more difficult with higher values of i_a° . The minimum $[\text{Cl}^-]$ required for pit initiation increases with decreasing solution temperature, *ie* with decreasing solution aggressiveness. The potential for pit initiation tends to be higher at lower solution temperatures and/or at higher pH's. $[\text{Cl}^-]$, anodic charging rate, solution temperature and pH influence pit initiation by affecting the efficiency of oxide repair at local breakdown sites in the passive oxide film.

INTRODUCTION

In previous papers[1], the galvanostatic oxidation of nickel in Na_2SO_4 solutions was studied in detail. It was shown that the increase in anodic potential during charging was most likely associated with an increase in the stability of the oxide film towards breakdown, and most of the anodic charge was accounted for by Ni^{2+} in solution rather than oxide growth. Neither the general shape of the anodic charging profile nor the high current efficiency for Ni^{2+} dissolution ($\sim 80\%$) changed substantially with different charging rates (i_a°), electrolyte pH or temperature, the fraction of the current contributing to oxide growth being constant at $\sim 20\%$. It thus appeared that oxide development occurred in essentially the same manner over a wide range of conditions, the state of the oxide being only dependent on the anodic charge passed. It is recognized that the state of the passive oxide plays a crucial role in determining the stability of a metal towards pitting (*cf*, *eg*, the case of 316 stainless steel[2-4]); therefore, the lack of a major influence of i_a° , pH and temperature on the galvanostatic development of the NiO film should be a distinct advantage in studies of the mechanism of pit initiation.

Another advantage of the galvanostatic method is that the electrode is free to adopt the appropriate potential for a particular state of the oxide and charging rate; with the potentiostatic (or potentiodynamic) methods, the anodic potential (V_a) is imposed on the electrode (*cf*[5]) which must then develop an oxide with a character associated with that specific V_a . In the latter case, prior knowledge of the complex influence of pH and temperature on the potential dependence of the oxide development reaction is required. Obviously, the potentiostatic method must be used to determine the induction time and the minimum potential for pitting. However, the galvanostatic method should be useful in identifying the role of $[\text{Cl}^-]$, pH and temperature in the pitting process, and

the present paper considers these factors in the pitting of nickel in Na_2SO_4 solutions.

EXPERIMENTAL

Polycrystalline specimens, 1×2.5 cm, were prepared from zone-refined nickel sheet of 99.996% purity[6]. They were degreased with benzene, chemically polished, electropolished for 2 min at 23°C in a 57 vol. % sulfuric acid solution at 0.5 A cm^{-2} , and then annealed at 800°C in a vacuum of 10^{-8} Torr. The specimens were electropolished again immediately before use in an experiment, and were galvanostatically anodized without cathodic reduction of the prior film.

Potentials are referred to the saturated calomel electrode which is 0.245 V with respect to the standard reversible hydrogen electrode. Solutions were de-aerated 0.15 N Na_2SO_4 with a pH of either 2.8 or 6.0; solution temperatures were 5, 25 or 45°C .

RESULTS AND DISCUSSION

The following reactions have been previously suggested[1, 7, 8] for localized breakdown and repair of oxide films on metals:

- (i) Breakdown $\text{MO} + 2\text{H}^+ \rightarrow \text{M}^{2+} + \text{H}_2\text{O}$,
- (ii) Repair: $\text{M} + \text{H}_2\text{O} \rightarrow \text{MO} + 2\text{H}^+ + 2e$
and
- (iii) Parallel metal dissolution: $\text{M} \rightarrow \text{M}^{2+} + 2e$.

Breakdown of the oxide film is considered to occur *via* chemical dissolution at local defects or weak points within the film, and repair is an inefficient reaction since parallel metal dissolution can occur during the

time the film is reforming. If the efficiency of local film repair is sufficiently low, pitting will occur[5]. The results to follow show the influence of $[\text{Cl}^-]$, pH, temperature and the state of the oxide on Cl^- initiated pitting of nickel. They are discussed in terms of local breakdown and repair of the passive oxide film.

(i) Anodic charging at different Cl^- concentrations

Figure 1 shows the effect of various concentrations of Cl^- on the galvanostatic charging profiles for electropolished nickel at 25°C in pH 2.8 Na_2SO_4 . The presence of Cl^- in the solution does not affect the initial part of the anodic charging curve, but the

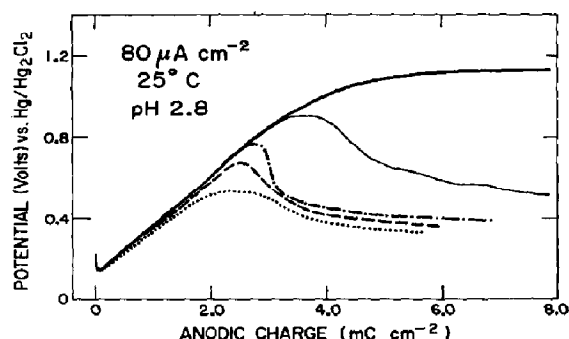


Fig. 1. Anodic galvanostatic charging profiles for electropolished nickel at $80 \mu\text{A cm}^{-2}$ and 25°C in pH 2.8 Na_2SO_4 with various Cl^- ion concentrations: (—) 0 M; (— — —) 0.025 M; (- - -) 0.05 M; (- · - ·) 0.1 M; (·····) 0.3 M.

potential begins to change in the cathodic direction as pits are initiated; the potential for pit initiation is more anodic than that required to sustain pitting. Supposedly an anodic overvoltage is required before the Cl^- ion can effectively interfere with local film repair and thereby generate essentially oxide-free active areas where the anodic current can be more easily consumed. The potential at which pitting begins decreases with increasing $[\text{Cl}^-]$ since it becomes progressively easier to initiate pitting at higher $[\text{Cl}^-]$, which is again understandable in terms of the ability of the Cl^- to interfere with oxide formation and therefore local film repair[5]. The shift in the plateau potential to more negative values is directly dependent on the bulk $[\text{Cl}^-]$. Obviously, the more Cl^- in solution, the larger the active area which can be generated and the lower the anodic overvoltage for a particular charging rate. The plateau potential remains in the passive

region even at the highest $[\text{Cl}^-]$, i.e. while the anodic current is being consumed by nickel dissolution, the potential does not shift into the active potential region ($\sim -0.4\text{ V}$). This may be due to a nickel dissolution reaction which is somewhat hindered by a defective oxide in the pit areas, and/or by an anodic overpotential effect since a small surface area is consuming the anodic current. Whatever the reason, steady-state nickel dissolution can occur in the passive potential region during galvanostatic anodic charging, and this is in agreement with the previous model for anodic charging of nickel (in Cl^- -free solutions) where it was proposed that a defective NiO film was present, with local breakdown and repair events responsible for most of the charge consumed in the passive region[1].

(ii) Anodic charging at different charging rates

The effect of different anodic charging rates on the anodic galvanostatic profiles for a solution containing 0.025 M Cl^- is shown in Fig. 2(a). At this low $[\text{Cl}^-]$, increasing the i from 40 to $400 \mu\text{A cm}^{-2}$ greatly increases the anodic charge which must pass before pit initiation; at the higher charging rate, pitting only begins after some time in the O_2 evolution region. These results suggest that a certain period of time is required for the local Cl^- ion concentration to increase sufficiently to block film repair and thereby initiate pitting[5, 9–18]. But time is not the only factor which is important in achieving the required high local $[\text{Cl}^-]$; also important are the local current densities which are responsible for increasing the $[\text{Cl}^-]$ through electrical migration effects. For this reason, pitting begins at $400 \mu\text{A cm}^{-2}$ well before the passage of $10 \times$ the charge involved at $40 \mu\text{A cm}^{-2}$ (Fig. 2a). At higher Cl^- ion concentrations, (e.g. 0.1 M), the charge passed before pitting occurs is exactly the same at 40 and $400 \mu\text{A cm}^{-2}$ (Fig. 2b); the two charging curves in Fig. 2(b) are quite similar except for the anticipated anodic potential shift with increased charging rate. The higher bulk $[\text{Cl}^-]$ is now able to supply all the local Cl^- demanded to satisfy the migration currents arising because of local film breakdown and repair. From previous work[1], these local currents are thought to be $\sim 10 \times$ higher at $400 \mu\text{A cm}^{-2}$ than at $40 \mu\text{A cm}^{-2}$.

(iii) Anodic charging at different temperatures

Figure 3(a) shows the anodic charging profiles, at $80 \mu\text{A cm}^{-2}$, in the presence of various Cl^- ion concentrations at 5°C , i.e. in a less aggressive environment than 25°C . The background profile is identical to that

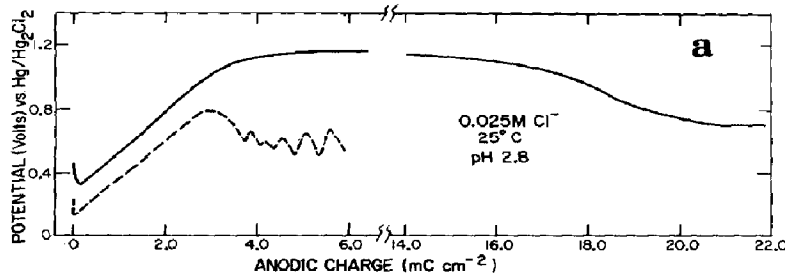


Fig. 2. (a) Anodic galvanostatic charging profiles for electropolished nickel at 25°C in pH 2.8 Na_2SO_4 + 0.025 M Cl^- at 40 (---) and 400 (—) $\mu\text{A cm}^{-2}$.

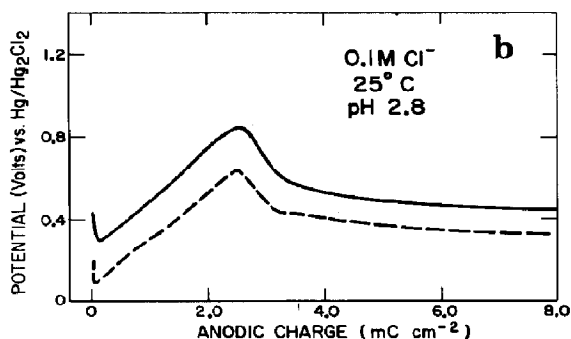


Fig. 2. (b) As in (a) but with 0.1 M Cl^- .

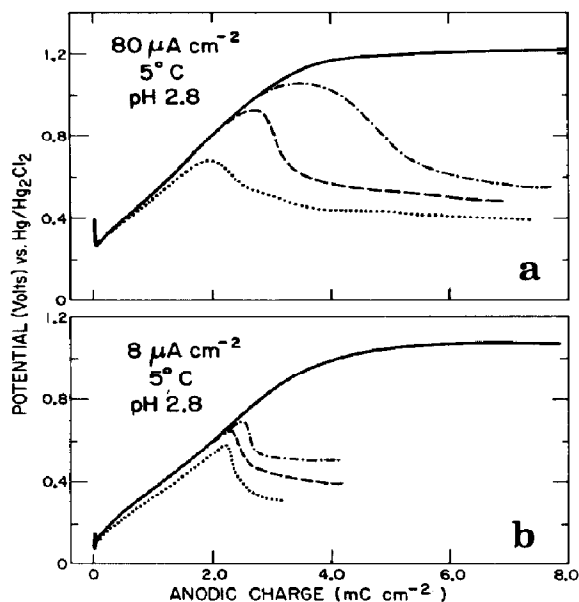


Fig. 3. (a) Anodic galvanostatic charging profiles for electropolished nickel at $80 \mu\text{A cm}^{-2}$ and 5°C in pH 2.8 Na_2SO_4 with various Cl^- concentrations: (—) 0 M; (---) 0.025 M; (---) 0.05 M; (---) 0.1 M; (---) 0.3 M. (b) As in (a) but at $8 \mu\text{A cm}^{-2}$.

obtained at 25°C with the exception of a $\sim 0.10\text{V}$ anodic potential shift of the entire profile (cf Fig. 1). At 5°C and $80 \mu\text{A cm}^{-2}$, there is no indication of pitting in 0.025 M Cl^- even after the passage of 25 mC cm^{-2} of anodic charge; pits do initiate in 0.05 M and 0.1 M Cl^- but with more difficulty than at 25°C (cf Fig. 1). In 0.3 M Cl^- , pit initiation occurs after passage of the same anodic charge at 5°C as at 25°C . It thus appears that the influence of electrolyte temperature on pit initiation decreases with increasing $[\text{Cl}^-]$ and, at a sufficiently high $[\text{Cl}^-]$, the solution temperature has little effect on the conditions necessary for pit initiation. Figure 3(b) shows the charging profiles obtained at 5°C at a lower charging rate of $8 \mu\text{A cm}^{-2}$. Here, the variation in the pit initiation potential with $[\text{Cl}^-]$ is much less than at $80 \mu\text{A cm}^{-2}$; the results look similar to those obtained at 25°C and $80 \mu\text{A cm}^{-2}$ (cf Fig. 1). It appears that the lower charging rate compensates for the lower solution temperature so that

changes in the $[\text{Cl}^-]$ play less of a role in pit initiation. The most probable explanation for these results is that at the lower solution temperature, the mobility of the Cl^- ion is less, so that either a higher bulk concentration of Cl^- is required for pit initiation or the anodic charging must be slower so that more time is available to achieve the locally high $[\text{Cl}^-]$ necessary to initiate pitting. Also, the decrease in solution temperature perhaps increases the efficiency of local film repair so that less anodic charge flows during each breakdown and repair event; the lower the local anodic charge flow, the less Cl^- that will migrate into the local breakdown area. At 45°C and $80 \mu\text{A cm}^{-2}$, pitting readily occurs even at the lowest $[\text{Cl}^-]$, i.e. 0.025 M (Fig. 4). In this highly aggressive solution, the spread of pitting potentials is less than at 25°C , i.e. variations in $[\text{Cl}^-]$ have less influence on pit initiation. With increasing electrolyte temperature, the threshold concentration of Cl^- needed to initiate pitting thus decreases at a particular charging rate and pH.

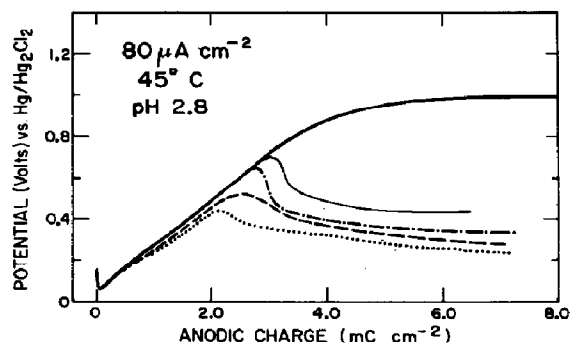


Fig. 4. Anodic galvanostatic charging profiles for electropolished nickel at $80 \mu\text{A cm}^{-2}$ and 45°C in pH 2.8 Na_2SO_4 with various Cl^- concentrations: (—) 0 M; (---) 0.025 M; (---) 0.05 M; (---) 0.1 M; (---) 0.3 M.

(iv) Anodic charging at different pH's

An increase in solution pH from 2.8 to 6.0 does not result in any major changes in the charging profiles at 25°C and $80 \mu\text{A cm}^{-2}$ (Fig. 5a). The higher pH does make pit initiation a little more difficult, especially at lower $[\text{Cl}^-]$; however, the changes are quite small when one considers that the H^+ and OH^- concentrations have changed by three orders of magnitude.

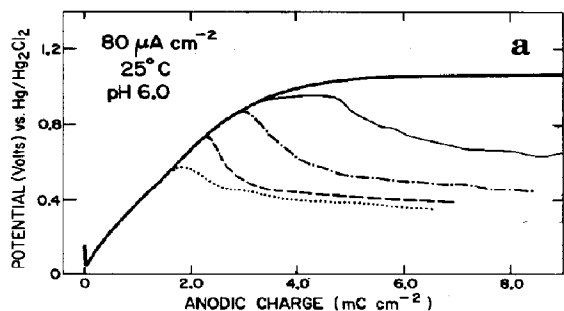


Fig. 5. (a) Anodic galvanostatic charging profiles for electropolished nickel at $80 \mu\text{A cm}^{-2}$ and 25°C in pH 6.0 Na_2SO_4 with various Cl^- concentrations: (—) 0 M; (---) 0.025 M; (---) 0.05 M; (---) 0.1 M; (---) 0.3 M.

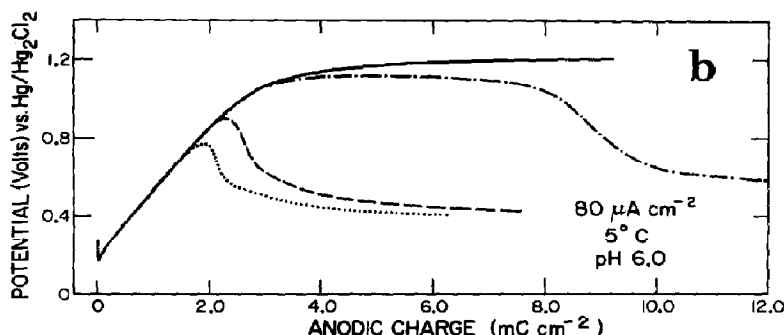


Fig. 5. (b) As in (a) but at 5°C.

The results are consistent with the lack of influence of solution pH on the charging profiles for nickel in Cl^- -free solutions, the state of the oxide film only depending on the amount of anodic charge passed[1]. The influence of a pH change from 2.8 to 6.0 is more pronounced at 5°C (Fig. 5b), pitting being slow to initiate even at 0.05 M $[\text{Cl}^-]$ at this lower temperature. The decrease in solution temperature probably lowers the mobility of the Cl^- ion and thus the $[\text{Cl}^-]$ in the vicinity of the pit. The results indicate that a change in solution pH is more likely to influence the pitting susceptibility if the solution temperature and $[\text{Cl}^-]$ are low, i.e., if the other variables make pitting more difficult.

In summary, the key to pit initiation appears to be the ability of the chloride ion to interfere with oxide formation[5] and thereby decrease the repair efficiency. This causes further metal dissolution and therefore even more Cl^- migration into the breakdown area. The process is thus self-sustaining and eventually the oxide film cannot effectively repair itself, and pitting occurs. The extent of local Cl^- enrichment depends on the bulk $[\text{Cl}^-]$ and also on the anodic potential (V_a) since the higher the V_a the higher are the local currents for metal dissolution after breakdown has occurred. At lower bulk $[\text{Cl}^-]$, a higher V_a is required to achieve the locally high $[\text{Cl}^-]$ necessary to initiate and sustain pitting. An accompanying decrease in pH is due to metal cation hydrolysis (eg [17]) $M^{2+} + \text{H}_2\text{O} \rightarrow M(\text{OH})^+ + \text{H}^+$, and this will also adversely influence film repair. It should be noted that the pH decrease in the pit area is due to the Cl^- interfering with oxide film repair and thereby generating more metal cations which are free to hydrolyze. The Cl^- probably has no direct influence on the kinetics of the metal cation hydrolysis reaction *per se*. Temperature, solution pH, and anodic charging rate have a major influence on the conditions of pit initiation when the

$[\text{Cl}^-]$ in solution is low; the extent of this influence decreases with increasing $[\text{Cl}^-]$. These results can be understood in terms of the effect of the various parameters on the efficiency of oxide film repair.

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