Electrodissolution kinetics of an Fe–Ni alloy in acidic chloride media of 1.0 M ionic strength

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Anodic dissolution of an Fe–5 Ni alloy in deoxygenated acidic chloride solutions of 1.0 M ionic strength has been studied. Steady state partial current densities of the iron and nickel components were obtained by atomic absorption spectrophotometry analysis of the solutions. Alloy and component electrodissolution rates show two anodic Tafel regions indicating simultaneous parallel reactions as reported previously for pure iron. Anodic Tafel slopes of 0.075 and 0.04 V dec⁻¹ were obtained in the lower (A) and higher (B) polarization regions, respectively. The kinetic results for the alloy are consistent with the Cl⁻ accelerated mechanism in Region (A) and the Bockris or OH⁻ accelerated mechanism in Region (B) for both iron and nickel components as proposed previously for pure iron.

1. Introduction

Anodic dissolution of iron and nickel in the absence and presence of chloride ions has been studied by a number of investigators (e.g., [1–18]). Although a complete understanding of the kinetics and mechanisms of iron and nickel electrodissolution has not yet been achieved, nevertheless much basic information has been gained during the past twenty years. On the other hand, few fundamental studies of the more complex systems of Fe–Ni alloys have been reported. For the pure iron system it has been shown that the addition of chloride ions to acidic media significantly affects the kinetics and mechanism of Fe electrodissolution [10, 19]. There is also evidence that there are similar effects in nickel electrodissolution [18]. For this reason, it would be of interest to examine the chloride effect on Fe–Ni alloys.

There have been a few anodic dissolution studies of Fe–Ni alloys in H₂SO₄ [20–22] and in acidic chloride media [23]. However, the kinetic information obtained in these studies was rather limited and precluded consideration of alloy electrodissolution mechanisms. This paper reports initial electrodissolution kinetic studies of a Fe–5 wt % Ni alloy in acidic chloride solutions of constant 1 M ionic strength. The results are compared with those obtained previously for pure iron [9] and pure nickel [18].

2. Experimental details

Electrodes were prepared from 0.95 cm diameter rod of Fe–5.32 wt % (5.08 g atom %) Ni alloy (Magnetics Co.). The rod was turned on a lathe to cross-sectional areas of 0.625 and 0.10 cm². The electrodes were polished with alumina paper (grit no. 240, 400 and 600), and then degreased with hot benzene in a Soxhlet column for 4 h, annealed under vacuum (10⁻⁵ torr) at 510°C for 1 h, allowed to cool slowly to room temperature and stored in a dessicator until used.

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Descriptions of the rotating disc electrode unit and the three-electrode electrochemical cell have been given previously [24]. A PAR potentiostat (model 173) with log current converter unit (model 376) and a PAR universal programmer (model 175) provided potential control. A Perkin–Elmer atomic absorption spectrophotometer was used for solution analyses.

Deionized water, which was then double distilled, and analytical reagent grade chemicals were used to prepare the electrolyte solutions, 1 M (NaCl + HCl) and 1 M (HCl + HClO₄). For solutions containing perchlorate ions, a fibre junction salt bridge filled with 4.2 M NaCl was inserted between the reference electrode (saturated calomel electrode) and the electrolyte. The solutions were deoxygenated with prepurified nitrogen gas (Liquid Carbonics) for 15 h before immersion of the rotating disc electrode. Before passage through the solution, the prepurified nitrogen gas was first passed through a heated Vycor glass column containing copper filings at 450° C.

After immersion of a fresh electrode in the solution, steady state corrosion potentials were usually attained within 1–2 h; polarization was then initiated. Potential steps were applied from the corrosion potential (in increments of 25 or 50 mV) for a normal polarization time of 30 min (steady state polarization was usually achieved within a few minutes). At the end of each potential step the electrode was returned to the corrosion potential (usually attained within 3–5 min). Solution samples were then taken for atomic absorption spectrophotometry analysis. At low rates of electrodissolution, polarization times were increased to 3–5 h since changes in metal ion concentrations in the solution at the normal 30 min polarization time were too small for accurate determinations. A fresh electrode was used for each polarization run.

All potentials reported in this paper have been corrected for IR drops and liquid junction potentials.

3. Results

The corrosion potentials of the rotating alloy discs in acidic chloride solutions were found to be independent of rotation rate (rotation rates were varied up to 5000 r.p.m.). The dependence of the corrosion potential on pH is shown in Fig. 1 where

$$\frac{\partial E_{\text{corr}}}{\partial \text{pH}} = -0.05 \text{ V pH}^{-1}$$

(1)

Its dependence on chloride ions is shown in Fig. 2 where

$$\frac{\partial E_{\text{corr}}}{\partial \log [\text{Cl}^-]} = -0.05 \text{ V dec}^{-1}$$

(2)

The corrosion currents were determined by anodic Tafel extrapolation and polarization resistance measurements. The dependence of the corrosion current on pH,

$$\frac{\partial \log i_{\text{corr}}^a}{\partial \text{pH}} = -0.2$$

(3)

and on chloride ions,

$$\frac{\partial \log i_{\text{corr}}^a}{\partial \log [\text{Cl}^-]} = 0.2$$

(4)

are also shown in Figs 1 and 2, respectively. The superscript ‘a’ refers to the alloy.

Equation 1 is in good agreement with that reported by Economy et al. [21] for Fe–5 Ni in H₂SO₄. Equation 3 is one-half the value reported by Chin [9] for iron in acidic chloride solutions; he also reported $\partial \log i_{\text{corr}} / \partial \log [\text{Cl}^-] = 0.3$ for iron compared to a value of 0.2 for the alloy (Equation 4).

Fig. 3 shows the dependence of anodic dissolution of the alloy in acidic chloride solutions on pH.