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ELECTROLYTIC DISSOLUTION OF NUCLEAR FUELS

Part II. Nichrome in Nitrate Solutions

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December 29, 1961

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A B S T R A C T

The electrolytic dissolution of Nichrome in nitrate systems is not complicated by the secondary passivation phenomenon observed in 304 stainless steel dissolution. The potential-current density curves in the transpassive region follow the Tafel equation ($\eta = a + b \log I$) where the slope (b) is equal to 0.038 volt. Under some conditions concentration polarization is present at high current densities ($\geq 1 \text{ amp/cm}^2$) but can be eliminated in all practical dissolver solutions by operating at 70°C.

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I. SUMMARY

On the basis of previous work on the electrolytic dissolution of type 304 stainless steel and other iron, nickel, and chromium alloys in nitrate systems, the general behavior of Nichrome dissolution in the transpassive region was predicted. A limited number of experiments was performed to confirm the predictions and to establish the optimum operating conditions for Nichrome dissolution. The experiments consisted of measurement of the potential-current density relationships as a function of solution composition and temperature.

The potential-current density curves follow the Tafel equation ($\eta = a + b \log I$) where the slope (b) is equal to 0.038 volt for all the solutions and temperatures studied. In the Tafel region the current density at constant potential is independent of hydrogen ion concentration, but does depend on nitrate ion concentration. The dissolution rate at constant potential increases as the nitrate ion concentration is decreased. In this region the energy of activation for dissolution is 13.2 Kcal/mole. In some cases a limiting current density due to concentration polarization is observed at current densities greater than 0.1 amp/cm²; this limiting current density also increases as the nitrate ion and Nichrome cation concentration decrease. However, at a higher temperature

of 70°C in a typical dissolver solution containing 116 g/l Nichrome concentration polarization is absent up to 4 amps/cm², so that operating temperatures near 70°C are recommended.

II. INTRODUCTION

Electrolytic dissolution in nitric acid shows promise as a single head-end treatment for reprocessing a variety of fuel element materials, e.g., stainless steel, Nichrome, aluminum. A nitrate system has the advantage that it may be used directly in well-established subsequent reprocessing steps. At the same time electrolytic dissolution allows complete control of the dissolution rate.

From the literature⁽¹⁻⁶⁾ and previous work in this laboratory⁽⁷⁾ pertaining to the electrolytic dissolution of iron, nickel, chromium, and their alloys (304 stainless steel in particular), the qualitative behavior of Nichrome dissolution in the transpassive region could be predicted. A comparison of the potential-current density curves of pure iron with that of pure nickel at potentials above 1.0 volt showed that nickel is much less passive than iron. It was also determined that the addition of chromium to iron increased its dissolution rate in the potential range above one volt, and that iron containing more than 35% chromium behaves essentially like pure chromium, in that secondary passivation is absent. Since nickel is less passive than iron, a smaller amount of chromium alloyed with nickel should be sufficient to eliminate secondary passivation. Therefore, it was reasoned that Nichrome (80% Ni, 20% Cr) would

dissolve in the transpassive region in a manner similar to pure chromium and not exhibit secondary passivation. In the absence of secondary passivation oxygen evolution would not be competitive at normal dissolution rates ($\approx 1 \text{ amp/cm}^2$). The limiting current densities, due to concentration polarization, observed for stainless steel and chromium at high nitric acid concentrations were also predicted for Nichrome dissolution, as was the general effect of solution composition and temperature. Only a limited number of experiments was required to confirm the above predictions. Measurements of Nichrome dissolution rate (current density) as a function of potential, solution composition and temperature were undertaken to determine the feasibility, limitations and optimum operating conditions of dissolution.

III. EXPERIMENTAL

The electrolysis cell was essentially the same as used in previous work and is described in detail elsewhere⁽⁸⁾. Platinum was used for the cathode, and the reference electrode was a saturated calomel electrode (S.C.E.). Nichrome rod (80% Ni, 20% Cr) was machined to fit into a Teflon holder in such a manner that $1/2 \text{ cm}^2$ of surface area was exposed to the solution. Prior to each experiment, the exposed surface of the Nichrome electrode was refaced by machining and the resulting work-hardened surface was removed by electrolytic dissolution in a solution of the same composition as used in the ensuing experiment.

The polarization curves were determined in 1, 5 and 10M nitric acid as well as in a typical dissolver solution containing nickel and chromium

nitrate (in the Nichrome ratio) made up to 4.5M in nitrate with 1M nitric acid added. Experiments with all these solutions were carried out at 25°C. In addition the 10M nitric acid and the "typical dissolver solution" were studied at 70°C.

The potential-current density relationships were obtained with an electronic potentiostat and covered a current range from approximately 10^{-6} amp/cm² to > 1 amp/cm². Potential-current readings were taken at 40 mv intervals for both increasing and decreasing values and the complete curve determined four times. The current was found to be reproducible to within ± 10 per cent.

IV. RESULTS

The potential-current density curves follow the Tafel equation ($\eta = a + b \log I$) where the slope (b) is equal to 0.038 volt for all the solutions and temperatures studied. Hence, it may be assumed that the dissolution mechanism is invariant in the Tafel region under these conditions. In some cases a limiting current density due to a product concentration polarization is reached at high current densities, but in all cases the Tafel equation is obeyed up to currents of 10^{-1} amp/cm². The prediction that secondary passivation (as observed in stainless steel dissolution) would be absent was verified.

The effect of solution composition on the dissolution rate (current density) at constant temperature is shown in Figures 1 and 2. Hydrogen ion concentration was found to have no effect on the dissolution rate in the Tafel region (Figure 1). Isolation of its effect on the limiting

Figure 1

Effect of H^+ Concentration on the Anodic Polarization of Nichrome at 25°C: a. $1.0M HNO_3 + 4.5M NO_3^-$ (80% Ni^{+2} , 20% Cr^{+3}), b. $5.5M HNO_3$

Figure 2

Effect of Nitric Acid Concentration on the Anodic Polarization of Nichrome at 25°C

current density was difficult, since it is experimentally impossible to change either the hydrogen or Nichrome cation concentration singly without changing the nitrate concentration. In this work it was desired to maintain the nitrate concentration constant in all experiments. Therefore, any influence of either hydrogen or Nichrome cations could not be determined independently without introducing another anion whose influence on the polarization curves would also be unknown. The effect of hydrogen ion on the limiting current density may be inferred from the fact that the reaction rate in the Tafel region is independent of hydrogen ion concentration. It is logical to assume that the overall reaction remains the same (with the rate independent of H^+ concentration) in the limiting current density region. The only difference is that the rate determining step changes from activation controlled (Tafel region) to mass transport controlled (limiting current density region). Also, since the rate of mass transport of products from the anode would be a direct function of the product concentration gradient, the influence of hydrogen ion would be, at most, a second order effect. It is therefore concluded that the difference in the values of the limiting current density observed in Figure 1 is due to the presence of Nichrome cations in one case (a) and their absence in the other (b).

Figure 2 shows that at constant potential the current density increases with decreasing nitrate ion concentration (vide supra) in both the Tafel and limiting current density regions. The variation of the limiting current density with solution composition as shown in Figures 1

and 2 is typical of anodic concentration polarization. The substitution of Cr^{+6} for Cr^{+3} had no effect on the polarization curves.

The effect of temperature on the dissolution rate at constant solution composition is shown in Figures 3 and 4. From these data the energy of activation $\Delta H^\ddagger$ in the Tafel region (at 1.1 volts versus S.C.E.) was calculated to be 13.2 Kcal/mole. The value of the limiting current density is increased with increasing temperature, and in a typical dissolver solution (containing 116 g/liter of Nichrome) at 70°C, concentration polarization is absent at current densities up to 4 amps/cm² (Figure 4). However, in 10M nitric acid at 70°C concentration polarization is still present to some degree at the currents of operating interest. This is due to the higher nitrate ion concentration.

A semi-quantitative estimate of the magnitude of concentration polarization for Nichrome at other temperatures can be made by consulting the work on 304 stainless steel dissolution.⁽⁷⁾ For this reason a study of Nichrome dissolution at other temperatures was felt to be unnecessary.

V. CONCLUSIONS

In the limiting current density region the reaction rate for Nichrome dissolution is controlled by the mass transport of reaction products away from the metal/solution interface. Therefore, in practice, the dissolution rate in this region can be increased by agitation, higher temperature and the use of solutions in which nickel and chromium nitrates have a higher solubility (low excess nitric acid). It is concluded that an

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Figure 3.

Effect of Temperature on the Anodic Polarization
of Nichrome in 1.0M HNO₃

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Figure 4

Effect of Temperature on the Anodic Polarization of Nichrome
in a Solution Containing 1.0M HNO₃ + 4.5M NO₃⁻ (80% Ni⁺², 20% Cr⁺³)

operating temperature of 70°C is sufficient to eliminate or minimize concentration polarization from the practical standpoint, provided the nitric acid concentration is not greater than 10M.

Stability will not be a problem with Nichrome product solutions because of the very high solubility of nickel nitrate (≈ 600 g/l of nickel at room temperature).

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