

Potentiostatic pulse technique to determine the efficiency of hydrogen absorption by alloys

B. G. POUND

Materials Research Laboratory, SRI International, Menlo Park, California 94025, USA

Received 17 October 1990; revised 27 February 1991

A potentiostatic pulse technique was used to determine the efficiency of hydrogen entry and trapping in two precipitation-hardened (Inconel 718 and Incoloy 925) and two work-hardened (Inconel 625 and Hastelloy C-276) nickel-base alloys in an acetate buffer (1 M acetic acid/1 M sodium acetate) containing 15 p.p.m. As_2O_3 . The data were examined as a function of charging time and overpotential. The trapping efficiency increases with charging time (t_c) and is linearly dependent on $(t_c)^{1/2}$ for sufficiently short times. The range of linearity is determined by the apparent trapping constant for the alloy. The entry efficiency is independent of charging time but it can vary with overpotential depending on the value of the charge transfer coefficient (α) for the hydrogen evolution reaction. In the case of Inconel 718 and Hastelloy C-276, the value of α was 1.4, which is consistent with a mechanism for hydrogen evolution involving fast discharge followed by slow electrochemical desorption.

1. Introduction

The susceptibility of an alloy to hydrogen embrittlement is strongly influenced by its hydrogen ingress characteristics. Two key characteristics are the efficiency of hydrogen entry and the efficiency of hydrogen trapping. The entry efficiency is represented by the amount of hydrogen entering the alloy relative to the total amount formed cathodically on the alloy surface. Some of the hydrogen that enters the alloy is trapped at structural heterogeneities and this component of the absorbed hydrogen defines the trapping efficiency. The traps are classified as reversible or irreversible depending on the binding energy of the hydrogen atom at the heterogeneity. In the case of an irreversible trap, the binding energy is high enough that the rate constant for release of the hydrogen is considered negligible whereas a reversible trap can release hydrogen, often sufficiently fast to permit local equilibrium between lattice and trapped hydrogen.

Both the entry and trapping efficiencies can be determined using a diffusion/trapping model to analyse anodic current transients obtained by a potentiostatic pulse technique [1-3]. An electrode of the test metal or alloy is charged with atomic hydrogen at a constant potential (E_c) for a time (t_c). During charging, adsorbed hydrogen is transferred across the metal surface and diffuses into the bulk. The electrode potential is then stepped to a more positive value, E_A (5-10 mV negative of the open-circuit potential, E_{oc}), producing a current transient associated with the oxidation of hydrogen atoms after they diffuse back to the metal surface.

In the diffusion/trapping model, the effect of trapping is taken into account mathematically by modifying Fick's second law of diffusion [1-3]. The approach is to include a trapping term, $k_a c$, in which the rate of

trapping is assumed to be proportional to the concentration, $c(x, t)$ of diffusing hydrogen at point x :

$$\frac{dc}{dt} = D_a \frac{d^2c}{dx^2} - k_a c \quad (1)$$

This equation has been solved analytically for two cases under conditions imposed by the pulse technique: (1) diffusion control, in which the rate of hydrogen ingress is controlled by diffusion in the bulk metal; and (2) interface control, in which the rate of ingress is controlled by the flux across the interface. For all alloys studied so far, the interface-control form of the model was found to be applicable. Hence, data for the anodic charge are analysed as a function of charging time to evaluate the flux of hydrogen atoms entering the metal (J) and the apparent trapping constant (k_a) measured for irreversible traps in the presence of reversible traps.

The charge (q_T) irreversibly trapped under conditions of interface control is given in nondimensional form [1] by

$$Q_T = [R^{1/2} - 1/2R^{1/2}] \operatorname{erf}(R)^{1/2} + \exp(-R)/\pi^{1/2} \quad (2)$$

The nondimensional terms are defined by $Q_T = q_T/[FJ(t_c/k_a)^{1/2}]$ and $R = k_a t_c$ where q_T is the dimensionalized charge in C m^{-2} , F is the Faraday constant, and J is the ingress flux in $\text{mol m}^{-2} \text{s}^{-1}$. Thus, values of k_a and J can be used to calculate q_T . The charge associated with the entry of hydrogen into the metal (q_{in}) also can be determined from its nondimensional form of $Q_{in} = (R)^{1/2}$ by using the value of k_a . The data for q_{in} , q_T , and the cathodic charge (q_c) can then be used to obtain two ratios: (a) q_T/q_{in} , corresponding to the fraction of hydrogen in the metal that is trapped; and (b) q_{in}/q_c , representing the fraction of charge

associated with hydrogen entry during the charging step.

The technique and model have been applied to a range of metals and alloys including steels, nickel-base alloys, and titanium. The values of k_a and J obtained for these alloys have been given elsewhere [3–5]. In this paper, the hydrogen ingress characteristics for two precipitation-hardened alloys (Inconel 718 and Incoloy 925) and two work-hardened alloys (Inconel 625 and Hastelloy C-276) are analysed in terms of the entry and trapping efficiencies as represented by q_T/q_{in} and q_{in}/q_c . The extent of hydrogen ingress is determined by the surface coverage of adsorbed hydrogen, which in turn depends on the mechanism of the hydrogen evolution reaction. Hence, the entry efficiency was further examined in relation to the hydrogen evolution mechanism.

2. Experimental procedure

The composition of each alloy is given in Table 1. Inconel 718 and Incoloy 925 were used in the as-received condition with yield strengths of 1238 and 758 MPa, respectively, whereas Inconel 625 and Hastelloy C-276 were cold-worked 17 and 27%, respectively, to obtain their final yield strengths of 1195 and 1237 MPa.

Details of the electrochemical cell and instrumentation have been given previously [3]. The test electrodes of each alloy consisted of a 5 cm length of rod press-fitted into a Teflon sheath so that only the planar end surface was exposed to the electrolyte. The surface was polished with SiC paper followed by 0.05 μm alumina powder. The electrolyte was an acetate buffer (1 M acetic acid/1 M sodium acetate) containing 15 p.p.m. As_2O_3 as a hydrogen entry promoter. The electrolyte was deaerated with argon for 1 h before measurements began and throughout data acquisition. The potentials were measured with respect to a saturated calomel electrode (SCE). All tests were performed at $22 \pm 2^\circ\text{C}$.

The test electrode was charged with hydrogen for times from 0.5 to 50 s. Anodic current transients were

Table 1. Alloy composition (wt %)

Element	Inconel 718	Incoloy 925	Inconel 625	Hastelloy C-276
Al	0.60	0.30	0.18	
C	0.03	0.02	0.03	0.002
Co	0.16			0.83
Cr	18.97	22.20	22.06	15.27
Cu	0.04	1.93		
Fe	16.25	28.96	4.37	5.84
Mn	0.10	0.62	0.17	0.48
Mo	3.04	2.74	8.70	16.04
Nb + Ta	5.30		3.50	
Ni	54.41	40.95	60.33	57.5
P	0.009		0.012	< 0.005
S	0.002	0.001	0.001	< 0.002
Si	0.11	0.17	0.38	< 0.02
Ti	0.98	2.11	0.27	
Other	0.003 B			3.90 W 0.12 V

obtained for each charging time over a range of overpotentials ($\eta = E_c - E_{oc}$). The open-circuit potential of the test electrode was sampled immediately before each charging time and was also used to monitor the stability of the surface film; reduction of the film was evident from a progressive shift of E_{oc} to more negative values with each t_c at a sufficiently high charging potential. The potential, E_A , was offset negative to the open-circuit potential to avoid significant metal dissolution. In practice, the presence of a small, constant current due to metal dissolution does not matter since the net steady state current is added as a correction to the current in the H oxidation transient.

3. Results

3.1. Trapping behaviour

3.1.1. Model. The effect of trapping constant on the trapping efficiency was modeled by varying k_a over a wide range (0.005–0.5 s^{-1}). The variation in q_T/q_{in} is shown as a function of charging time in Fig. 1. At low values of k_a , q_T/q_{in} follows an approximately linear dependence on $(t_c)^{1/2}$, although the reason for this relatively simple relationship is not apparent from the complex dependence of q_T on t_c . Some deviation from linearity occurs at long charging times, which is to be expected in view of the quite different t_c dependence of q_T and q_{in} . As k_a increases, the linear region is restricted to shorter charging times with the subsequent non-linearity becoming more pronounced at high t_c .

The slope (m) of the linear region is proportional to $(k_a)^{1/2}$ (Fig. 2) and is given by

$$m = 0.69(k_a)^{1/2} + 0.002 \quad (3)$$

The constant contributes $\leq 4\%$ for $k_a \geq 0.005 \text{ s}^{-1}$, so that $q_T/q_{in} \approx 0.69(k_a t_c)^{1/2}$. Clearly, q_T/q_{in} , unlike q_{in}/q_c , is independent of potential because each component

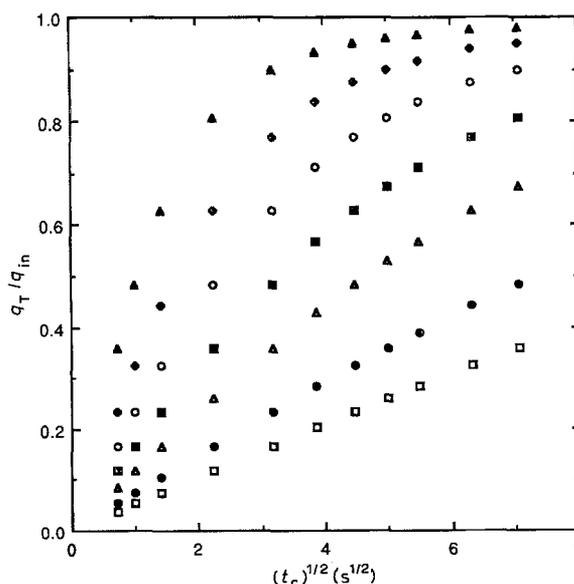


Fig. 1. Dependence of q_T/q_{in} on charging time for different values of k_a : (\square) 0.005, (\bullet) 0.010, (Δ) 0.025, (\blacksquare) 0.050, (\circ) 0.100, (\blacklozenge) 0.200, (\blacktriangle) 0.500 s^{-1} .

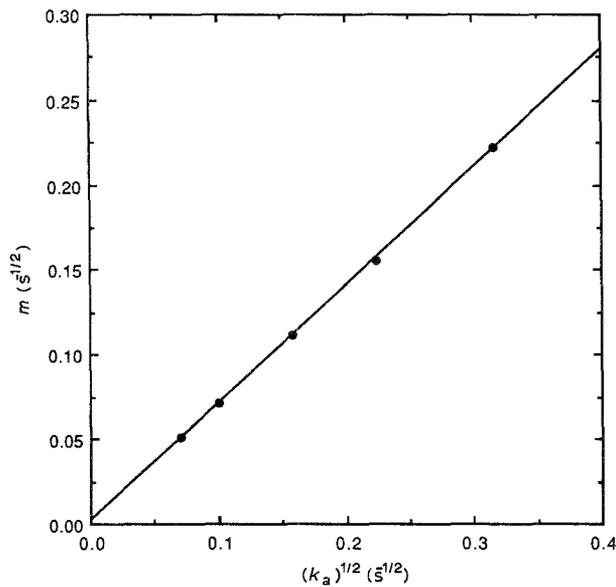


Fig. 2. Effect of k_a on the slope (m) obtained from the dependence of q_T/q_{in} on $(t_c)^{1/2}$.

of the trapping ratio has the same dependence on the entry flux.

3.1.2. Alloys. The apparent trapping constants reported earlier for each alloy are summarized in Table 2. These values were used to calculate the particular trapping efficiencies for the alloys of interest. The ratio of q_T to q_{in} in each case is shown as a function of t_c in Fig. 3. The fraction of hydrogen trapped for the two nickel-base alloys (Inconel 625 and Incoloy 925) with low trapping constants is found to vary approximately linearly with $(t_c)^{1/2}$ apparently due to the relatively low influence of trapping on hydrogen ingress. In contrast, the effect of the higher trapping constants for Inconel 718 and Hastelloy C-276 is observed in the non-linearity of q_T/q_{in} over longer charging times.

3.2. Entry behaviour of alloys

The charging current and therefore the cathodic charge (q_c) were low for Incoloy 925 and Inconel 625, so it was not possible to determine reliable values of q_{in}/q_c . However, in the case of Inconel 718 and Hastelloy C-276, the cathodic charge was somewhat higher, which reduced the excessive sensitivity observed in q_{in}/q_c for the other two alloys.

The fraction of hydrogen entering Inconel 718 is essentially constant with t_c for overpotentials from -0.15 to -0.25 V (Fig. 4). However, q_{in}/q_c increases almost linearly with t_c at -0.10 V and varies slightly even at -0.15 V. For a given charging time, q_{in}/q_c

Table 2. Apparent trapping constants

Alloy	k_a (s^{-1})
Inconel 718	0.031 ± 0.002
Hastelloy C-276	0.025 ± 0.003
Incoloy 925	0.006 ± 0.003
Inconel 625	0.004 ± 0.002

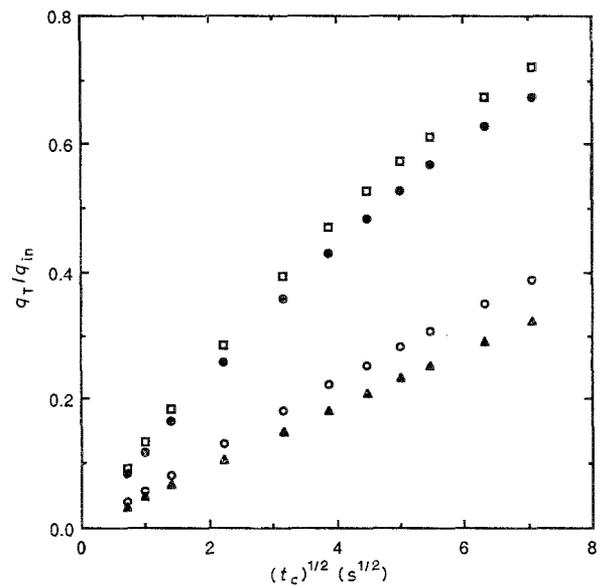


Fig. 3. Dependence of q_T/q_{in} on charging time for each alloy. The apparent rate constants are given in parentheses for the particular alloy: (□) Inconel 718 (0.031); (○) Incoloy 925 (0.006); (▲) Inconel 625 (0.004); (●) Hastelloy C-276 (0.025).

decreases with increasing overpotential, as shown more clearly in Fig. 5. The entry efficiency for Hastelloy C-276, like that for Inconel 718, is largely independent of t_c at higher overpotentials (Fig. 6) and decreases with increasing overpotential (Fig. 7). The decrease in entry efficiency for the Inconel and Hastelloy indicates that the rate of hydrogen desorption increases relative to the rate of hydrogen entry.

4. Discussion

4.1. Trapping efficiency

The trapping efficiency of an alloy as a function of charging time is determined essentially by the trapping constant for the alloy; that is, the ratio does not depend on any other parameter such as ingress flux.

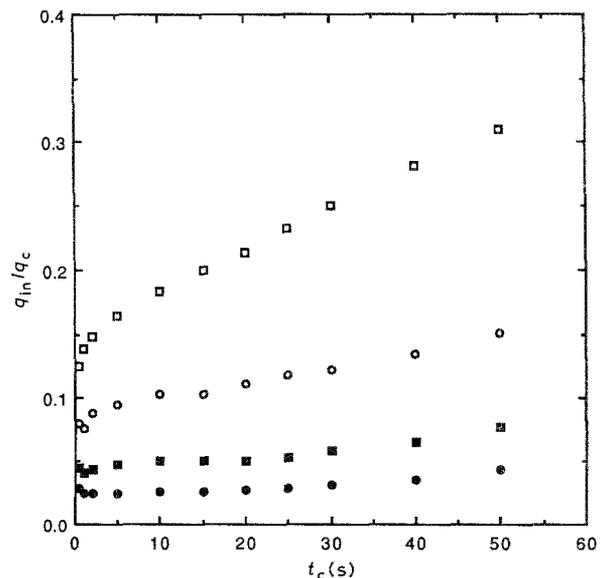


Fig. 4. Dependence of q_{in}/q_c on charging time for Inconel 718 at various overpotentials: (□) -0.10 , (○) -0.15 , (■) -0.20 , (●) -0.25 V.

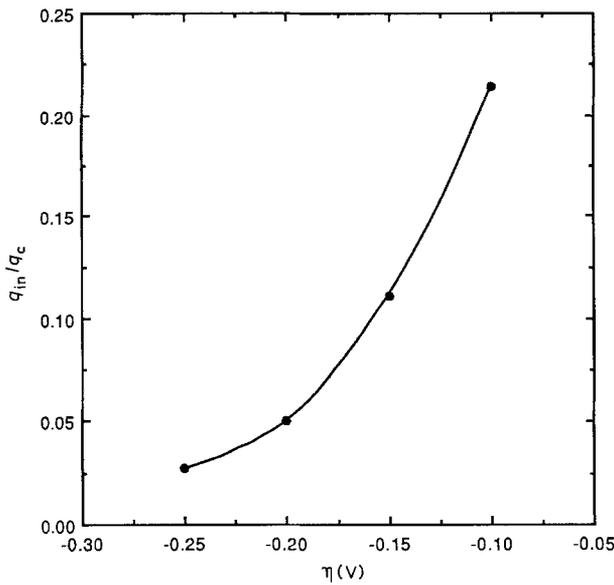


Fig. 5. Dependence of q_{in}/q_c on overpotential for Inconel 718 at a charging time of 20 s.

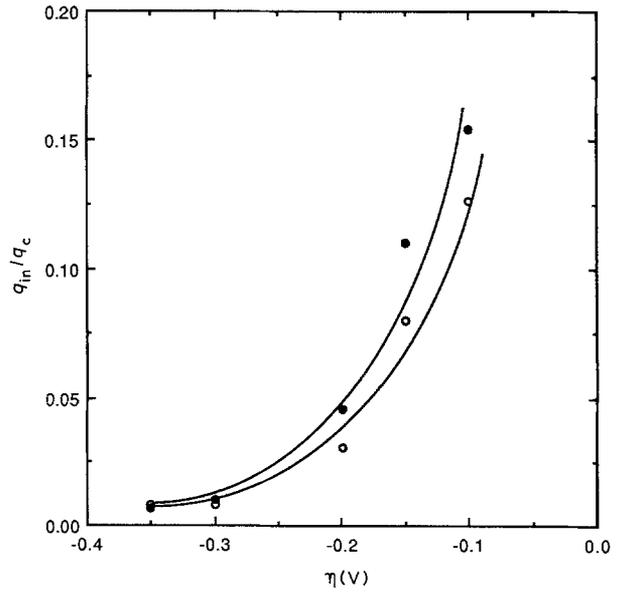


Fig. 7. Dependence of q_{in}/q_c on overpotential for Inconel 718 at charging times of 20 s (O) and 40 s (●).

Hence, the alloys fall into two groups according to whether their apparent trapping constants are high ($\geq 0.025 \text{ s}^{-1}$) or low ($< 0.010 \text{ s}^{-1}$). Clearly, due to the similarity in apparent trapping constants, the alloys in each group have similar trapping efficiencies despite having quite different thermo-mechanical treatments and types of irreversible traps. For example, in the case of Inconel 718 and Hastelloy C-276, hardening is achieved by aging and cold-working, respectively, and the principal irreversible traps appear to be carbonitride particles and grain boundary phosphorus, respectively [4, 5], but there is little difference in the trapping efficiency of the two alloys.

The reason for the lack of difference is that the apparent trapping constants used to calculate q_T and q_{in} reflect both irreversible trapping and reversible trapping, according to Equation 4:

$$k_a = k/(1 + K_r) \quad (4)$$

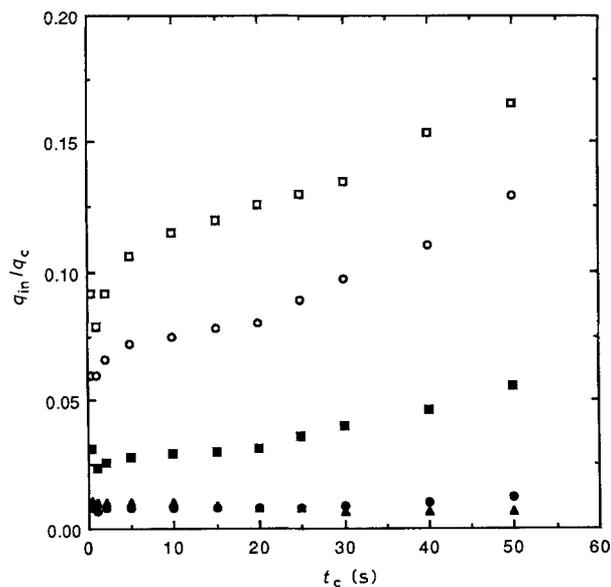


Fig. 6. Dependence of q_{in}/q_c on charging time for Hastelloy C-276 at various overpotentials: (□) -0.10, (O) -0.15, (■) -0.20, (●) -0.30, (▲) -0.35 V.

where k is the irreversible trapping constant and K_r is an equilibrium constant for reversible traps. Hence, k_a accounts for the effect of the appropriate irreversible trap modified by the reversible trapping behaviour associated with microstructural heterogeneities. In particular, defects such as grain boundaries and dislocations that vary with the amount of thermo-mechanical processing can generally be characterized by K_r , so k_a is able to represent the overall trapping behaviour of alloys having different compositions and microstructures.

4.2. Entry efficiency

4.2.1. Effect of charging conditions. The entry efficiency can be expressed by

$$q_{in}/q_c = FJt_c \int_0^{r_c} i_c dt \quad (5)$$

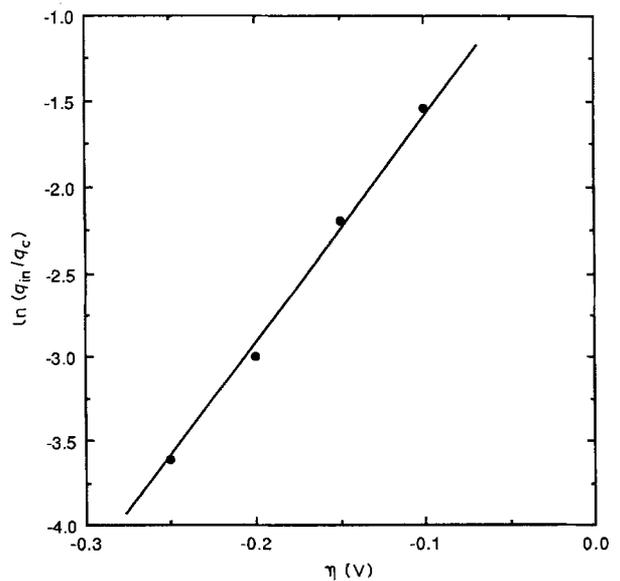


Fig. 8. Logarithmic dependence of q_{in}/q_c on overpotential for Inconel 718 at a charging time of 20 s.

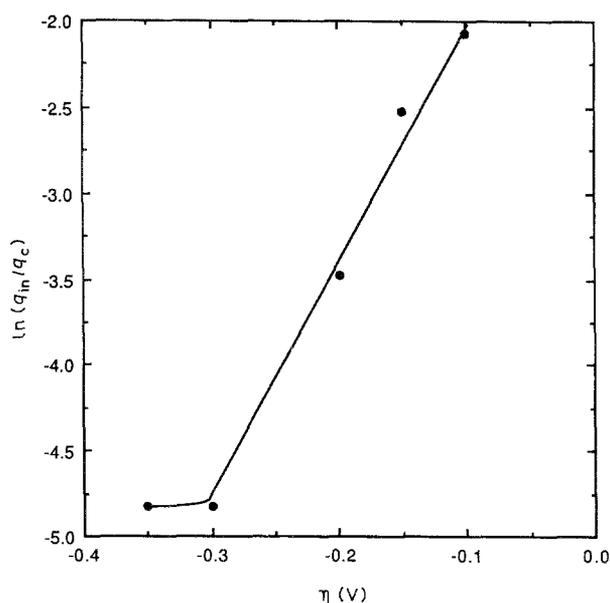


Fig. 9. Logarithmic dependence of q_{in}/q_c on overpotential for Hastelloy C-276 at a charging time of 20 s.

where i_c is the charging current. If i_c is invariant with time, then $q_c = i_c t_c$, so that q_{in}/q_c is given by FJ/i_c . The entry efficiency should therefore be independent of t_c for a constant charging current. However, the surface coverage, and therefore J , as well as i_c may vary with overpotential, depending on the mechanism of the hydrogen evolution reaction.

In the diffusion/trapping model used to analyse the pulse data, the layer of adsorbed hydrogen is assumed to adjust very rapidly to a potential step. Under this condition, the dependence of q_{in}/q_c on overpotential is given by (see Appendix):

$$\ln(q_{in}/q_c) = Y - (w - \alpha)\eta F/RT \quad (6)$$

where the values of Y and w depend on the type of mechanism for hydrogen evolution. The variation in the entry efficiency with overpotential is clearly dependent on the charge transfer coefficient (α) and w . For mechanisms involving fast discharge, w can have a value of 0.5 in the case of activated Temkin adsorption of 1 in the case of Langmuir and non-activated Temkin adsorption. If $\alpha = w$, q_{in}/q_c will be independent of overpotential. However, if $\alpha > w$ or $\alpha < w$, q_{in}/q_c will decrease or increase, respectively, as the overpotential is made more negative.

4.2.2. Nickel alloys. The entry efficiencies for Hastelloy C-276 and Inconel 718 behave similarly. The q_{in}/q_c ratios for both alloys are essentially independent of charging time at overpotentials ≤ -0.15 V and -0.20 V, respectively, and therefore follow the predicted behaviour at sufficiently negative overpotentials. The dependence on t_c observed at low overpotentials suggests that i_c decreased enough during each charging time to be considered time-dependent. As predicted from Equation 6, q_{in}/q_c for both alloys is exponentially dependent on overpotential (Figs 8 and 9). The lack of change in q_{in}/q_c for the Hastelloy between

-0.3 and -0.35 V is probably due to the surface coverage reaching saturation at the corresponding charging potentials. The term $(w - \alpha)$ was evaluated from the variation of q_{in}/q_c with overpotential and was found to be 0.4. Hence, the value of α could be either 0.9 if activated Temkin adsorption were involved or 1.4 if Langmuir or non-activated Temkin adsorption occurred.

The kinetics of hydrogen evolution have been analysed by McBreen and Genshaw [6] for different mechanisms with both Langmuir and Temkin adsorption of the hydrogen atoms formed during discharge. The value of 1.4 obtained for α from the experimental data corresponds most closely to the theoretical value of 1.5 for a mechanism involving fast discharge and slow electrochemical desorption with either Langmuir or non-activated Temkin adsorption.

The other experimental value of 0.9 in the case of activated Temkin adsorption is assumed to reflect mechanisms with a theoretical value of 1.0, but the two mechanisms involving fast discharge followed by slow desorption (chemical in one case and electrochemical in the other) both have the appropriate value of α [6]. However, slow desorption typically leads to relatively high surface coverages, and so tends to favour the electrochemical route. In addition, hydrogen evolution on nickel is known to occur by rapid proton discharge followed by rate-determining electrochemical desorption [7]. Hence, although the type of adsorption (Langmuir or Temkin) cannot be distinguished, both values of α for the Hastelloy and Inconel indicate that the mechanism involves fast discharge-slow electrochemical desorption. Moreover, this mechanism is consistent with that found for nickel.

5. Summary

- (i) The trapping efficiency is approximately given by $0.69(k_a t_c)^{1/2}$ for sufficiently short charging times. The magnitude of the apparent trapping constant determines the maximum charging time to maintain the square root dependence of q_T/q_{in} on t_c .
- (ii) The entry efficiency is independent of charging time but it can be an exponential function of overpotential depending on the values of the charge transfer coefficient (α) and another mechanism parameter (w). If $\alpha = w$, q_{in}/q_c is independent of η but if $\alpha > w$ or $\alpha < w$, the ratio decreases or increases, respectively, as the overpotential is made more negative.
- (iii) The entry and trapping efficiencies behave similarly for Hastelloy C-276 and Inconel 718. The q_{in}/q_c ratios, as predicted, are independent of charging time (except at low overpotentials) and are exponentially dependent on overpotential.
- (iv) The value of α for these two nickel alloys in the acetate-As₂O₃ electrolyte is 1.4, which is consistent with a mechanism involving fast discharge followed by slow electrochemical desorption.

Appendix: Dependence of entry efficiency on overpotential

If the charging current is assumed to be constant, the entry efficiency can be expressed as

$$q_{in}/q_c = FJ/i_c \quad [A.1]$$

The charging current is given by

$$i_c = i_0 \exp[-\alpha F\eta_f/RT] \quad [A.2]$$

where i_0 is the exchange current density, α is the charge transfer coefficient, η_f is the conventional overpotential defined as $(E_c - E_r)$, and E_r is the reversible potential for the overall H^+/H_2 reaction. In this work, η is represented by $(E_c - E_{oc})$. Therefore, η_f can be written as $(\eta - E'_r)$ where $E'_r = E_r - E_{oc}$.

The potential dependence of the surface coverage, and consequently the flux, is determined by the mechanism of the hydrogen evolution reaction. The surface coverage is assumed to respond rapidly enough to changes in potential so as to maintain a quasi-equilibrium. Therefore, only those mechanisms that involve fast discharge need to be considered.

Langmuir adsorption

Under Langmuir conditions, the flux can be related to the surface coverage (θ) by

$$J = d\theta \quad [A.3]$$

where d is a generalized rate constant and the occupancy of interstitial sites immediately below the surface of the metal is assumed to be very low [6]. The surface coverage is given by the following isotherm [8]:

$$\theta = \frac{K \exp[-F\eta_f/RT]}{(1 + K \exp[-F\eta_f/RT])} \quad [A.4]$$

where K is a constant at a given pH. At sufficiently low potentials, $K \exp(-F\eta_f/RT) \ll 1$, and therefore $\theta \sim K \exp(-F\eta_f/RT)$. Hence, the entry efficiency can be expressed as

$$q_{in}/q_c = \frac{FdK \exp[-\eta_f F/RT]}{i_0 \exp[-\alpha \eta_f F/RT]} \quad [A.5]$$

Rewriting Equation [A.5] in terms of η gives

$$q_{in}/q_c = \frac{FdK \exp[(1 - \alpha)E'_r F/RT]}{i_0 \exp[(1 - \alpha)\eta F/RT]} \quad [A.6]$$

and therefore

$$\ln(q_{in}/q_c) = X - (1 - \alpha)\eta F/RT \quad [A.7]$$

where X is a constant given by $\ln(FdK/i_0) + (1 - \alpha)E'_r F/RT$.

Temkin adsorption

Two cases can be considered:

1. Non-activated adsorption for which the flux is assumed to be given by

$$J = d \exp(r\theta/RT) \quad [A.8]$$

where $r = fRT$ and f is a free energy parameter. The surface coverage term can be expressed as [8]

$$\exp(r\theta/RT) = K' \exp[-F\eta_f/RT] \quad [A.9]$$

where K' is a constant.

Hence, the entry efficiency can be written as

$$q_{in}/q_c = \frac{FdK'}{i_0 \exp[(1 - \alpha)(\eta - E'_r)F/RT]} \quad [A.10]$$

or

$$\ln(q_{in}/q_c) = X' - (1 - \alpha)\eta F/RT \quad [A.11]$$

where X' is a constant given by $\ln(FdK'/i_0) + (1 - \alpha)E'_r F/RT$.

2. Activated adsorption for which the flux is assumed to be given by

$$J = d \exp(\alpha' r\theta/RT) \quad [A.12]$$

where α' is a symmetry factor and will normally be close to 0.5 for the case of activated adsorption [8]. The charging efficiency is obtained by using Equation [A.9] to yield

$$q_{in}/q_c = \frac{FdK'^{\alpha'} \exp[-\alpha' F\eta_f/RT]}{i_0 \exp[-\alpha F\eta_f/RT]} \quad [A.13]$$

Therefore,

$$q_{in}/q_c = \frac{FdK'^{\alpha'}}{i_0 \exp(\alpha' - \alpha)F\eta_f/RT} \quad [A.14]$$

If α' is assumed to have its usual value of 0.5, then Equation A.14 can be rewritten as

$$q_{in}/q_c = \frac{FdK'^{0.5}}{i_0 \exp[(0.5 - \alpha)(\eta - E'_r)F/RT]} \quad [A.15]$$

and therefore

$$\ln(q_{in}/q_c) = X'' - (0.5 - \alpha)\eta F/RT \quad [A.16]$$

where X'' is a constant given by $\ln(FdK'^{0.5}/i_0) + (0.5 - \alpha)E'_r F/RT$.

Acknowledgments

Financial support of this work by the U.S. Office of Naval Research under Contract N00014-86-C-0233 is gratefully acknowledged.

References

- [1] R. McKibbin, D. A. Harrington, B. G. Pound, R. M. Sharp and G. A. Wright, *Acta metall. mater.* **35** (1987) 253.
- [2] B. G. Pound, R. M. Sharp and G. A. Wright, *ibid.* **35** (1987) 263.
- [3] B. G. Pound, *Corrosion* **45** (1989) 18; **46** (1990) 50.
- [4] *Idem*, *Acta metall. mater.* **38** (1990) 2373.
- [5] *Idem*, *ibid.*, in press.
- [6] J. McBreen and M. A. Genshaw, in Proceedings of the Conference on Fundamental Aspects of Stress Corrosion Cracking, Columbus, Ohio (1967) p. 51.
- [7] J. O'M. Bockris and A. K. Reddy, 'Modern Electrochemistry', Vol. 2, Plenum Press, New York (1973) p. 1250.
- [8] E. Gileadi and B. E. Conway, in 'Modern Aspects of Electrochemistry', Vol 3 (edited by J. O'M. Bockris and B. E. Conway), Butterworths, London (1964) p. 347.