DRAFT SF 298

1. Report Date (dd-mm-yy)

2. Report Type

3. Dates covered (from... to)

4. Title & subtitle
The Resistance of High-Strength Alloys to Hydrogen Embrittlement
Tri-Service Committee on Corrosion Proceedings

5a. Contract or Grant #

5b. Program Element #

5c. Project #

5d. Task #

5e. Work Unit #

6. Author(s)
Dr. Bruce G. Pound

7. Performing Organization Name & Address

8. Performing Organization Report #

9. Sponsoring/Monitoring Agency Name & Address
Tri-Service Committee on Corrosion
USAF WRIGHT-PATTERSON Air Force Base, Ohio 45433

10. Monitor Acronym

11. Monitor Report #

12. Distribution/Availability Statement
Approved for Public Release
Distribution Unlimited

13. Supplementary Notes

14. Abstract

15. Subject Terms
Tri-Service Conference on Corrosion

Security Classification of

16. Report

17. Abstract

18. This Page

19. Limitation of Abstract

20. # of Pages

21. Responsible Person
(Name and Telephone #)

000955

TRI-SERVICE CONFERENCE ON CORROSION

21-23 JUNE 1994

SHERATON PLAZA HOTEL
ORLANDO, FLORIDA

PROCEEDINGS

The Resistance of High-Strength Alloys to Hydrogen Embrittlement

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Abstract

The resistance of an alloy to hydrogen embrittlement (HE) is strongly influenced by the presence of microstructural heterogeneities, which can provide sites to trap hydrogen. The entry and trapping of hydrogen in a range of high-strength alloys have been investigated with a technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP). Data were analyzed by using a diffusion/trapping model to determine entry and trapping parameters for high-strength steels, precipitation-hardened and work-hardened nickel-base alloys, and titanium alloys. For most of the alloys studied, the observed resistance to HE appeared to be determined primarily by the alloy's intrinsic susceptibility as defined by the trapping characteristics; that is, the H entry flux generally has only a secondary effect on the resistance to HE. However, in one case, the HE resistance was attributable to a low entry flux. This type of case highlights the need for characterizing alloys in terms of both trapping capability and rate of H entry to account for differences observed in their HE resistance.

Introduction

Microstructural heterogeneities in alloys provide potential trapping sites for hydrogen and so can play a crucial role in determining an alloy's resistance to hydrogen embrittlement (HE). This role originates in the fact that the interaction of these heterogeneities with hydrogen can strongly influence the series of events leading to failure.[1] The accumulation of hydrogen at second-phase particles and precipitates, for example, is generally considered to promote microvoid initiation via the fracture of particles or the weakening of particle-matrix interfaces. Traps with a large saturability and a high binding energy for hydrogen are highly conducive to HE,[2,3] whereas alloys containing a high density of well-distributed irreversible (high binding energy) traps that have a low saturability should be less susceptible. Thus, the intrinsic susceptibility of an alloy to HE is highly dependent on the type of microstructural defect, with large irreversible traps typically imparting a high susceptibility.

The basic concept of trap theory is that the local concentration of hydrogen trapped at a defect must exceed some critical value (C_k) for cracks to be initiated.[1,3] It should be recognized, however, that the mechanism by which such an accumulation triggers HE is not addressed. The value of C_k, and therefore the intrinsic susceptibility of an alloy, is determined by the type of trap, its size, concentration (density), and other parameters. A decrease in C_k will render the alloy more susceptible. However, whether embrittlement will actually occur is also affected by the amount of trapped H, which depends on factors such as the entry kinetics, exposure time, and transport mode. In some cases, an alloy may prove resistant during exposure because the amount of H that enters is small enough that the critical concentration at the traps is not exceeded. Likewise, when alloys have a similar intrinsic susceptibility in terms of their trapping characteristics, the difference in their actual resistance to HE is likely to be determined by the amount of H absorbed by each alloy.

Over the last few years, the entry and trapping of hydrogen in a wide range of high-strength alloys have been investigated at SRI.[4-8] The rates of H entry and rate constants for irreversible trapping were determined using an electrochemical technique referred to as hydrogen ingress analysis by potentiostatic pulsing (HIAPP).[4,9] The research was aimed in part at characterizing the intrinsic susceptibility of the alloys to HE in terms of their irreversible trapping constants. The relative intrinsic susceptibilities then could be compared with results for the actual resistance to HE observed in tests by other workers. In this paper, the irreversible trapping constants and, where necessary, H entry fluxes for the different alloys are compared, with the objective of providing a basis for explaining differences in the resistance of these alloys to HE.

Experimental

The alloy of interest is cathodically charged with hydrogen at a constant potential E_c for a time t_c, after which the potential is stepped in the positive direction. H diffuses back to the entry surface and is reoxidized, thereby generating an anodic current transient. Data are obtained over a range of charging times, typically from 5 to 60 s, at different overpotentials ($\eta = E_c - E_{oc}$) relative to the open-circuit potential

(E_{oc}), which is measured immediately before each charging time. E_{oc} is also used to monitor the stability of the alloy surface, since any oxides present should not be reduced during charging.

The pulse technique was applied to high-strength steels,[4,5] precipitation-hardened and work-hardened nickel-base alloys,[5,6] and titanium.[7] The composition of each alloy is given in Table 1. Table 2 shows the yield strength of the alloys and the thermomechanical treatment used in each case.

Table 1
Alloy Composition (wt%)

	4340	18Ni	718	925	C-276	625	716	TiGr2
Al	0.031	0.13	0.60	0.30		0.18	0.22	
B		0.003	0.003					
C	0.42	0.009	0.03	0.02	0.002	0.03	0.011	0.021
Co		9.15	0.16		0.83		<0.01	
Cr	0.89	0.06	18.97	22.20	15.27	22.06	20.99	
Cu	0.19	0.11	0.04	1.93				
Fe	bal	bal	16.25	28.96	5.84	4.37	5.32	0.17
Mn	0.46	0.01	0.10	0.62	0.48	0.17	0.01	
Mo	0.21	4.82	3.04	2.74	16.04	8.70	8.10	
O	0.001							0.16
Nb+Ta			5.30			3.50	3.47	
Ni	1.74	18.42	54.41	40.95	57.5	60.33	60.5	
P	0.009	0.004	0.009		<0.005	0.012	0.004	
S	0.001	0.001	0.002	0.001	<0.002	0.001	0.001	
Si	0.28	0.04	0.11	0.17	<0.02	0.38	0.02	
Ti		0.65	0.98	2.11		0.27	1.35	bal
W		0.01			3.90			
Other	0.005N	0.05 Ca 0.02 Zr			0.12 V			<0.005H 0.007N

Test electrodes of each alloy were fabricated from a length (1.3-3.8 cm) of rod press-fitted into a Teflon sheath so that only the planar end surface was exposed to the electrolyte. The surface was polished before each experiment with SiC paper followed by 0.05-µm alumina powder. Details of the electrochemical cell and instrumentation have been given elsewhere.[4] The alloys were exposed in a deaerated solution containing 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium acetate with 15 ppm As_2O_3 added to promote H entry. The potentials were measured with respect to a saturated calomel electrode (SCE). All tests were performed at 22 ± 2°C.

Table 2
Thermomechanical Treatment of Alloys

Alloy	Heat Treatment[a]	Test Condition	Yield Strength (MPa)
4340	Annealed	HRC 41	1206
		HRC 53	1792
18Ni	Aged (482°C, 4 h)	As received	1954
K-500	Cold drawn, unaged	As received	758
		Aged (600°C, 8 h)	1096
35N	Cold drawn and aged	As received	1854
718	Hot fin., solution treated	As received	1238
925	Hot fin., annealed, aged	As received	758
C-276	Hot rolled	27% cold work	1237
625	Hot fin., annealed	17% cold work	1195
716	Annealed, aged	4% cold work	1186
Ti Gr2	Annealed (620°C, 1 h)	As received	380

[a] Provided by producer.

Analysis

Although permeation methods have been used extensively, they suffer from several disadvantages, as discussed elsewhere.[10] The main theoretical limitation is that most, if not all, diffusion/trapping models for these methods are based on an input boundary condition of constant concentration. Hence, these models are strictly applicable only for charging conditions without any entry limitation.

In the case of HIAPP, a model has been developed to allow for the effect of trapping on diffusion for cases involving either a constant concentration or a constant flux at the input surface.[4,9] The constant flux model was found to apply to all alloys studied to date. In this model, the rate of hydrogen ingress is controlled by diffusion but the entry flux of hydrogen is restricted, which results in interface-limited diffusion control. Solution of the diffusion equation for a constant flux condition gives the following expression for the total anodic charge (C m^{-2}):

$$q'(\infty) = FJ\,t_c\{1 - e^{-R}/(\pi R)^{1/2} - [1 - 1/(2R)]\mathrm{erf}(R^{1/2})\} \tag{1}$$

where F is the Faraday constant, J is the ingress flux in mol m^{-2} s^{-1}, and R $= k_a t_c$. The charge $q'(\infty)$ is equated to the charge (q_a) associated with the experimental anodic transients. q_a can be associated entirely with absorbed H, since the adsorbed charge is almost invariably negligible.

k_a is an apparent trapping constant measured for irreversible traps in the presence of reversible traps. It is related to the irreversible trapping constant (k) by kD_a/D_L where D_a is the apparent diffusivity and D_L is the lattice diffusivity of H. The magnitude of k depends on the density of particles or defects (N_i) providing irreversible traps, the radius (d) of the trap defects, and the diameter (a) of the metal atom[11]:

$$k = \frac{4\pi d^2 N_i D_L}{a} \tag{2}$$

The term, d^2N_i, represents the trapping capability and underlies the use of k as an index of an alloy's intrinsic susceptibility to HE.

For the constant flux model to be applicable, it must be possible to determine a trapping constant for which J is independent of charging time. Data for q_a could in fact be fitted to Eq. (1) to obtain values of k_a and J that satisfied this requirement at each potential. Experimental and fitted values of q_a for various charging times are compared in Fig. 1, which illustrates the level of agreement obtained for the alloys in this work.

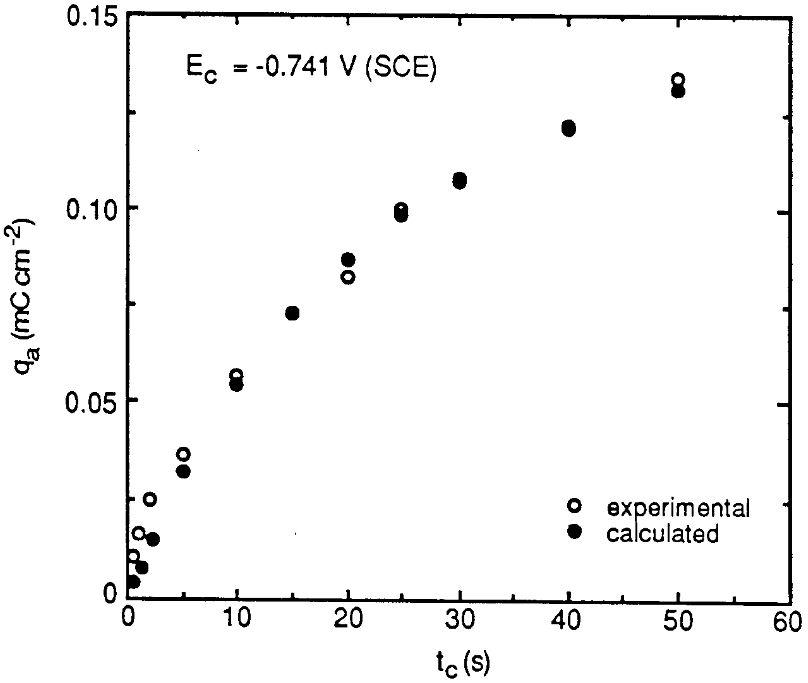

Figure 1. Dependence of anodic charge on charging time for Ti grade 2.

Results

The alloys were studied as a series of groups, which were then merged to provide an overall comparison of the irreversible trapping constants. The values of k_a and k for each group are summarized in Table 3. The first group consisted of a high-strength steel (AISI 4340), and two nickel-containing alloys (K-500 and 35N).[4] The aim was to determine whether the irreversible trapping constants might assist in explaining differences observed in HE resistance between high-strength steels and nickel-base alloys. The values of both k and J for the steel were higher than those for alloys K-500 and 35N. Hence, both the irreversible trapping characteristics and the amount of H entering could account for the steel being less resistant to HE than the two nickel-containing alloys.

Table 3
Trapping Parameters

Alloy	k_a (s^{-1})	D_L/D_a	k (s^{-1})
4340 Steel	0.008 ± 0.001	500	4.0 ± 0.5
K-500 Unaged	0.017 ± 0.003	2.0	0.034 ± 0.006
Aged	0.021 ± 0.003	2.0	0.042 ± 0.006
35N	0.026 ± 0.002	1	0.026 ± 0.002
718	0.031 ± 0.002	4.0 ± 0.5	0.124 ± 0.024
925	0.006 ± 0.003	4.6 ± 0.6	0.034 ± 0.004
18Ni Steel	0.005 ± 0.002	300 ± 90	1.50 ± 1.05
	0.010 ± 0.005[a]	300 ± 90	3.00 ± 2.40
C-276	0.025 ± 0.003	2.6 ± 0.8	0.090 ± 0.030
	0.019 ± 0.010[a]	2.6 ± 0.8	0.068 ± 0.051
625	0.004 ± 0.002	2.6 ± 0.8	0.014 ± 0.010
716	0.054 ± 0.004	3.8 ± 0.8	0.20 ± 0.06
Ti grade 2	0.028 ± 0.002	1	0.028 ± 0.002
	0.012 ± 0.006[b]	1	0.012 ± 0.006

[a] Quasi-irreversible trapping; [b] Hydride formation.

Two further groups of alloys were then studied: precipitation-hardened alloys (718, 925, and 18Ni maraging steel)[5] and work-hardened alloys (625 and C-276).[6] Alloys 625, 718, and 925 were each characterized a single type of irreversible trap, whereas alloy C-276 and 18Ni maraging steel were characterized by both an irreversible trap and a quasi-irreversible trap. In irreversible trapping, the rate constant for release is assumed to be zero, whereas for the quasi-irreversible case, the release constant is not zero but is too small to achieve local equilibrium between the lattice and trapped H.[5] The maraging steel had the highest value of *k*, followed by alloys 718, C-276, 925, and 625. It is apparent from its value of *k* that the maraging steel is intrinsically somewhat less susceptible than 4340 steel. Test results have in fact shown that 18 Ni(250) maraging steel is more resistant to cracking than 4340 steel,[12] so the differing susceptibility of the two steels was matched by their actual resistances to HE.

A similar parallel was found to exist for the 18Ni steel and alloy 718. Stress-rupture tests during electrolytic charging have shown that 18Ni (1723 MPa) maraging steel undergoes severe HE, whereas alloy 718 exhibits negligible embrittlement.[13] Likewise, gas-phase charging tests showed from the reduction in strength that the maraging steel was less resistant than alloy 718, although the embrittlement in both cases was characterized as extreme.[13]

No Ni-base alloys in the 900 series were included in the electrolytic embrittlement tests. However, gas-phase studies on alloy 903 have shown that short exposure to high-pressure hydrogen is not detrimental, though prolonged exposure, particularly at higher temperatures, can reduce ductility.[14] In contrast, alloy 718 undergoes extreme embrittlement under gas-phase charging, as noted above. These results suggest that alloy 903 and, by implication, alloy 925 are less sensitive than alloy 718 to HE. Hence, the irreversible trapping constants of the three precipitation-hardened alloys are consistent with their relative resistances to HE observed in failure tests.

A similar comparison of the resistances of alloys C-276 and 625 is complicated by their sensitivity to cold work. However, the ranking of these alloys can be assessed indirectly from results for alloys C-276 and G.[15] Time-to-failure and crack propagation data showed that alloy C-276 has a greater tendency to HE than alloy G cold-worked to an equivalent degree. Alloys G and 625 are comparable in their levels of Cr, Mo, and Nb+Ta, so they might be expected to be similar in their resistance to HE. For the degree of cold work involved, alloy C-276 should therefore be less resistant to HE than alloy 625,[6] which coincides with the order of their trapping constants.

A lack of relevant data in the literature makes it difficult to determine whether the two cold-worked alloys fit in with the other alloys on the basis of their *k* values. The difficulty in evaluating the position of the cold-worked alloys is compounded by some uncertainty in these values. Nevertheless, the trapping constants for alloys 625 and 718 show a significant difference, and the sequence of values is consistent with results from C-ring and U-bend exposure tests that indicated alloy 625 is more resistant to cracking than alloy 718.[16]

If allowance is made for the uncertainty in *k*, the position of alloy 625 is comparable to that of alloy 35N. Tests using C-ring specimens of these alloys showed that the time-to-failure of unaged alloy 625 with 59% cold reduction is intermediate between those for 35% and 51% cold reduced alloy 35N in the aged condition.[17] Alloy 625 with 17% cold work, as was used in the present study, should withstand a longer exposure time than the same alloy with 59% cold work and therefore should be at least as resistant to HE as alloy 35N in the condition of interest (40-50% cold reduced and aged). In fact, the 625 specimen may be more resistant than the 35N alloy, as implied by their values of *k*. Thus, the order of the trapping constants parallels the relative resistance of these alloys to HE.

Ti grade 2 was also examined.[6] It exhibited two values of *k*, depending on the overpotential (Fig. 2) and therefore on the level of H in the alloy. Hydride precipitates have been observed in Ti grade 2 at H levels above ~100 ppm, but gross embrittlement does not result until much higher levels.[18] Thus, the similarity observed in the values of *k* for low-H Ti grade 2 and alloy 925 fits their relative resistance to HE in that both alloys must be exposed for long times to cause degradation of their mechanical properties.[14,18] Furthermore, the higher value of *k* for Ti grade 2 coincides with its decreased resistance to embrittlement at high enough H concentrations.

An exception to these trends was observed with alloy 716, which is an age-hardenable alternative to alloy 625.[16] Alloy 716 had a *k* of 0.2, which is the highest value among those for the nickel-base alloys and indicates that this alloy is intrinsically the most susceptible to HE. However, tests with C-ring and U-bend specimens have shown that it is comparable to alloy 625 of similar yield strength in being able to withstand exposure in aggressive environments.[16] A likely explanation is that, although alloy 716 has a high intrinsic susceptibility, the H concentration at the dominant traps remains below the critical level required to initiate cracking. The entry flux was found to be low in the acetate buffer and could well have been low enough in the cracking test environments to delay failure in most cases (up to 1000 h). Thus, the resistance to cracking observed for alloy 716 was believed to be associated with the low entry flux of hydrogen.

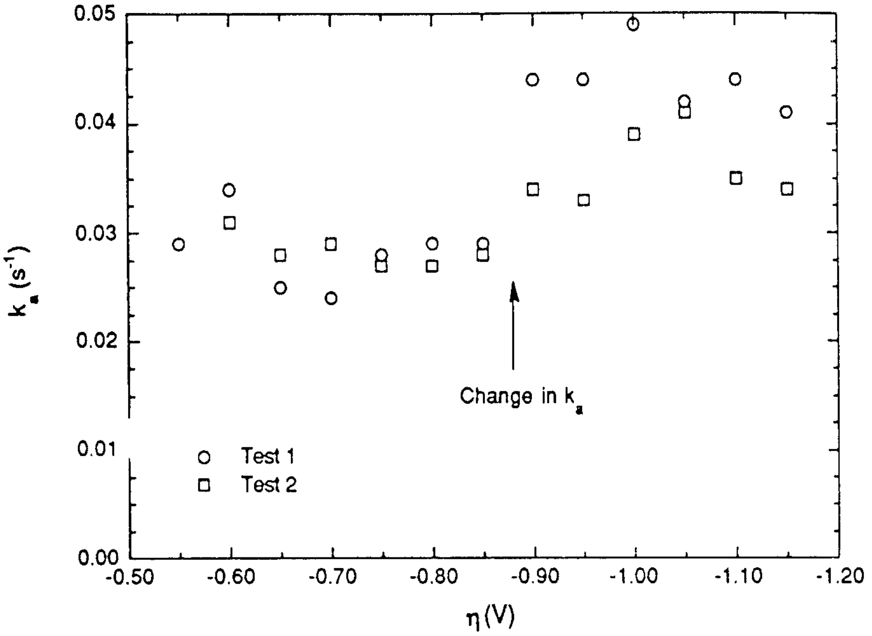

Figure 2. Variation in k_a with overpotential for Ti grade 2.

Discussion

The alloys studied were generally characterized by a single type of irreversible trap, but in some alloys the principal irreversible type of trap was supplemented by other traps of either a quasi-irreversible type or another irreversible type. Values of *k* associated with the principal irreversible traps are listed in Table 4 for all the alloys except 716. They are also presented graphically in Fig. 3 to highlight differences between them.

The steels, particularly 4340, exhibit high values of *k* that are indicative of a high intrinsic susceptibility to HE, whereas the nickel-base alloys are characterized by lower values of *k* and are therefore intrinsically less susceptible. Differences in the susceptibility of the nickel-base alloys are smaller than those for the steels but are clearly discernible. In particular, the trapping constants for alloys within groups defined by thermomechanical treatment (precipitation- and work-hardening) indicate that the susceptibilities can vary significantly.

For most alloys, there appears to be a correlation between the intrinsic susceptibility, as represented by *k*, and the actual resistance to HE observed in failure tests. This correlation suggests that the observed resistance to HE is determined primarily by the alloy's intrinsic susceptibility — that is, by the irreversible trapping characteristics. Thus, the entry flux generally has only a secondary effect on the HE resistance.

Table 4
Irreversible Trapping Constants

Alloy	k (s^{-1})
4340 steel	4.0 ± 0.5
18Ni (300) steel	1.50 ± 1.05
718	0.128 ± 0.024
C-276 (27% cold work)	0.090 ± 0.030
K-500	0.040 ± 0.010
Ti grade 2 (high H)	0.040 ± 0.008
925	0.034 ± 0.004
Ti grade 2 (low H)	0.028 ± 0.002
35N	0.026 ± 0.002
625 (17% cold work)	0.014 ± 0.010

Exceptions to this correlation can be expected in cases where the ingress flux for an alloy is low enough that the alloy is relatively resistant to cracking even though it might have a high intrinsic susceptibility. Such an exception was observed with alloy 716. The intrinsic susceptibility of

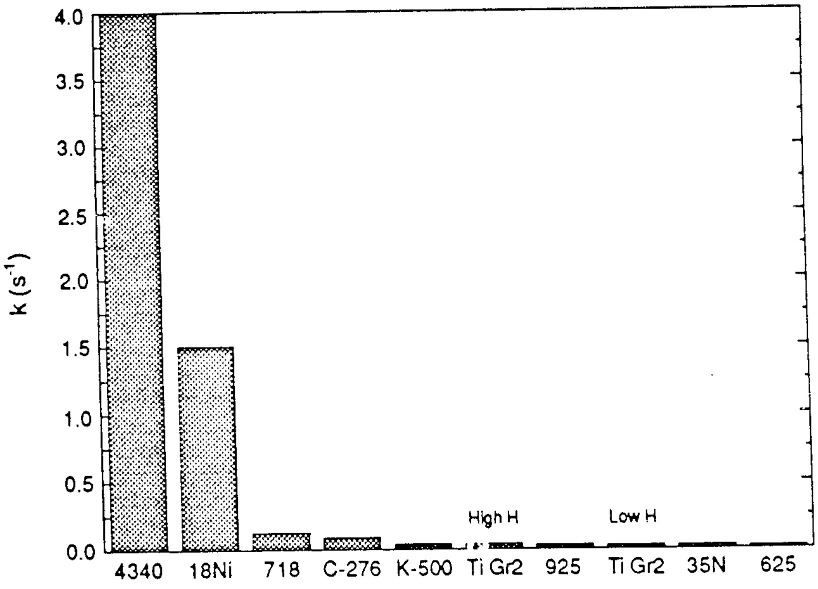

Figure 3. Variation in k for the different alloys.

this alloy was shown to be high ($k = 0.2$), yet the entry flux was apparently low enough that the alloy generally did not undergo cracking during exposure in aggressive environments for periods up to 1000 h.

The use of k to provide an index of HE susceptibility can be justified on the basis of Eq. (2), but there remains the question of why such a relatively simple parameter has the apparent ability in most cases to indicate the relative resistance actually observed to HE. Some insight may be gained by considering k, which encompasses the trapping capability (d^2N_i) as well as the alloy-specific characteristics of metal atom size and lattice diffusivity. The trapping capability has a strong influence on the critical concentration (C_k) required to initiate cracking at traps, while the diffusivity reflects the ease of H transport to different sites, including traps. Since the likelihood of crack initiation is highly dependent on both C_k and H accumulation, it is perhaps not surprising that k is effective as an index of susceptibility in being able to indicate the actual resistance of most alloys to HE. Underlying this rationale is the implication that, despite differences between alloys, the H entry flux is generally not low enough to become the controlling factor.

Finally, it should be noted that the density of particles or defects providing irreversible traps can be calculated from k, or k_a, by using Eq. (2). The trap radius (d) is estimated from the dimensions of heterogeneities that are potential irreversible traps, and trap densities are then calculated for the different values of d. In this way, the dominant irreversible trap can be identified by comparing the values of N_i with the actual concentrations of specific heterogeneities. Identification of the primary irreversible traps in the various alloys is described elsewhere.[4-8]

Summary

For a wide range of alloys, a correlation exists between the intrinsic susceptibility, as defined by the irreversible trapping constant, and the observed resistance to HE. Thus, the HE resistance appears to be determined primarily by the alloy's intrinsic susceptibility. This relationship implies that generally the H entry flux has only a secondary effect on the HE resistance, suggesting that it is not low enough to become the controlling factor for most alloys. However, in one case (alloy 716), the resistance to HE can be attributed to a low entry flux.

The irreversible trapping constant, by virtue of the observed correlation, appears to be an indicator of the relative resistance to HE for most alloys, and as such, it can be used to predict the relative resistance of alloys in a particular environment. However, the predicted relative resistance may not be reliable in cases where H entry is severely restricted. The ability of k to provide an indication of the relative resistance to HE seems to be attributable to its dependence on both the trapping capability and the diffusivity. The combination of these two characteristics is crucial for crack initiation and therefore provides a rationale for the correlation observed between *k* and the actual resistance to HE.

Acknowledgment

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

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