Dislocation Transport and Hydrogen Embrittlement

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Tensile tests of several austenitic stainless steels show that when smooth bar samples are exposed to very high pressure hydrogen significant degradation in mechanical properties is observed. This degradation is accompanied by fracture along interfaces such as grain and twin boundaries although microvoid coalescence remains a prominent fracture feature. The interface cracking and loss in ductility increases as the exposure pressure increases to 172.5 MPa and at the higher pressures the adverse effects of hydrogen are enhanced by warm working operations. Rationalization of these data show that dislocation transport of hydrogen is not required in the embrittlement process; constraint, local lattice dilation, hydrogen content of interfaces are the dominant variables influencing the hydrogen affected fracture processes.

The potential role of hydrogen transport by dislocations in hydrogen embrittlement processes has been discussed by numerous investigators since the concept was first proposed in the early 1950’s.¹² The first experimental evidence for such transport was reported in the late 1950’s when deformation enhanced hydrogen outgassing was observed in mild steels.³ However, the concept did not receive widespread attention until the early 1970’s when direct evidence for dislocation assisted hydrogen transport was observed.⁵ The use of the radioactive hydrogen isotope, tritium, to study transport kinetics greatly enhanced the experimental accuracy of hydrogen release measurements and permitted the demonstration of deformation enhanced hydrogen absorption.⁵ Subsequent to the tritium transport and release measurements, investigators associated dislocation transport as critical to hydrogen embrittlement processes.

The development of high localized hydrogen pressures,⁶ correlations between hydrogen compatibility and stacking fault energy,⁷ the effect of a dispersed phase on hydrogen compatibility,⁸ correlations between lattice misfit parameter and hydrogen performance of precipitation strengthened stainless steels,⁹ the sweeping of hydrogen to grain boundaries,¹⁰ environmental effects on fatigue crack growth,¹¹ and hydrogen participation in ductile rupture processes¹² have been rationalized and/or described in terms of hydrogen transport by dislocations. These rationalizations and numerous similar reports are experimentally based, typically qualitative and generally require the assumption that localized high concentrations of hydrogen are developed. A quantitative model for the localization of hydrogen by dislocation transport¹³ predicts extremely small values for kinetic supersaturation when a balance between hydrogen arrival and departure rates is obtained. This calculation leads to the conclusion that hydrogen embrittlement cannot be explained by kinetic supersaturation arguments.

The significance of this conclusion can be minimized by showing that when the binding energy of hydrogen to a trap is significantly higher than the binding energy of hydrogen to a dislocation, localized high concentrations can be developed by dislocation transport without the necessity of supersaturation.¹² However, in this latter case the necessity of dislocation transport is not immediately apparent; such transport may be unimportant in the embrittlement process. This paper attempts to clarify the importance of dislocation transport to hydrogen embrittlement processes by showing that most, if not all, embrittlement data described by the transport theory can be modeled without the necessity of deformation enhanced hydrogen localization. It is worthwhile to emphasize that dislocation transport of hydrogen has been clearly demonstrated,¹⁴,¹⁵ thus the following discussion does not question the validity of the dislocation transport process but rather it questions the role of that process in hydrogen embrittlement.

HYDROGEN TRANSPORT BY DISLOCATIONS

The semiquantitative model for hydrogen transport by dislocations was first published by Kolachev and coworkers¹⁷-¹⁸ and subsequently modified by several investigators.⁵,¹⁰,¹³,¹⁸ The model is based on the assumption that the concentration of hydrogen at the core of a dislocation, \( C_\perp \), can be estimated from the lattice hydrogen concentration, \( C \), through:

\[
C_\perp = C \exp \left( -\frac{G_B}{RT} \right)
\]  

where \( G_B \) is the binding energy of hydrogen to dislocations. Movement of the hydrogen laden dislocation will transport the associated hydrogen atmosphere whenever the maximum velocity of the dislocation is less than some critical velocity, \( V^* \), which can be approximated by:

\[
V^* = \frac{D}{RT} \left( \frac{G_B}{30 b} \right)
\]

where \( D \) is the diffusivity of hydrogen in the lattice, and \( 30 b \) is an estimate of the effective trapping radius of the dislocation with Burgers vector \( b \). By presenting \( V^* \) as the time derivative of distance and intergrating, Eq. [2] can be used to show that, during time, \( t \), the...
maximum distance of hydrogen transport by a dislocation, $X^*$, is:

$$X^* = \frac{\sqrt{\Delta t}}{\sqrt{\frac{4RT}{30b}}} \tag{2a}$$

This distance has been compared to the distance of transport by random walk diffusion, $X = 4\sqrt{\Delta t}$, to show that:

$$\frac{X^*}{X} = \sqrt{\frac{G_B}{R}} \sqrt{\frac{30b}{4\Delta t}} \tag{3}$$

This ratio reduces to:

$$\frac{X^*}{X} = 2 \times 10^6 \sqrt{\frac{G_B}{R}} \sqrt{\frac{b}{\Delta t}} \tag{3a}$$

at room temperature (293 K) if $G_B$ and $b$ are assumed to be typical of $\alpha$-Fe and given by $-6400$ cal/mol and $2 \times 10^{-10}$ cm respectively.

In ferritic steels at 293 K ($D \sim 10^{-6}$ cm$^2$/s) hydrogen transport by dislocations during a tensile test lasting $10^4$ s (2 to 3 h) may occur to depths $\sim 5 \times 10^5$ times greater than that predicted by random walk diffusion. The favorability of this ratio decreases as the magnitude of the binding energy and the diffusivity of hydrogen decrease. For example, the room temperature diffusivity of hydrogen is austenitic steels is $\sim 10^{-12}$ cm$^2$/s and, at most $G_B \sim -4000$ cal/mol. Under these conditions the ratio reduces to $3 \times 10^5$. This ratio is still larger than unity and the value of $X^*$ (0.13 cm) for a $10^4$ s tensile test is very significant when compared to the radius of the typical tensile specimen. Calculations similar to those just presented illustrate that, within the validity of the transport model, dislocations can carry hydrogen deep into a plastically deforming sample. However, experimental observations indicate that this transport model is oversimplified.

Measurements of the release of hydrogen from metals during plastic deformation have shown accelerated release from tritium charged Armco Iron, austenitic stainless steels, Inconel 718, commercially pure nickel and aluminum alloy 5086. The general form of the accelerated release during tensile tests is the onset of a rapid increase in release rate at the proportional limit or yield point of the alloy tested. Elastic strains apparently do not influence the release rate. The deformation enhanced release has been related to dislocation dynamics through measurements of the temperature dependence of release rate and evaluation of the form of the release rate curves. The data are consistent with the interpretation that the enhanced release "is due to those dislocations which egress from the specimen and carry with them their associated hydrogen". The fact that deformation enhanced release is observed in alloys that are very susceptible to hydrogen embrittlement (Inconel 718), in alloys that have a minimal susceptibility to hydrogen embrittlement (Type 304L stainless steel) and in alloys which are generally considered to be immune the hydrogen embrittlement (5083 Al) demonstrates that dislocation transport of hydrogen is not sufficient (and may not even be necessary) to cause hydrogen embrittlement in metals and alloys. However, the release data is consistent with the dislocation transport model. This is not the general case for tritium absorption measurements.

The sorption of hydrogen by metals during plastic deformation has not received as much experimental attention as hydrogen release although detailed concentration profiles are available for nickel and austenitic steel samples deformed in high pressure tritium environments. The data for nickel show that plastic deformation during exposure enhances tritium uptake but that the depth of significant tritium absorption is not as great as that observed in companion unstrained samples (Fig. 1(a)). Similar tests with Type 304L stainless steel samples give vastly different results (Fig. 1(b)). Comparison of the results shown in Fig. 1 indicates that the apparent hydrogen solubility and diffusivity in metals can either be increased or decreased by plastic deformation, depending on the particular metal (or exposure conditions). This is not predicted by the dislocation transport model and in fact, the decrease in the apparent diffusivity of hydrogen in plastically deforming nickel is in direct contradiction with predictions based on Eq. [3]. Because of this contradiction and because dislocation transport is observed in metals not apparently susceptible to hydrogen embrittlement the role of dislocation transport in embrittlement processes needs further definition.

Saturation of Dislocations

Hydrogen localization at dislocations, as predicted by Eq. [1], is limited to some saturation value, $C_d$.

Thus, $C_d$ only increases with increasing lattice hydrogen concentration until that saturation value is reached. The determination of $C_d$ is difficult and several estimates are available. Internal friction and permeation data have been used to estimate that $C_d$ equals 2 atoms of hydrogen per atom of iron in $\alpha$-Fe. However, hydrogen embrittlement data and the dislocation transport model have been used to show that $C_d$ is 1 in $\alpha$-Fe, if the dislocation transport model is operative. Deformation enhanced tritium release from Armco iron has been explained by assuming the $C_d$ is between 0.5 and 1.4. If $C_d$ is assumed to be 1, the dislocation core has been shown to be saturated when the lattice hydrogen concentration in $\alpha$-Fe is as low as 3 ppm. This critical lattice concentration is dependent on the binding energy and increases as the binding energy decreases. The volume slightly remote from the dislocation core does not become saturated until after $C_d$ is obtained. Therefore, a distinct saturation value may not be reached. However, $V^*$ and thus $X^*$ decrease linearly as the binding energy decreases and for practical purposes the amount of hydrogen transport by dislocations at any given strain-rate should saturate at a lattice hydrogen concentration which for practical purposes can be estimated from the binding energy and the saturation value.

The available estimates of the binding energy of hydrogen to dislocations in austenitic stainless steels are between $-2300$ and $-23,000$ cal/mol, moreover, detailed analyses of the binding are rather incomplete. Hydrogen effects on stacking fault energies are reasonably well known and result from chemical binding of hydrogen to partial dislocations. Hence, the role of chemical binding must be better understood and incorporated with binding contributions due to elastic misfit before accurate determinations of total binding energies can be made. However, most estimates of