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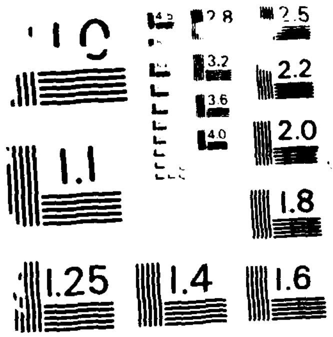

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STRESS CORROSION CRACKING AND HYDROGEN EMBRITTLEMENT

HYDROGEN EMBRITTLEMENT OF STEEL

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A brief outline is presented of experimental observations and theoretical interpretations of hydrogen embrittlement of steels. Detailed results on the effect of precharged hydrogen on reduction in ductility of low-strength steels under plane strain loading are discussed. Under such conditions hydrogen is shown to degrade the steels by promoting plastic instability in the form of shear bands, lowering the critical strain for various events without changing the locally ductile mode of fracture.

In "Environment Sensitive Fracture of Metals and Alloys," edited by R. P. Wei, D. J. Duquette, T. W. Crooker and A. J. Sedriks, Office of Naval Research, 1987.

Introduction

Years ago, Toh and Baldwin [1] showed that precharging of low strength steels with hydrogen at moderate fugacities degraded properties by lowering the elongation and reduction in area without much effect on flow stress. A "rule of thumb" in those days was that steels with yield strengths below 700 MPa were immune to catastrophic hydrogen embrittlement in the form of delayed brittle failure. Yet there were abundant controversies (see reviews in refs. [2-5]) with a number of competitive mechanisms for embrittlement (pressurization of voids, lowering of surface energy, lowering flow stress, increasing flow stress, and decohesion or bond-breaking at the crack tip), widely scattered diffusion data for H in steel, puzzlement about kinetics, and questions about the importance of dislocation transport of H.

The situation today is much improved, although some issues remain unresolved. Work on very pure iron [6,7] clearly showed that precharged or dynamically charged H lowers the flow stress of pure iron at low strain (≤ 0.20) and above 200 K. Later TEM work [8] indicated that gaseous charging of iron foils by H increases dislocation velocity. The scatter in H diffusivity is now attributed to trapping on defects [9], with good agreement for low dislocation density, high purity iron, the value at room temperature being about 10^{5} cm^2/s [5,10,11]. Work has defined different rate controlling processes under different conditions, for example any among diffusion in the environment, interface reaction of hydrogen containing gases, or diffusion in the steel can control mode I crack propagation kinetics in the presence of hydrogen for alloy steels, depending on gas pressure and hydrogen fugacity [12].

The critical strength, 700 MPa, rule has been shown to be inapplicable. Brittle, stable mode I crack propagation can occur in iron exposed to dry hydrogen gas at a pressure much less than one atmosphere [13] and in low strength steels exposed to high fugacity hydrogen, such as H_2S gas [14]. Also microstructure [15] and minor alloy additions [16] have an influence on the embrittlement tendency. In our own work, we have found that at moderate hydrogen fugacity (corresponding to a gas pressure of 240 MPa or less [17]), precharging of a low yield strength, 400 MPa, spheroidized steel causes a reduction in ductility but still leads to a mixed mode I-II ductile fracture [18]. Yet dynamic charging, that is, charging while straining, leads to a brittle mode I fracture at a strain little removed from the yield strain [18].

Hence, the issue of what causes the ductile, mixed mode, moderate strain failure to brittle, mode I, low strain failure transition depends on many variables and is still incompletely resolved. Under very ideal conditions of oriented cracks and low fugacity dry hydrogen, the transition in Fe-3% Si single crystals [19] seems to be a genuine transition between crack tip bond breaking and dislocation emission: the crack tip opening angle increases with decreased hydrogen fugacity from near zero to ≈ 70 degrees. A complicating factor in many cases is the screening of the crack tip by emitted or matrix dislocations [20]. The local crack tip process may be brittle, operating at the Griffith condition, yet the macroscopic stress intensity may be orders of magnitude larger because of dislocation activity away from the near tip region.

Our own work has focussed on the influence of hydrogen on ductile fracture by enhancing the onset of plastic instability in the form of shear bands. This has occurred at a time when there has been great activity from the viewpoint both of observations [21] and of theoretical mechanics calculations [22,23] for such instabilities. The remainder of our presentation concerns this type of degradation. While many materials were studied, we discuss for brevity only the work on spheroidized AISI 1090 steel.

The steel had a composition in weight percent of 0.88 C, 0.75 Mn, 0.017 P, 0.036 S, 0.19 Si, 0.17 Cu, 0.09 Cr, 0.06 Ni, 0.01 Mo, 0.003 Ti, balance Fe. The carbide volume fraction was 11 percent, the mean particle size was 0.8 μm and the mean particle spacing was 1.2 μm.

Indirect Evidence for Hydrogen Enhancement of Plastic Instability

In all cases, hydrogen was charged electrolytically in a 1N sulfuric acid solution containing 1 g/ℓ of the hydrogen recombination poison thiourea. Charging was done at a current density of 80 to 100 A/m^2. Permeation measurements [17] show that this corresponds to moderate hydrogen pressures of 200 to 240 MPa. The permeation measurements and measurements of reversible softening [24] of the steel after hydrogen charging show that these current densities are below the critical value of 135 A/m^2 (equivalent hydrogen pressure 270 MPa) that produces irreversible damage and softening. Precharging was performed for 2 h. Other experimental details such as precautions to avoid oxygenation of the solution, are presented elsewhere [18].

The first manifestation of the enhancement of plastic instability was the observation [25] of hydrogen induced Lüders band formation on polished, blunt-notched plane-strain tensile bars. Later work [18] was performed on U-notched, plane-strain, 3-point bend bars with varying notch root radii, producing varying internal stress concentrations, maximum at the elastic-plastic boundary. The results showed that tests in air or with precharged $\underline{H}$ were of the mixed mode I-II type, following the traces of the characteristic slip lines of plasticity theory, Fig. 1. As noted in Table I, $\underline{H}$ caused a reduction, by about a factor of two, in the critical strain to failure, independent of notch curvature and hence of stress concentration. Those observations showed that the failure was probably associated with plastic shear instability bands propagating in from the surface where the strain is a maximum.

Table I. Critical Maximum Principal Surface Strains, 3-Point Bend Specimens

	Radius of Curvature of Notch		
	0.59 mm	1.19 mm	1.59 mm
Void Initiation			
Uncharged	0.13	0.15	0.13
Precharged	0.06	0.07	-
Void Profusion			
Uncharged	-	0.36	0.35
Crack Initiation			
Uncharged	0.36	0.42	0.38
Precharged	0.21	0.23	0.22

Microstructural study of specimens strained to varying amounts showed that voids formed, also along the traces of characteristic slip lines, and eventually there was a profusion of voids formed at a strain slightly below the fracture strain. Table I indicates that hydrogen also reduces the critical strain for these events by about a factor of two.

Micrographs, for example, Fig. 2, showed that most of the voids formed between two carbide particles closely spaced along the direction of maximum principal tensile force. The void configuration can be understood in terms of incompatibility stresses, arising at particles in the path of a shear band, which add to the maximum applied principal stress. The overlap of the added tensile fields for two closely spaced particles favors void nucleation at such a pair. Moreover, as proved by analog experiments [18], void growth is also favored at such sites.

Thus, the indirect interpretation of the data was that hydrogen enhanced plastic instability in the form of shear bands emanating from the surface and following the shear paths of plasticity theory. The localized shear produced voids in the same path because of the incompatibility effect. The voids further enhanced shear localization and finally profuse void formation and crack opening because of occurrence of the mode I loading component.

Other work had indicated that the major effect of H was on void nucleation [26], on growth and coalescence [27], or failed to find a reduction in instability strain [28]. However, the former tests [26,27] were on notched round bars where instability is much less prominent while the latter [28] were on the plane stress region at the lateral surface of plane stress specimens. As indicated both by this set of experiments and by theory [22,23], only under plane strain conditions do the marked reductions in strain and pronounced shear instabilities occur.

On the other hand, theory [29] also indicated that voids can provide an added enhancement of shear localization. Thus the possibility existed that H actually promoted void nucleation near the surface and the voids caused the localization. However, theory [23] also predicted that an earlier form of instability would be rumpling of the surface. Thus, we proceeded to study surface rumpling of polished plane-strain specimens as a more direct test of the effect of H.

Direct Evidence for Hydrogen Enhancement of Plastic Instability

Polished surfaces of 3-point loaded bend bars were studied as a function of strain: rumpling was observed [30]. As summarized in Table II, H again

Table II. Critical Strain for the Onset of Surface Rumpling, 3-Point Bend Specimens

Theory	Experiment	
	Uncharged	Precharged
0.25	0.28	0.12

lowered the critical strain, in this case for rumpling, by about a factor of two [31]. Further studies [32] on plane strain tensile specimens and round bar tensile specimens verified the effect, and demonstrated the more severe influence of plane-strain loading, Table III. The results in air are in fair agreement with the theoretical prediction [23,30]

$$\frac{d\sigma/d\varepsilon}{\sigma/\varepsilon^*} = \varepsilon^* (1 - e^{-2\varepsilon^*}) \qquad (1)$$

Table III. Critical Strains, Tensile Specimens

	Round Bar		Plane Strain	
	Uncharged	Precharged	Uncharged	Precharged
Uniform elongation	0.21	0.20	0.24	0.17
Surface rumpling	-	-	0.18	0.07
Surface cracks	-	-	0.28	0.10
Failure	1.04	0.63	0.71	0.34

relating the critical strain for rumpling to the properties of the stress σ - strain ε curve.

Most recently [33], similar tests have been performed on plane-strain, U-notched, four-point bend specimens where the notch can be loaded in tension or compression. The critical strain for rumpling in compression, Table IV, was

Table IV. Critical Strain for the Onset of Surface Rumpling and Crack Initiation, 4-Point Bend Specimens

	Tension		Compression	
	Uncharged	Precharged	Uncharged	Precharged
Rumpling	0.26	0.14	0.15	0.12
Cracking	0.67	0.41	0.31	0.37

less than that in tension, in agreement with theory, Eq. (1). The effect of $\underline{H}$ was present in compression, but it was less marked than in tension. However, with $\underline{H}$ present, mixed mode microcracks formed in compression.

Thus, the direct tests confirmed the indirect tests and supported the hypothesis that the effect of $\underline{H}$ on the onset of plastic instability is a direct one. The mechanism of the enhancement is not clear. We can say that since $\underline{H}$ lowers ε^* while leaving $d\sigma/d\varepsilon$ and σ at ε unchanged, it is not an effect on the continuum plasticity level manifested in Eq. (1). The $\underline{H}$ must promote instability on a local, microstructural scale. In this connection, it is noteworthy that TEM studies have shown dislocation structures indicating that hydrogen promotes local deformation, between carbide particles, akin to shear localization and prior to microvoid formation [34].

Three possibilities are suggested. First, the lowering of surface energy of a slip step in the presence of hydrogen may promote a larger local slip event. The slip band in turn is effectively a mode II crack nucleus. Second, hydrogen both lowers the flow stress for dislocations (in iron and in spheroidized steel) and promotes planar slip on {110} planes. The absence of grain boundary compatibility effects near free surfaces would also tend to promote single slip. These effects again would tend to produce planar local slip events, near the surface, that could act as mode II crack nuclei. Third, a set of such crack nuclei could indirectly lead to a marked reduction of ε in Eq. (1) in a manner analogous to that of imposing an initial sinusoidal roughening in finite element calculations used to test the continuum theory [23]. Further work is needed to resolve the detailed mechanism.

Conclusions

A. Low strength steels, exemplified by spheroidized plain carbon alloys, fail as a consequence of shear instability in the form of localized shear bands. The critical strain is least under plane-strain conditions where initiation is favored at a free surface.

B. Metallographic observations indicate that the sequence of events leading to failure in plane strain is surface roughening, shear localization, void formation as a consequence of strain incompatibility in the shear path, crack initiation at a surface valley, and crack propagation in a mixed mode I-II manner along the shear path.

C. Precharged hydrogen reduces the critical strain for all of the above events by a factor of two but leaves the essential ductile nature of the fracture unchanged and has little effect on the flow stress at strains less than the critical value. Dynamically charged hydrogen changes the fracture to a mode I type with a drastic reduction in ductility. The detailed mechanism by which hydrogen enhances plastic instability is undetermined although possible models are suggested.

D. The critical strain for initiation of surface roughening is in fair agreement with continuum mechanical, theoretical predictions. The critical value in the presence of hydrogen is not in agreement, implying that hydrogen exerts its effect on a local microstructural scale.

Acknowledgment

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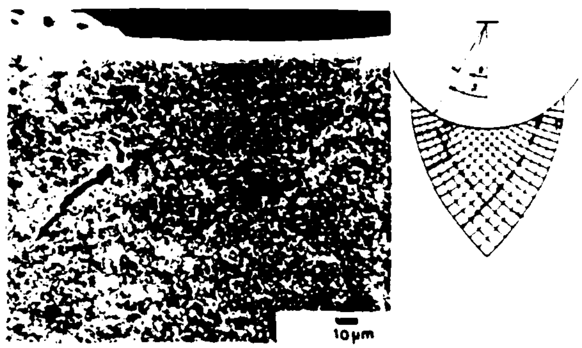

Fig. 1 - Cross-section showing microcrack starting at surface and following characteristic slip traces. Inset shows voids aligned along the characteristics.

Fig. 2 - Void between two closely spaced carbides aligned along maximum principal force direction (horizontal on page).

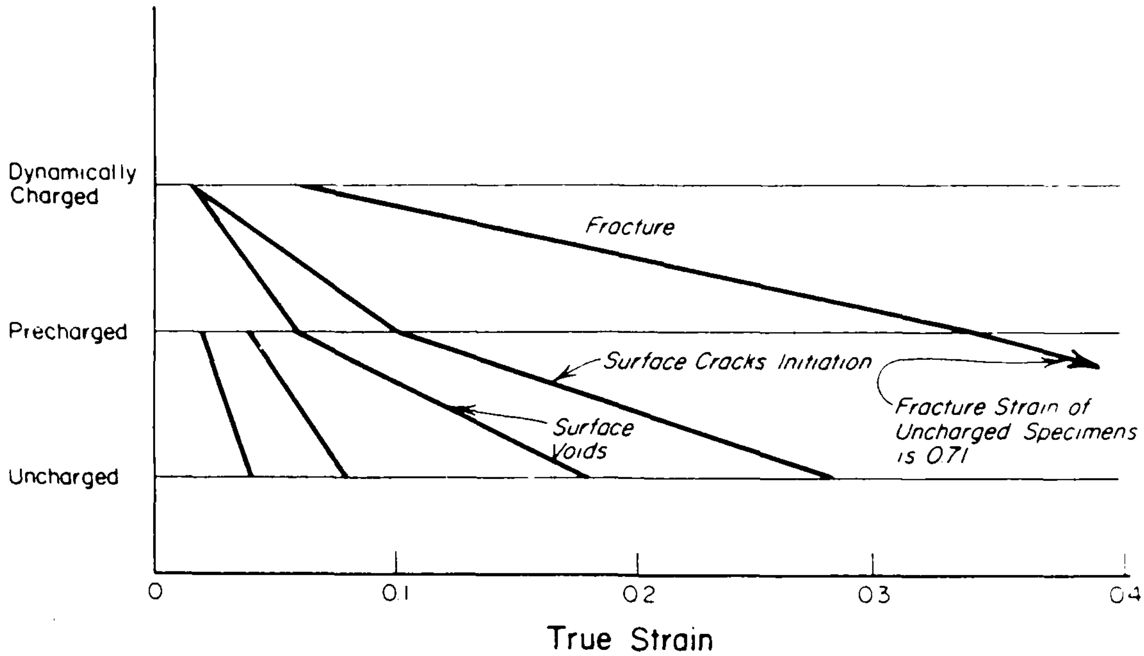

Fig. 3 - Equi-slip band diagram for plane-strain specimens tested under different charging conditions.

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