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Hydrogen-induced intergranular failure of iron

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Abstract

The hydrogen embrittlement of a commercial-grade pure iron was examined by using repeated stress-relaxation tests under simultaneous cathodic hydrogen charging. The hydrogen-charged iron, containing an estimated 25.8 appm H, fractured after repeated transients, with a total strain of ~5%. The fracture mode was intergranular. Thermal activation measurements show a decrease in activation volume and free energy, which is consistent with hydrogen enhancing the dislocation velocity. The microstructure beneath the intergranular facets displays a dislocation cell structure more complex than expected for intergranular fracture and this strain-to-failure. It is proposed that hydrogen accelerates the evolution of the dislocation microstructure through the hydrogen-enhanced plasticity mechanism and this work-hardening of the matrix along with the attendant hydrogen concentration at the grain boundaries are crucial steps in causing the observed hydrogen-induced intergranular failure.

Keywords: Iron; Hydrogen embrittlement; Transmission electron microscopy, Mechanical properties

1. Introduction

Hydrogen-enhanced or hydrogen-induced failure and the role of plasticity processes in these failures remains a topic of debate and is especially important in iron and iron-based alloys because of their importance as structural materials [1]. It is well established that hydrogen not only causes a reduction in the mechanical properties, but can cause a transition in fracture mode from ductile microvoid coalescence to intergranular failure [2–12]. The latter has often been associated with the presence of segregants such as phosphorus and sulfur, as well as hydrogen, at the grain boundary [13,14], although hydrogen at sufficient concentrations can induce intergranular failure by itself [7,15,16]. A challenge has been to identify the role, if any, of plasticity processes in establishing the conditions for hydrogen-induced intergranular failure. The most common evidence indicating some plasticity has occurred is the appearance of slip traces on the intergranular facets, but these are not sufficient to determine if the deformation processes are essential to establishing the intergranular failure or just a consequence of it.

Recently, Martin et al. [17], by using focused ion beam (FIB) machining to extract and thin samples for subsequent examination by transmission electron microscopy (TEM) from hydrogen-induced intergranular facets in Ni, revealed the microstructure immediately beneath the facets.

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Evidence of the slip traces on the facet surface was identified in the electron micrographs, although there was no simple correlation with the underlying microstructure, as it consisted of a dislocation cell structure with cells a few hundred nanometers in diameter and dense cell walls even beneath facets exhibiting just one slip trace. The unanticipated aspects of these observations were the cell dimensions, and the extent to which they extended, $>15 \times 10^{-6}$ m, beneath the facet for a strain-to-failure of just 13%. Indeed, Martin and Robertson [18] found that the microstructure was in an advanced development stage at a depth of several millimeters from the fracture surface. Martin et al. [17] explained the observed microstructural state within the framework of the hydrogen-enhanced plasticity mechanism and the hydrogen-shielding concept [19]. The hydrogen-enhanced dislocation velocity was used to explain the advanced state of the evolved microstructure and the cell dimensions were attributed to hydrogen shielding dislocation–dislocation interactions to permit them to exist in closer proximity. Although not noted by Martin et al. [17], the attendant hydrogen concentration within the cell walls will inhibit reorganization, as an additional driving force would have to be supplied to return the trapped hydrogen to solid solution during the transition. The transition from ductile transgranular to intergranular failure was explained by the accumulation of a high hydrogen concentration at the grain boundaries by diffusional as well as dislocation transport processes and the locally high work-hardening in the grain interior [17].

In this paper, the microstructure beneath the fracture surfaces in uncharged and hydrogen-charged commercially pure iron is compared. Essentially, this compares the microstructure developed during a knife-edge fracture with microvoids in the uncharged iron to intergranular fracture in hydrogen-charged material. To complement the electron microscopy and to aid in the interpretation of the results, the influence of hydrogen on the deformation processes was investigated by using thermal activation analysis. The results are discussed within the framework of the hydrogen-shielding mechanism of the hydrogen-enhanced localized plasticity mechanism. Hydrogen-induced intergranular failure is explained by a combination of dislocation interactions with the grain boundary modifying its internal structure; an increase of the local hydrogen content, including that on the grain boundary, due to the arrival of dislocations; and the formation of a local stress state due to the accumulated dislocation content. Transition from microvoid coalescence to intergranular failure is determined by those conditions reaching a critical combination of stress, grain boundary strain energy density and hydrogen concentration.

2. Experimental procedure

The iron (purity >99.995%) used was produced by Johnson Matthey Chemicals Ltd.; its chemical composition is shown in Table 1.

Table 1
The composition of the iron used in this study (wt. ppm).

Mg	Ca	Cr	Mn	Si	C	H	O	N	Fe
7	1	1	1	1	35	1.6	34	190	Balance

Tensile specimens 16 mm in length and 0.25 mm in thickness with a gage 5 mm in length and 1.2 mm in width were produced. Hydrogen was introduced into the specimens by cathodic charging during the mechanical test using an electrolyte of 0.5 mol l^{-1} sulfuric acid and 50 g l^{-1} thiourea with an applied current density of 75 mA cm^{-2}. Here it is noted that this is an aggressive cathodic charging condition. However, there was no evidence for surface blistering or for blister formation on interior grain boundaries. This is attributed to the short duration of the experiment, which is significantly less than the time reported by others for blister formation [20,21]. The hydrogen concentration was estimated to be ~25.8 appm [22,23]. The repeated stress-relaxation test developed by Spätig et al. [24] was applied to hydrogen-charged and uncharged specimens. At 293 K, the tensile samples were initially strained to 5% beyond the yield point at a strain rate of 1×10^{-4} s^{-1}. In each relaxation step, the crosshead of the tensile machine was stopped for 30 s and the decay of stress was recorded at 0.3 s intervals. Subsequently, the stress at the onset of the previous relaxation was restored before the crosshead was stopped again. This process was repeated until no further relaxation was recorded on halting the test.

To determine the microstructure beneath the fracture surface, FIB machining (using an FEI Dual Beam 235 FIB or an FEI Helios 600i) was used to extract site-specific samples for TEM analysis. This process has been shown to have no significant impact on the fracture surface morphology and not to generate complex line dislocation structures, suggesting that the underlying microstructure remains unaltered in a significant way by the preparation process; it is appreciated that there will be ion damage associated with the preparation process and this takes the form of small black dots [25].

3. Results

The results obtained from repeated stress-relaxation tests are summarized in Table 2 for uncharged and hydrogen-charged iron. The yield stress was determined to be 179 and 164 MPa in the uncharged and hydrogen-charged material, respectively. The hydrogen-charged iron was fractured during repeated relaxation processes (after 19 tests), with a total strain of ~5%. With hydrogen, the stress rate at the onset of relaxation is decreased from −0.98 to −3.28 MPa s^{-1}.

Table 2
Results of repeated transients of hydrogen-free and charged specimens.

Specimens	σ_y (MPa)	V_{eff} (b^3)	ΔF (meV)	$\rho_m(t)/\rho_m(0)$
Hydrogen-free	179.25	272.8	390	0 (after 90 s)
25.8 appm hydrogen	163.94	30.2	349	0.84