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Crack and blister initiation and growth in purified iron due to hydrogen loading

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ABSTRACT

Purified iron was loaded electrochemically with hydrogen in the presence of a hydrogen promoter, leading to the formation of cracks inside of the bulk and blisters on the surface. The mechanism for the crack initiation was investigated using SEM cross-section images and by investigating the fracture surface of a ruptured sample, where preexisting cracks were exposed for observation. Cracks were found to originate at inclusions. It was observed that blisters grow with time, leading to the conclusion that the underlying growth process is discontinuous. The surface morphology of the blisters consists of steps and in the underlying microstructure investigated by TEM shear bands were found. Hydrogen gas pressures in the range of half of the yield strength of iron were determined directly after hydrogen loading using density measurements. Therefore, the hydrogen gas pressure in the cracks was concluded to be the driving force for crack advance.

1. Introduction

The premature failure of materials, especially iron-based alloys, due to the influence of hydrogen is a well-known materials selection problem for various applications. The mechanism leading to unfavourable changes in the properties, or even to failure, of exposed materials is in most cases not fully understood.

The first detailed report about the observation of hydrogen embrittlement was published by Johnson in 1874 [1]. Many decades of research have been dedicated to the investigation of the influence of hydrogen on materials properties and the proposal of mechanisms for hydrogen embrittlement (HE) as well as hydrogen induced cracking (HIC). An overview of phenomena and mechanisms of hydrogen embrittlement is given in the review by Robertson et al. [2].

In addition to a degradation of tensile properties under stress, hydrogen has also been found to degrade the mechanical properties of iron-based alloys in the absence of stress, usually under conditions of high hydrogen activities, such as during corrosion and cathodic charging. This has been related to the formation of blisters on the surface or cracks in the interior (HIC or step-wise cracking) [3–8]. It has been proposed that these cracks are caused by the precipitation and accumulation of gaseous hydrogen (H_2) at microstructural features such as grain boundaries or inclusions in the metal, which in turn leads to a pressure build-up at these sites. The actual pressure in the blisters is debated with some measurements suggesting pressures in the range of hundreds of psi (~2 MPa) [6] to direct measurements of pressures corresponding to 20% of the yield strength in individual cracks [9], and calculations, such as those by Schuyler [10], suggesting that the pressure needs to be approximately half the yield strength of the material (~50 MPa for iron). The cracks are proposed to grow discontinuously: when a crack grows faster than hydrogen pressure is maintained, the crack growth will halt whenever the crack pressure drops below the critical pressure until diffusion allows sufficient accumulation of molecular hydrogen to continue crack growth [11]. Once initiated, crack propagation is assumed to follow in the maximum shear direction determined by the stress field of the main crack [12–17]. Despite a great deal of study, there is still a lack of understanding of the mechanism by which these cracks form.

A lot of work has concentrated on studying the effect of different steel doping or contamination elements [4,14,18–20]. This is of

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Table 1
Trace elements in a high purity iron sample measured by ICP-MS.[3]

Elements	Mn	Cu	Cr	Co	Ge	Ni
Content [ppm]	6.9 ± 2.4	7.4 ± 2.7	6.5 ± 3.1	4.8 ± 2.2	9.5 ± 5.7	3.2 ± 3.9

interest because proposed and confirmed nucleation sites are grain boundaries, inclusions, voids, laminations or anomalous microstructures. In particular, inclusions have long been associated with an increased susceptibility to HIC. The elongated MnS inclusions that form during cold-rolling processing of steels are considered the most dangerous in terms of HIC susceptibility [18]. Rounded inclusions, such as MnS, MnO or Al_2O_3, are associated with a decreased HIC susceptibility, though rounded inclusions still have interfaces that are likely to fail. It is generally thought that without an elongated shape there is no driving force for cracking to proceed [21]. In the absence of these secondary phase nucleation sites, voids formed by the accumulation of vacancies are proposed to be a primary site. Vacancies are stabilized by hydrogen [22], and therefore agglomerations of vacancies can form, creating nucleation sites for blisters [23].

In this paper, a very simple case of hydrogen induced cracking is investigated in detail and a mechanism for crack formation and crack propagation is proposed. Purified iron was chosen as a model system in order to avoid the influence of different phases or precipitations, for the reasons stated above. The samples were heat-treated to achieve a low density of grain boundaries. The purified iron samples were loaded electrochemically in the presence of a hydrogen promoter, until cracks and blisters on the surface formed.

The focus of this study was to investigate the microstructure, and in particular the initiation sites of cracks, in more detail. Therefore, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used. To examine the HIC morphology more closely, post-hydrogen loading samples with cracks were ruptured to reveal the crack initiation sites. The pressure in the cracks was determined from a pressure measurement in a vacuum chamber, in which the hydrogen degasses after loading and from the volume of the cracks obtained via the Archimedes principle, i.e. measuring the buoyancy of the sample. From these finding, a complete mechanistic model for HIC is proposed.

2. Experimental details

2.1. Preparation and composition of the samples

High purity iron was produced by remelting and degassing.[2] Samples of 1.5 mm thickness were ground with SiC-paper up to 4000 grit, and subsequently heat treated for 5 h at 1153 K in high vacuum (~10^{-7} mbar), and followed by furnace cooling to avoid stress build-up during cooling. The median grain diameter of the heat treated material is 0.5 mm.

The trace elements of a purified iron sample were measured by inductively coupled plasma mass spectrometry[3] (ICP-MS). The sampling volume was a cylinder of 100 μm in diameter and in 22 μm depth. Results averaged over ten different locations are summarized in Table 1; elements with a content of less than 1 ppm are not included. Some elements, such as carbon, oxygen and sulfur cannot be measured with ICP-MS.

[2] Purified iron was produced at Max-Plank-Institut für Eisenforschung in Düsseldorf.

[3] Measurements were done by Dr. Klaus Simon, Geochemistry Division of the Geowissenschaftliches Zentrum (GZG) at Georg August University of Göttingen.

2.2. Electrochemical hydrogen loading

The annealed iron samples were charged electrochemically in constant current mode using a platinum counter electrode. The electrolyte was a solution of 0.1 M sulphuric acid with 1 wt% ammonium thiocyanate as hydrogen promoter. The electrolyte was prepared following the method described by Suzuki et al. [24]. Current densities in the range of 0.01–100 mA/cm^2 were used. The loading time was varied from 30 min to 5 h.

2.3. Investigation after loading

Directly after electrochemical hydrogen loading the hydrogen concentration in a set of samples was determined using a Bruker Galileo G8 Hydrogen Hot Extraction Analyzer; cleaning procedure took about 2 min. Sample size was 7 mm × 7 mm with a thickness of 1.5 mm.

To characterize crack and blister morphology, samples sized 1 cm^2 with a thickness of 1.5 mm or more were charged. Smaller samples were cross-sectioned to reveal internal crack distribution. The larger samples were subsequently cut into dog-bone specimens and tensile-loaded to failure to reveal the HIC surfaces. Samples were examined in a FEI Nova NanoSEM scanning electron microscope. In this microscope, point scans by energy dispersive x-ray spectroscopy (EDX) were performed to characterize the chemical composition of inclusions.

By means of a FEI Nova Nano Lab 600 Focused Ion Beam (FIB), TEM-lamellae were prepared by the lift-out technique to investigate the microstructure using Philips CM12 and CM120 transmission electron microscopes.

2.4. Density and pressure measurement

To analyze the hydrogen gas pressure in the cracks, density measurements based on the Archimedes principle were performed. A Sartorius balance was modified so that samples could float in a fluid of high density (Sodium polytungstate stabilized by chromium salts) while measuring the weight. The amount of hydrogen leaving the sample was obtained from a pressure measurement in a vacuum chamber, where the sample is degassing after electrochemical loading. The pressure increase in the vacuum chamber (volume = (86.2 ± 0.6) cm^3) due to the degassing hydrogen from the cracks in the sample is in the range of 9 mbar. The pressure was corrected by a continuous, very small increase of the pressure due to leaking.

2.5. Permeation measurement

The annealed iron sample of 1.5 mm thickness was exposed to a cathodic current on one side over an area of 1.8 cm^2. On the opposite side, a KircTec-Probe [25] was spot-welded to the iron sample, in order to measure the permeation of hydrogen through the sample. The KircTec-Probe material has a higher affinity to hydrogen than iron. Thus the hydrogen concentration at the adjacent iron side of the spot weld is reduced to zero and a corresponding concentration gradient builds up from the cathodic side to the probe. The resulting hydrogen flux increases the H-concentration within the material of the KircTec-Probe, which is monitored continuously. Compared to a double-cell set-up of the