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Effect of deformation and charging conditions on crack and blister formation during electrochemical hydrogen charging

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ABSTRACT

Hydrogen induced cracks were introduced in an ultra-low carbon (ULC) steel by subjecting it to electrochemical hydrogen charging. The damage characteristics were investigated for three material conditions, i.e. cold deformed, recovered, and recrystallized state. The aim of the work was to understand the effect of deformation induced defects on the hydrogen induced cracking of this material. Additionally, the effect of the charging conditions, i.e. charging time and current density, on the cracking characteristics were verified. The blister surfaces and related hydrogen induced cracks were studied by optical microscopy, scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD). Deformed samples were considerably more sensitive to hydrogen induced cracking, which demonstrates the important role of dislocations in hydrogen induced damage mechanisms. Permeation tests were performed in order to elucidate the role of hydrogen diffusion in the process. Charging conditions had a clear influence on the hydrogen induced cracking behavior of the material. This should be taken into account when designing experimental parameters in order to obtain results valid under real life conditions.

1. Introduction

Experimental electrochemical charging of steels with hydrogen mimics, on the one hand, well hydrogen generation and entry in the material from corrosion or applications such as arc welding [1]. On the other hand, intensive electrochemical charging can induce both surface and internal damage in a material [2]. The technique can as such be applied to simulate situations where hydrogen induced cracking (HIC) occurs. Hydrogen flakes as found in reactor pressure vessels [3] could, for instance, be artificially reproduced. The internal pressure theory [4–6] explains the phenomenon of HIC in high fugacity hydrogen environments, such as high pressure hydrogen gas environments or extreme cathodic charging conditions. It states that HIC results from the formation of high pressure hydrogen gas bubbles in internal voids and microcracks. When an alloy is exposed to a hydrogen environment, atomic hydrogen is absorbed in the metal and diffuses inside. Its movement can be interrupted by microstructural discontinuities, such as voids, second phase particles, grain boundaries, and microcracks, which act as trap sites [7]. At such sites, atomic hydrogen can recombine to form molecular gaseous hydrogen, which is incapable of further migration and locally creates a very high internal pressure [8]. The result is the formation of overpressurized gas-filled cavities, which cause plastic deformation of the surrounding lattice and promote crack formation. If the internal pressure rises to levels which exceed the tensile strength, crack propagation occurs, even in the absence of externally applied loads. The internal pressure is temporarily relieved due to crack propagation, which therefore occurs discontinuously. As proof some wavy lines perpendicular to the crack propagating directions were observed on the fracture surface of a blister [9,10]. In a next stage microcracks propagate further and connect, creating a series of stepwise cracks through the material [11]. When the phenomenon takes place close to the sample surface, it is referred to as blistering. The high pressure then pushes material upwards, resulting in a surface blister [2].

Different blister initiation sites and initiation mechanisms have been proposed in literature for alloys charged in a high fugacity hydrogen environment. Numerous studies [9,10,12,13] revealed that inclusions and second phase particles in steels act as major

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nucleation sites for blisters. Numerous authors [1,14,15] state that the presence of a second phase is not a prerequisite for blister formation and claim that vacancy-hydrogen interaction plays a role in the initiation process. Garofalo et al. [16] stated that the hydrogen induced propagation of internal cracks in steel is promoted by hydrogen gas in voids or microcracks which may be formed by plastic deformation or are present as porosities from the casting process. Griesche et al. [1] visualized small pores with diameters of ~1 μm all over the hydrogen induced crack surfaces. These pores were located along grain boundaries, which are strong hydrogen traps. In summary, crack nucleation during hydrogen charging has been related to a localized concentration and subsequent recombination of hydrogen at suitable heterogeneities such as grain boundaries, second phase particles, microvoids and tangled dislocations [17].

Huang et al. [18] and Dong et al. [19] revealed that HIC susceptibility depends on the hydrogen entrapment in steel. Multiple authors [20,21] discovered that the density of hydrogen traps increases with increasing cold work. Kumnick and Johnson [21] showed by permeation transient measurements that the hydrogen trap density increases from 10^{20} m^{-3} for annealed ARMCO iron to a little over 10^{23} m^{-3} for heavily deformed iron. The presence of deformation induced defects can, therefore, cause a substantial change in hydrogen diffusivity and solubility as reversible trapping in these deformation induced defects can occur [22–24]. Furthermore, Huang and Shaw [25] and Szklarska-Smialowska and Xia [26] found that cold deformation promotes hydrogen embrittlement.

A lack of information concerning the effect of deformation on blister and internal damage formation exists. The current study, therefore, analyzed the blistering phenomenon in ultra-low carbon (ULC) steel with variable concentrations of deformation induced defects, i.e. cold deformed, recovered, and recrystallized material. The material was cathodically charged using different current densities and charging times in order to characterize the evolution of surface and internal damage with varying charging conditions. A thorough microstructural characterization of blisters and internal cracks was performed by optical microscopy, scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD). Additionally, permeation tests were performed in order to elucidate the role of hydrogen diffusion in the process.

2. Experimental procedure

2.1. Material

Ultra-low carbon steel was chosen as the material of study in order to avoid the effect of complex microstructural characteristics on blister/internal crack characterization. The steel contains 214 wt.ppm C, 88 wt.ppm N, 38 wt.ppm S, 73 wt.ppm P, 0.25 mass% Mn, 0.002 mass% Ti, and 0.047 mass% Al. Three material conditions were studied, i.e. cold deformed (60% reduction), recovered, and recrystallized. The corresponding microstructures are shown in Fig. 1. All three materials consisted of ferrite grains. Only a few hydrogen trapping site types were present in these materials, i.e. grain boundaries, dislocations, vacancies, and microvoids with increasing amounts for recrystallized, recovered, and cold deformed material and additionally, some precipitates. In order to obtain a recrystallized microstructure, a cold rolled plate was annealed in a salt bath at 760 °C for 4 min and air cooled. The recovered material was obtained by annealing of a cold rolled plate at 640 °C in a salt bath for 1 min, followed by water quenching. Oval shaped samples with a major axis of 20 mm and a minor axis of 15 mm and a thickness of 1.2 mm were machined. The major axis of the samples coincides with the rolling direction of the plate.

2.2. Hydrogen charging

Hydrogen was introduced in the samples by cathodic charging in a 0.5 M H_2SO_4 electrolyte containing 1 g/l of thiourea. Thiourea was added to the electrolyte in order to promote hydrogen atom absorption into the metal rather than hydrogen recombination to its molecular form. Charging occurred in a polycarbonate cell where the sample, connected as cathode, was positioned symmetrically in between two platinum anodes. All samples were charged at room temperature using different combinations of charging times (30′, 2 h, 1 day, 2 days, and 4 days) and current densities (2.5, 5, 10, and 20 mA/cm^2).

2.3. Hydrogen electrochemical permeation tests

Hydrogen electrochemical permeation tests were performed according to the Devanathan and Stachurski method [27] to determine the hydrogen diffusion coefficient. The permeation cell consisted out of two compartments filled with 0.1 M NaOH solution. The employed electrolyte in these tests differs from the one used for hydrogen charging of the samples as the employed current density and long duration of the permeation test are likely to cause hydrogen induced damage, which would make the obtained results invalid [28]. The two compartments were stirred with nitrogen bubbling and kept at ambient temperature. Polished circular samples (2 cm diameter) with 1 mm thickness were clamped in between the compartments. To the hydrogen entry side, which acts as cathode, a current density of 3 mA/cm^2 was applied, while the hydrogen exit side was potentiostatically kept at −500 mV with respect to a Hg/Hg_2SO_4 reference electrode. From such tests a permeation curve with the normalized current as a function of time was drafted. The apparent hydrogen diffusion coefficient could be calculated from the permeation curve using the following formula:

$$D_{app} = \frac{L^2}{7.7t}\left(m^2/s\right) \quad (1)$$

where t is the time (s) when the normalized steady-state value has reached 0.1 and L is the specimen thickness (m).

2.4. Microstructural characterization

Surface imaging by optical microscopy allowed the detection of blisters permitting determination of their morphology, distribution, size, and areal density. Cross sections were analyzed in order to obtain information on the morphology and depth of internal cracks in the charged samples. These sections were polished using standard metallographic techniques and subsequently etched with Nital 2% for 10s. A first preliminary investigation of the internal microstructural damage was performed by optical microscopy, followed by a scanning electron microscopy (SEM) study. Subsequently, the most interesting features were investigated with electron backscatter diffraction (EBSD). FEI Quanta 450 with field emission gun (FEG) was used as SEM. EBSD data was acquired at 20 kV acceleration voltage, emission current of 200 μA, specimen tilt of 70° and a scan step size of 0.25 μm on a hexagonal scan grid. TSL-OIM Data Analysis V6.1 software was used for post processing and analysis of the orientation data.

3. Results

3.1. Effect of deformation induced defects

Each material exhibited a different behavior when in contact with hydrogen, i.e. the blistering behavior varied strongly for the