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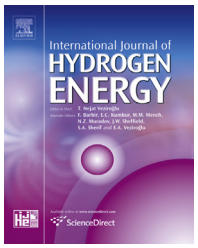

Hydrogen embrittlement in nickel, visited by first principles modeling, cohesive zone simulation and nanomechanical testing

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ABSTRACT

Hydrogen (H) can have dramatic consequences on material properties, especially by reducing the fracture toughness. Degradation by H initiates through mechanisms at the nano-scale, and is normally not detectable prior to the final leakage or component fracture. Computational techniques are therefore being developed in order to provide both a wider understanding of the phenomenon and engineering tools for prediction of materials susceptibility toward hydrogen embrittlement. This work presents a preliminary study for the development of a novel computational approach in which density functional theory (DFT), nanoscale experiments and finite element (FE) modeling are combined and interrelated in order to improve the understanding of hydrogen induced intergranular cracking. Two low angle and low coincidence grain boundaries types have been considered: Σ_3 and Σ_5. Density Functional Theory has been applied to investigate the influence of an increasing number of H atoms on the cohesive strength of these grain boundaries in pure Nickel. This provided relations between the number of H atoms (coverage of the grain boundary) and the cohesive strength, which is further applied in cohesive zone FE modeling of a triangular nanometer sized fracture mechanics cantilever beam. For verification of the model such specimens will be tested experimentally both with and without in-situ electrochemical charging.

The simulation results show that the model is suitable for describing the combined effect of grain boundary misorientation and the reduced cohesive energy due to hydrogen on the grain boundary propensity to cleave.

Introduction

Stress corrosion cracking (SCC) and hydrogen embrittlement (HE) are threats to the structural integrity of offshore oil and gas pipelines and components and can cause costly downtime and repair. The main source of atomic hydrogen (H) in oil & gas fields is the corrosion protection systems, where H is formed at the cathode at normal protection potentials and enters the steel by absorption. Another source may be welds,

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caused by the presence of moisture during repair welding. Lately, there are reports about the tendency of premature failure of materials despite being considered "safe" considering the design criteria and resistance towards HE (*e.g.* super duplex stainless steel (SDSS) and nickel-base alloys) [1,2].

Modern steels are designed on the basis of introduction of different interfaces into the microstructure and reduction of the grain size. It is already known that grain boundary (GB) density, as well as their types and misorientation, play a fundamental role in the macro-behavior of polycrystalline metallic materials, including the resistance to crack nucleation and propagation [3,4]. On the other hand, interfaces and grain boundaries may act as preferential sites for trapping and segregation for H atoms, finally leading to intergranular embrittlement and cracking. In the case of aging offshore steel infrastructure the role of the grain boundaries and interfaces become more important since these traps are potential initiation sites for failure as well as sources of H to the failure sites through high diffusion rate paths. While hydrogen embrittlement is a well-known phenomenon, the mechanisms involved are still not fully understood. Two of the most established micromechanical models of hydrogen-assisted fracture are the hydrogen enhanced decohesion model (HEDE) [5–8] and the hydrogen enhanced local plasticity model (HELP) [9–11]. Adsorption induced dislocation emission (AIDE) [12] and the thermodynamic framework of Defactant concept proposed by Kirchheim [13] are others. Recently it has been shown that quantum effects need to be considered in order to achieve a correct understanding of the degradation mechanisms in construction materials [14,15].

A logical approach for understanding the hydrogen effect on the GB under stress is to study the mechanical behaviour of bi-crystal cantilevers, containing a single defined GB [16]. Bicrystalline cantilevers including one single predefined interface is prepared by means of focused ion beam (FIB). With the application of cathodic polarization it is possible to charge the cantilevers with H. The small size of the cantilevers assures a uniform concentration of H and fast saturation of the GB with H. The results can then be compared to similar cantilevers deformed in H free condition. This makes it possible to quantify and verify the effect of H on the interface cohesion energy.

The work presented is preliminary in nature: the main goal is to investigate and evaluate the suitability of the proposed multiscale modelling approach for providing a better understanding of hydrogen induced GB separation as well as a tool for experimental design. Density functional theory is applied to investigate the influence of different levels of atomic H on the cohesive strength and embrittlement mechanism involving grain boundaries and interfaces. Input from atomistic modeling provides quantitative information to cohesive zone (CZ) elements, implemented in the FE code ABAQUS. The cohesive elements are placed between grains which are consistently oriented in order to represent specific GB on a continuum level. The critical energy for the collapse of the element is therefore linked to the H coverage of the GB. Finally, the procedure is applied for the simulation of nanometer sized fracture mechanics cantilever beams of a Nickel bi-crystal.

Materials and methods

Nickel is the simplest relevant model system to establish the basic methodology and competence before establishing projects on more industrial relevant alloys.

Bulk samples in form of thin discs with 10 mm diameter and 2 mm thickness were prepared from as-received 99.99% pure Nickel according to the description in Ref. [17] to produce two dimensional samples, i.e. the GB perpendicular to the sample surface, so that any geometrically-caused parameters affecting the results will be excluded. The discs were characterized using electron backscatter diffraction (EBSD) to verify the GB types and then electro polished to prepare a perfectly clean surface.

Cantilevers with 4 μm length and 2 μm width were milled using a FEI Helios NanoLab 600 DualBeam FIB. Milling of cantilevers was performed in two steps: first a balk roughly to the final length and width of the cantilever was milled using 30 kV and 0.9 pA beam current (Fig. 1a). Next the balk was milled from the sides by rotating 90° to release it from the bulk sample. and milled from both sides within rotating by 180° (Fig. 1b). In this second step the FIB stage was tilted back to 7°, and so the cross section of the cantilever became a triangle with an angle of 45° (Fig. 1c). This step is also called fine milling step using lower voltage of 10 kV and current of 0.2 pA. In this way, the damaged layer in the first step by the high voltage/current is removed for the most part. The GB was located at the one fourth total length of the cantilever from the cantilever end.

Prepared cantilevers will be tested under bending test in air and in the hydrogen contained atmosphere, which will be presented in upcoming reports. As an ongoing study, this part was presented to show that by performing experimental tests, we verify our simulation studies.

Theory and calculations

Input from existing atomic scale modeling such as the work of Jiang et al. [18] has already been used in the past [19,20] to improve the predictive capacity of continuum models. In this work, however, the aim is to set up a framework in which atomic scale experiments and modeling are tailor-made to answer challenges faced at the continuum and FE level.

Atomistic level – DFT

Spin polarized DFT calculations at the PBE-GGA level [21] were performed for Ni $\Sigma_5(012)$ and $\Sigma_3(111)$ symmetrical grain boundaries (GBs) using the Vienna ab-initio simulation package (VASP) [22,23]. The criterion for energy convergence was a change of the total energy less than 10^{-5}. The plane-wave energy cut-off was 450 eV and a $7 \times 7 \times 3$ Gamma sampling of k-points was used to model the Brillouin zone. The energy cut-off and k-points were tested by comparing the energy of models with one and two hydrogen atoms. The chosen values gave relative energy convergences better than 1 meV. The closed GB unit cells consisted of 80 and 96 Ni atoms as illustrated in Fig. 2, into which an increasing amount of H was