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Abstract

MultiHy is an EU-FP7-NMP project that aims to develop advanced, industrially-relevant numerical models for hydrogen embrittlement (HE). The primary focus of the project is the description of H transport in advanced materials with complex microstructures. By focusing on H transport we aim to develop a robust, transferrable methodology for predicting the susceptibility of materials to HE based on detailed microstructural information using computational methods and supported at all levels by experimental measurements. The models will be demonstrated by investigating the role of microstructure in three contrasting industrial case studies involving HE. The goals of the project will be achieved by development of a multiscale modelling framework that will enable the extraction and propagation of information pertaining to critical microstructural features from the nanometer up to the component scales. The key aspect of this modelling effort is the incorporation of atomistically-derived diffusion barriers for critical H trapping sites into continuum and component level models. The gap between the atomistic and continuum hierarchies will be bridged by kinetic Monte Carlo calculations that will provide a basis for derivation of a novel set of equations for H diffusion. These equations will be applied in continuum and component models for boundary conditions representative of those that occur in service.

Introduction

Hydrogen embrittlement (HE) is a serious problem afflicting all structural metals to some extent. Given the ubiquity of H in service environments, this represents a very serious threat to the integrity of structural components across all industries. A new project called MultiHy (multiscale modelling of hydrogen embrittlement), funded under the EU’s 7th Framework Program, aims to develop advanced multiscale models to assist in the evaluation of the HE susceptibility of materials and components in realistic service conditions based on microstructural information. The four-year, 5.3mil€ project will be carried out by a consortium of eleven partner from six European countries: Fraunhofer IWM, Germany; Queen’s University Belfast, UK; EADS, Germany; BMW Group, Germany; National Physical Laboratory, UK; Swansea University, UK; University of Salamanca, Spain; The Norwegian University of Science and Technology, Norway; ThyssenKrupp, Germany; voestalpine, Austria; and SKF, Netherlands. This paper will outline the scope and objectives of the project and provide an overview of the scientific and technical background that influenced its development.

The significance of H transport and trapping

The deleterious effect of H on the mechanical properties of metals and alloys has been studied extensively since the 1930s [1,2,3,4,5]; however, there is still considerable debate regarding the mechanisms for HE, in particular regarding the specific mechanism for H-assisted damage (i.e. role of H in the fracture process). The mechanisms for H-assisted damage with the soundest experimental and theoretical basis are: (i) Hydrogen enhanced decohesion (HEDE); (ii) Hydrogen enhanced localised plasticity (HELP); (iii) Hydrogen enhanced strain induced vacancy formation (HESIV); and (iii) Delayed hydride cracking (DHC). These have been reviewed in detail elsewhere [6,7,8,9]. Various doubts exist regarding the validity of each of these mechanisms. This confusion is
exacerbated by the dependence of these mechanisms on material properties, defect distribution, microstructure as well as mechanical and environmental conditions. These dependencies are often so complex that different mechanisms can occur for the same alloy under different mechanical and environmental conditions. It is also possible that combinations of several mechanisms can occur simultaneously and synergistically, since some involve common background processes.

Figure 1 - Distribution of roles to consortium partners in different length scales (orange indicates numerical modelling and green experimental characterisation of materials).

Figure 2 - The consortium is comprised of a roughly even number of industrial and academic entities, with a balance of capabilities in the fields of theoretical modelling and physical evaluation.

A common factor in all H-assisted damage mechanisms is the crucial role of H transport and trapping [4,10,11]. Depending on the mode of H transport, it may be either the rate limiting process or an intrinsic part of the fracture process itself. The lifetime of a HE-susceptible component is often dominated by the time taken for H to accumulate in sufficient quantities at the fracture site, with crack propagation occurring very rapidly after initiation. In such cases the component lifetime may be characterised by the crack incubation time. The rate of H transport can also affect the mode of fracture, as this is dependent on the amount of H available at the fracture site. Various modes of H transport are possible, with both the rate and mode of H transport dependent on the structure of the material at all length scales.

H transport and, therefore, HE susceptibility are profoundly affected by the strength and distribution of trap sites. Trap sites may include point defects and their complexes, solute atoms, second phase particles, grain or phase interfaces, twin boundaries, and dislocations. The influence of traps on H transport depends on their binding energy and whether they are reversible (acting as sinks or sources, depending on conditions) or irreversible (always acting as sinks) [12,13,14,15,16]. The binding energies of traps can be evaluated by numerical modelling on the atomistic level and, to some extent, by experimental techniques such as thermal desorption spectroscopy (TDS) and permeation testing. There is a limited body of literature on the determination of diffusion barriers for atomic complexes, crystallographic defects and simple microstructural features using numerical simulations; however, a complete database of diffusion barriers that are encountered in real material microstructures is far off. This project will represent the first coordinated European effort to expand on this body of work and to compile diffusion barriers relevant to real engineering systems.

Scope and objectives of the project
The primary objective of the proposed project is to develop an advanced multiscale modelling framework to assist in the evaluation of the HE susceptibility of materials and components in realistic service conditions based on microstructural information. It is anticipated that this will have a particularly high impact on the development and application of advanced, high-strength alloys with complex microstructures. Such materials can be highly susceptible to HE; however, existing numerical models are unable to relate the influences of microstructural features in such materials to measurable macroscopic HE susceptibility indicators. The modelling will focus on determining the rate and mode of H transport in the material with the aid of experimental measurements. H transport will be related to the degradation and reliability of materials and components by developing a robust and transferrable methodology for determining the critical local conditions causing HE initiation and the key microstructural features affecting H transport to the fracture site. This will be achieved by combining our understanding of H transport on different length scales, from atomistic calculations through to component-level H diffusion models.

A secondary objective of the proposed project is to develop a mechanistic understanding of H-microstructure interactions in three industrial problems involving degradation of advanced materials. The case studies are:

- Delayed H-assisted cracking in pulse-plated (PP) Ni used for the main and upper stage combustion chambers of the Ariane 5 satellite launcher;
- HE of advanced high strength steel (AHSS) used for automobile chassis components;
- H-assisted rolling contact fatigue of wind turbine bearings in service.

The evaluations of microstructural influences in these case studies will serve to validate and demonstrate the applicability of the modelling framework. It will also provide opportunities to find long term solutions to these specific problems, e.g. through microstructural modification. The diversity of these case studies will exemplify the ubiquity of H-related material degradation across all industrial sectors, and the flexibility of the H transport model to be applied in very different systems.

Figure 3 - The model will be applied in order to resolve existing problems in three different industrial sectors: (i) delayed cracking in pulse-plated Ni used in Ariane 5 rocket combustion chambers; (ii) H-assisted degradation of AHSSs for automobile chassis components; and (iii) hydrogen-assisted rolling contact fatigue in wind turbine bearings.

The project will not attempt to model H-assisted damage mechanisms. Though there exists numerous sophisticated models for H-assisted damage mechanisms, there is an inherent uncertainty regarding the predominant damage mechanism in any system. A consequence of this uncertainty is the inability of numerical models for H-assisted damage mechanisms to be related to measurable macroscopic parameters. The project aims to circumvent this uncertainty by focusing on H transport rather than the damage mechanisms directly and characterising damage in terms of the local material conditions corresponding to the experimentally-determined macroscopic thresholds.
The project also does not aim to develop a universal, market-ready software tool for evaluating the susceptibility of materials and components to HE. This goal is believed to be unfeasible within the scope of this project. The project will result in the development of advanced, experimentally-validated models capable of predicting the susceptibility of specific materials and components to HE that can be integrated into existing commercial software packages. Plans for ongoing projects and ventures to further develop the model towards an integrated, engineering-oriented tool will be developed during the project, with the aim of being implemented at the end of the EC funding cycle.

**Macroscopic modelling of hydrogen embrittlement**

It is evident that the processes associated with HE are remarkably complex to model. Nevertheless, there exists a considerable body of literature on numerical modelling of HE at the macro scale. The models usually fall into one of two categories: (i) models of H transport in the vicinity of a crack or notch, sometimes coupled with fracture criteria based on one or more of the H-assisted damage mechanisms (usually DHC or HEDE) [17,18,19,20,21,22]; or (ii) models of H transport in the vicinity of a dislocation, or of the influence of H atmospheres on the elastic interaction between dislocations in an array [23,24]. A deficiency common to each of the models is the use of a large number of simplifying assumptions regarding the microstructure, material properties and thermodynamics of the system. It is generally assumed that H transport occurs by interstitial diffusion only. Typically, the materials are taken as isotropic with H diffusivity being constant and equal in all directions. The incorporation of detailed microstructural information (e.g. short circuit diffusion along grain boundaries or the influence microstructural inhomogeneities other than simple trap sites) is beyond the current state-of-the-art. Furthermore, it is usually assumed that the interstitial H does not affect the stiffness of the matrix and that the lattice expansion due to a single H atom occupying an interstitial site is purely dilatational and reacts only with the hydrostatic component of the local stress. Most models also consider the mechanical response of the material as linear-elastic and the overall system to be isothermal, though some have considered the dependence of H transport on trapping by static dislocations resulting from plasticification (but not H transport by dislocations). As a consequence of these simplifications, the existing models are unable to resolve the influences of microstructural features and material properties on the microscopic processes involved in HE and, therefore, on the HE behaviour at the component level. Quasi-continuum models for DHC and HEDE have been correlated with measured fracture mechanics parameters using model materials over a limited range of conditions; however, these models have tended to contain a large number of adjustable parameters, and there remains much uncertainty regarding the conditions in which these damage mechanisms occur. Quasi-continuum models of localised softening due to HELP also exist; however, in such models the degree of softening is characterised by arbitrary linear parameters and, as is admitted by their proponents [25], they provide only a first-order approximation of the softening effects. Thus, the applicability of even the most sophisticated macroscopic H-assisted damage models to real engineering systems is equivocal.

**Atomistic modelling of hydrogen interactions**

The importance of atomistic simulations in materials science has increased tremendously within the last two decades [26]. Ever growing computational power has allowed to study systems containing up to one billion atoms and to follow their dynamical development for tens of nanoseconds. Unfortunately, simulations over such extensive time and length scales are possible for a limited number of materials and processes. This is because there exists only a few real materials can be described by models of interatomic interactions that are both quantitatively predictive and computationally efficient. Thus, whilst atomistic simulations provide valuable qualitative insights and quantitative trends about materials behaviour, they usually need to be coupled with
macroscopic models or theories in order to make meaningful predictions of macroscopic material properties.

Examples of atomistic simulations of H interactions in crystalline materials in the literature are few. The studies can be divided roughly into two categories according to the description of interatomic interactions. In the first category, a full quantum-mechanical treatment of the electronic structure (so called first-principles or ab initio methods) is employed. These, essentially parameter-free, methods offer accuracy and predictive power but are elaborate and computationally demanding. In the second category, properties of materials are reproduced via simplified interatomic potentials that are justified to a greater or lesser extent by some theoretical developments. These empirical approaches excel in computational speed but are less accurate and reliable.

First-principles calculations are mostly limited to studies of bulk phases, point defects, high-index surfaces and simple grain boundaries. In a pioneering study, Elsässer et al. [27,28,29] calculated adiabatic potentials for vibrational states of H in FCC lattices of γ-Fe and Ni and BCC of α-Fe using first-principles calculations based on density functional theory. These calculations predicted that H resides in the tetrahedral sites of bcc Fe, whereas in the close-packed FCC lattices of Ni and gamma-Fe the octahedral site are energetically preferable. These findings were later confirmed by experiments [30,31] and other first-principles calculations [32,33]. The energetics of H segregation at a symmetrical tilt grain boundary in Ni was studied by Yamaguchi et al. [34,35]. A combination of first-principles calculations with the adaptive kinetic Monte Carlo method was used for the first time to simulate a long-timescale diffusion of H at several distinct grain boundaries in Al [36]. The most surprising finding of these simulations is that the investigated grain boundaries impede rather than enhance H diffusion because they either trap or block diffusing H atoms. There exist several studies of H-vacancy interactions in Al [37], α-Fe [38], and the ternary Fe-C-H system [39]. All these calculations confirm a strong binding of H to vacancies and formation of stable defect complexes. The only first-principles study of the influence of H on dislocation core properties was carried out by Lu et al. [40] for Al. They again observed a strong binding of H to the dislocation core and a significant increase of the activation energy for cross slip. Finally, Jiang and Carter [41] and van der Ven and Ceder [42] investigated the decohesion of Al and Fe surfaces with varying H coverage. Based on their first-principles results, Serebrinsky et al. [43] developed a quantum-mechanically informed continuum model of H-assisted cracking.

Simulations using empirical potentials can be used to model the interaction of H with extended lattice defects (general grain boundaries, dislocations, cracks) but the predictive power of these studies is to a great extent limited by the reliability of the interatomic potential. For the Ni-H and Fe-H systems there exists a number of simulations based on the embedded atom method (EAM) potentials [44,45,46]. Several groups have applied EAM potentials developed for the Ni-H system to study: (i) H adsorption at surfaces [47]; (ii) binding of H at grain boundaries [48,49]; (iii) H interactions with dislocation cores [50,51,52,53,54,55]; (iv) the effect of H on nanovoid nucleation at grain boundaries [56]; (v) nanoindentation in the presence of H; and (vi) and the influence of H on crack propagation [57]. While the EAM potentials seem to describe reasonably well the atomic interactions in the FCC Ni-H system, this class of potential performs much worse for BCC transition metals and their compounds. EAM-type potentials for α-Fe and other BCC metals show severe deficiencies in the description of extended lattice defects, especially dislocations. Recent efforts to improve parameterizations of these potentials have not been very successful. Development of reliable interatomic potentials for atomistic simulations of lattice defects in iron and iron-based materials is particularly challenging. Energetics and structural stability of magnetic materials is strongly influenced by magnetic effects and details of the electronic structure. Therefore, these materials cannot be described adequately by the EAM potentials, which are only density dependent. The only schemes that have been proved reliable for the description of chemical
bonding in BCC transition metals are the bond-order potentials [58,59,60,61], which are based on the tight-binding method [62,63].

**Bridging the scales**

Despite recent extensive advancements atomistic simulations have inherent limitations. The determination of many material properties requires statistical averaging over large ensembles or many atomic events, which may occur on time scales much longer than those accessible in a typical simulation. This temporal aspect is one of the most severe shortcomings of atomistic simulations. Currently such simulations are only able to follow the dynamic development of a system for much less than one microsecond. Thus, direct simulations of diffusion or thermally activated processes are excluded from direct evaluation by atomistic methods. In order to overcome the time scale problem, novel techniques have been developed. One of the most successful approaches that enables simulation of long-range diffusion and trapping is the kinetic Monte Carlo (KMC) technique. This method does not consider any details of atomic interactions but instead explores the dynamics between well defined states, which correspond to particular atomic arrangements in crystal environment. The direct treatment of the state-to-state transitions enables to reach far greater time scales than those in atomistic simulations, typically seconds or beyond. The crucial input for KMC is the knowledge of the potential energy surface, i.e. the energies of individual states and the energy barriers between them. A major challenge is to map accurately the PES and to create a complete catalogue of possible events along with their transition probabilities. This input can be extracted from atomistic calculations provided they are sufficiently reliable. As both the qualitative and quantitative outcome of the KMC simulations is extremely sensitive to these input quantities, the accuracy of the atomistic simulations is of outmost importance.

First model KMC simulations that predicted the effective diffusion coefficients in a crystal containing traps were done by Kirchheim more than 20 years ago [64]. These parameter studies were very useful since they validated for the first time analytical models of trapping and revealed that changes of PES in the vicinity of trapping sites have a strong effect on the computed diffusion coefficients. However, they were not extended to a specific material with a realistic microstructure. Material specific KMC simulations of H diffusion were performed for the first time only very recently [33]. This study is also the first one that is based fully on input data derived from atomistic simulations. One important aspect of KMC in the context of H diffusion in a crystal containing various defects is the need to employ off-lattice KMC, which is able to reproduce the distortions of the atomic structure in the vicinity of defects. This aspect makes it more complicated but is unavoidable for a correct assessment of diffusion coefficients.

**Application of models to reliability and lifetime assessment**

Any model related to H-assisted degradation must incorporate fracture criteria. In lieu of direct treatment of H-assisted damage mechanisms by computation means, the fracture criteria will be furnished by the local conditions (e.g. in terms of H concentrations and stress-strain conditions) at the instant of fracture. These conditions will be determined using a combination of experimental and numerical modelling techniques, and incorporated into the model at the component level as the fracture criteria. This approach requires a robust and transferrable methodology for determining the “critical condition” from experimentally-determined macroscopic thresholds using numerical simulation. The development and validation of this methodology will be a key focus of MultiHy.

A fundamental concept of H-assisted degradation is that fracture occurs at some critical combination of H concentration and the local stress-strain state. The stress-strain components relevant to this fracture condition are the maximum principal stress, $\sigma_1$, and the equivalent plastic
strain, $\varepsilon_{eq}$ [22]. Thus, the critical local H concentration at the fracture point, $C_{cr}$, may be defined as a function of $\sigma_1$ and $\varepsilon_{eq}$:

$$C_{cr}(x,t) = C_{eq} \left( \sigma_1(x,t), \varepsilon_{eq}(x,t) \right)$$

Equation 1

where $t$ and $x$ denote the time and location of fracture. In the current project, this critical condition will be defined (in terms of $C_{cr}$, $\sigma_1$ and $\varepsilon_{eq}$) using the atomistically-informed H transport based on the macroscopic threshold stresses and stress intensities for crack initiation, which will be measured experimentally (e.g. by in-situ tensile testing) as a function of externally-applied conditions (i.e. mechanical loads, temperature and H influx). The results will then be incorporated into the component-level H transport models as the fracture criteria, so that the lifetime of the component can be interpolated within a range of externally-applied conditions.

The assessment of degradation and reliability of materials and components will also be enhanced by the use of boundary conditions that are based on measurements taken in-service or during component laboratory tests. A significant part of the project will be devoted to the collection and analysis of data pertaining to the process or service conditions causing HE in each CS. The data will include process parameters and component test conditions, as well material characteristics (e.g. concentration and distribution of absorbed H and residual stresses) after processing or testing.

Project overview

The project will address the deficiencies of the existing numerical models for HE that prohibit their application to real engineering systems. These are: (i) the inability to resolve the influences of fine microstructural features and material properties at the component level; and (ii) the inherent uncertainty arising from the use of fracture criteria based on systemically-ambiguous H-assisted damage mechanisms. This will be achieved by focusing on H transport and the critical local conditions causing crack initiation and by developing an accurate description of the dependence of the driving forces for H diffusion on microstructure and material properties using a combination of atomistic, KMC and finite element modelling. This will be achieved by focusing on H transport and the critical local conditions causing crack initiation, and by developing an accurate description of the dependence of the driving forces for H diffusion on microstructure and material properties using a. This “bottom up” approach will involve four levels:

- **LEVEL 1** Construction of a comprehensive database of binding energies, diffusion barriers and chemical potentials for H in a complex, 3-dimensional microstructure using atomistic and kinetic Monte Carlo simulations.
- **LEVEL 2** Derivation of novel continuum descriptions of H diffusion including the effects of multiple traps with different energy configurations.
- **LEVEL 3** Implementation of the continuum models using FE codes that can be scaled up to the component level.
- **LEVEL 4** Validation of the consistency of the modelling chain at all stages by dedicated experiments.

In addition to the 4 levels associated with the development of the modelling framework, the project contains two additional levels where the developed methodology will be applied to real industrial problems in order to demonstrate its applicability.

- **LEVEL 5** Application to three industrial case studies.
- **LEVEL 6** Assessment of material reliability and lifetime.
Figure 4 – Structure of the project.

References
