

# **Protocols for designing H resistant alloys through multiscale modelling: The HeMS Project**

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Hydrogen is a ubiquitous element that harms advanced alloys, fostering embrittlement and decreasing component life. There is renewed interest in the topic due to the need for hydrogen storage required for emerging technologies. Hydrogen in steels represents a challenge due to the complexity of the interactions associated to it, the difficulty in establishing the mechanisms through which it alters mechanical properties, and the ability to detect it. Multiscale modelling therefore represents an ideal tool for overcoming these challenges. After reviewing our recent contributions to the computer aided design of novel ultra-hard steels resistant to hydrogen embrittlement [Materials and Design 43 (2013) 499–506], we embark in outlining our multiscale modelling based approach to hydrogen embrittlement and alloy design: the HeMS project ([www.hems.ox.ac.uk](http://www.hems.ox.ac.uk)). HeMS combines density functional theory, atomistics and micromechanical approaches to gain fundamental understanding into the mechanisms governing hydrogen embrittlement. Employs thermokinetics modelling for microstructural design and computational plasticity for describing microstructure evolution upon exposure to hydrogen. Adopts statistical and artificial intelligence techniques for examining the results of models and experiments. And develops new experimental techniques to determine hydrogen migration in complex steels. This presentation summarises our previous achievements in alloy design, and our on-going work to control hydrogen embrittlement through understanding of its multiscale effects.

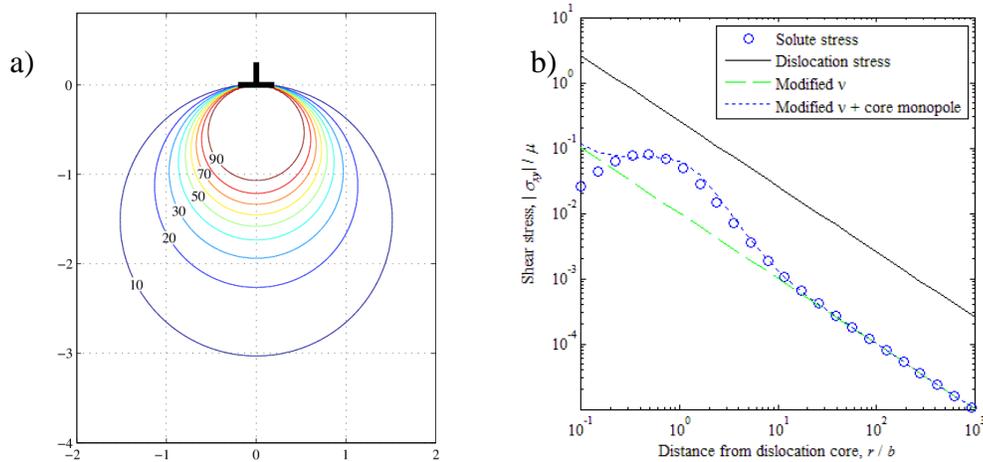
# Hydrogen Effects on Dislocation Dynamics and Metal Plasticity

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Hydrogen in solid solution can modify the behavior of metals in numerous, seemingly contradictory ways. For instance, hydrogen is believed to enhance localized plasticity while simultaneously decreasing overall ductility. Dislocation dynamics (DD) simulations can provide insight into these effects. While hydrogen modifies dislocation behavior in multiple ways, we focus on two major effects: changes in the driving forces on the lines and modification of the dislocation mobility. In the limit of fast diffusion, where the solute distribution is always in equilibrium with the dislocation stress fields, we show that the elastic stress field due to the solutes can be decomposed into near-core and far-field components (see Fig. 1). The near-core field can be well approximated by a single line of dilatation below the dislocation, and the far-field stresses can be determined by calculating the dislocation stress field with a modified Poisson's ratio. The dislocation mobility in the presence of hydrogen solutes can be determined using atomistic simulations. Using 3D DD simulations that incorporate these effects in an FCC metal, we predict the effects of hydrogen on the behavior of dislocation populations and the stress-strain curve.



**Fig.1:** (a) H concentration,  $c/c_0$ , where  $c_0$  is the stress-free concentration, under an edge dislocation in Pd [1]. Grid spacing is  $b$ , the Burgers vector magnitude. (b) Shear stress  $\sigma_{xy}$  along the glide plane due to the solute atmosphere [1]. *Modified v* was calculated using the dislocation stress expression with a modified Poisson's ratio and *Modified v + core monopole* adds to this result the stresses due to a solute monopole below the dislocation core. The *Dislocation stress* field is also shown for reference.  $c_0=1$  at. % in these figures.

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[1] W. Cai, R. B. Sills, D. M. Barnett, W. D. Nix, Modeling a Distribution of Point Defects as Misfitting Inclusions in Stressed Solids, *J. Mech. Phys. Solids*, in press (2014).

# **Effect of microstructure on hydrogen trapping in bcc Fe-Ti-C steel - A quantitative parameter study**

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Hydrogen embrittlement is one of the most devastating and unpredictable, yet least understood, mechanisms of failure experienced by engineering components. H has the tendency to segregate at microstructural defects such as dislocation cores, grain boundaries and interfaces on incoherent particles. Hydrogen, itself as interstitial component, can be trapped by these or other sorts of traps, e.g. substitutional impurities. Such interactions take place at scales ranging from electronic to the microstructural realm. Since the trapping mechanism of H was suggested by Darken and Smith [1] in 1949, hydrogen trapping has been substantiated, experimentally and theoretically. Recently published works by Fischer [2] and Svoboda [3] present equations for the role of several sorts of traps in Fe based alloys. By applying their concepts in the framework of thermo-kinetic simulation we present computational studies including the diffusion process of H, dependent on the depth and molar volume of different kinds of traps. Combining phase transformation kinetics to trap models we calculate the ratio of trapped to non-trapped (free) amount of H. H atoms, able to diffuse through the metal, may recombine to form hydrogen molecules, which develop pressure within the bulk. This pressure can increase to levels where hydrogen induced cracking may occur. To reduce the extent of damage, the microstructure should consist of a homogeneous distribution of hydrogen traps, which will distribute the H atoms innocuously. We will demonstrate that the trapping effect on diffusion of H in pure iron is negligible, whereas the variation of microstructural defects in Fe-based alloys can have a remarkable influence on the mobility of hydrogen in the bulk. In order to obtain a relatively simple illustrative model, the iron based system is alloyed just with titanium and carbon. Incoherent TiC particles are found to have strong interaction energy with hydrogen.

In the model we take as our main variables the four dominant influencing parameters, namely:

- Grain size.
- Dislocation density.
- Austenitization temperature.
- Dilute Ti and C solutions.

We demonstrate the characteristics of H diffusion in Fe and Fe-based alloys under varying the trap population of the material by usage of thermo-kinetic simulations. It is anticipated by our models, that suitable choice of trap type can reduce the susceptibility to hydrogen induced cracking.

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[3] J. Svoboda, G. Mori, A. Prethaler, F.D. Fischer, Corrosion Science 82, 93 (2014)

## **Cyclic and High-Strain Rate Plasticity in Penta-Twinned Silver Nanowires – Atomistic Experiments and Modeling**

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In recent years there has been a major thrust to develop novel nanomaterials, e.g., nanowires (NWs), exhibiting unique mechanical and electrical properties. These nanostructures are envisioned as building blocks for the next generation of electronic devices, biosensors, energy harvesting systems and other applications. In this context, identification of scale dependent properties is essential. However, such endeavor has proven challenging from both experimental and modeling perspectives. Here we follow a combined computational-experimental approach to characterize the plastic mechanisms in penta-twinned silver nanowires.

Employing a MEMS-based tensile testing technique, we performed *in situ* TEM tensile experiments. The measurements showed that nanowires exhibit increasing strength and ductility as the diameter of the nanowire is reduced. TEM imaging during mechanical straining enabled the visualization of dislocation structures (plastic zones) nucleating at several localized regions along nanowires. These experimental observations were interpreted by means of molecular dynamics simulations (MD), which reveal atomistic detail of the plasticity mechanisms. We found that penta-twinned Ag NWs deform plastically via surface nucleation of stacking fault decahedrons (SFDs). These stacking fault decahedrons form chains, along the wire length, resulting in multiple plastic zones. The signature of these SFDs, visualized in simulations, was identified in TEM as well.

We also report on recent improvements of our MEMS testing system, namely, closed-loop feedback control to achieve displacement-controlled testing, and low-noise electronic sensing for cyclic and high-strain rate mechanical experiments. We show that the signal-to-noise ratio afforded by the feedback system, results in an unprecedented increase in the resolution of stress-strain signatures, which enables a better mechanistic understanding and a more direct comparison to MD predictions. In particular, we have characterized the cyclic behavior of the nanowires. Load and unload cycles reveal increasing hysteresis with increasing unloading strain, which points to the existence of the Bauschinger effect in nanowires. On the other hand, high strain rate experiments with rates as high as 1/s have been performed, revealing increased hardening and decreased plastic localization with increasing strain rate.

### **3D mesoscopic simulation of fatigue-crack shielding and blunting in FCC metals**

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When subjecting ductile crystalline solids like FCC metals to low-amplitude cyclic loading, plastic strain localizations can appear which may lead to the formation of cracks and subsequent fracture. Crack propagation then depends on the dynamics and the interactions of the dislocations accumulated and patterned in a plastic zone ahead of the crack tip.

Modeling these phenomena is a long-standing and complex problem. So far, existing models are essentially 2D and only few attempts in 3D have been made. 3D dislocation dynamics (DD) simulations are then needed to quantitatively investigate the plastic flow restraining crack propagation through shielding and blunting mechanisms. Only in 3D the influence of crystal symmetry, exact slip system activity and thermally activated processes like dislocation cross-slip can correctly be taken into account.

To model this complex boundary value problem, the Discrete-Continuous Model (DCM) [1] is used to reproduce the properties of realistic dislocation microstructures in large volume elements (e.g.  $40 \times 40 \times 40 \mu\text{m}^3$ ) with a sharp initial crack and cyclically loaded. In this presentation, the first results of the 3D simulations are presented and compared with results from the literature considering a 2D geometry.

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## **Role of plasticity-induced crack closure in fatigue crack growth in metals**

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The premature contact of crack surfaces attributable to the near-tip plastic deformations under cyclic loading, which is commonly referred to as plasticity induced crack closure (PICC), has long been focused as supposedly controlling factor of fatigue crack growth (FCG). Nevertheless, when the plane-strain near-tip constraint is approached, PICC lacks of straightforward evidence, so that its significance in FCG, and even the very existence, remain debatable. To add insights into this matter, large-deformation elastoplastic simulations of plane-strain crack under constant amplitude load cycling at different load ranges and ratios, as well as with an overload, have been performed. Modeling visualizes the Laird-Smith conceptual mechanism of FCG by plastic blunting and re-sharpening. Simulation reproduces the experimental trends of FCG concerning the roles of stress intensity factor range and overload, but PICC has never been detected. Near-tip deformation patterns discard the filling-in a crack with material stretched out of the crack plane in the wake behind the tip as supposed PICC origin. Despite the absence of closure, load-deformation curves appear bent, which raises doubts about the trustworthiness of closure assessment from the compliance variation. This demonstrates ambiguities of PICC as a supposedly intrinsic factor of FCG and, by implication, favors the stresses and strains in front of the crack tip as genuine fatigue drivers.

## Theoretical study of hydrogen interacting with TiC nanoparticles in iron

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Brittle fracture of steels resulting from hydrogen embrittlement (HE) presents a serious industrial problem. One of possible means to lower the HE susceptibility is to reduce the amount of diffusible hydrogen in the material. It is widely believed that nano-sized transition-metal-carbide precipitates (e.g. TiC, NbC, or VC) can provide efficient traps for H. But in spite of various experimental evidences, the trapping mechanisms at the atomic scale are not yet well understood.

In this theoretical study, we investigate the interaction of H atoms with TiC particles in the matrix of body-centered cubic iron using first-principles calculations based on density functional theory (DFT). Our atomic-scale results show that the different possible trap sites, namely at coherent Fe/TiC interfaces, interfacial misfit-dislocation cores, and carbon monovacancies in TiC, exhibit large differences in their trapping strength and effectiveness.

A detailed analysis of the computational results with respect to available experimental results reveals a rather consistent interpretation for the trapping mechanisms.

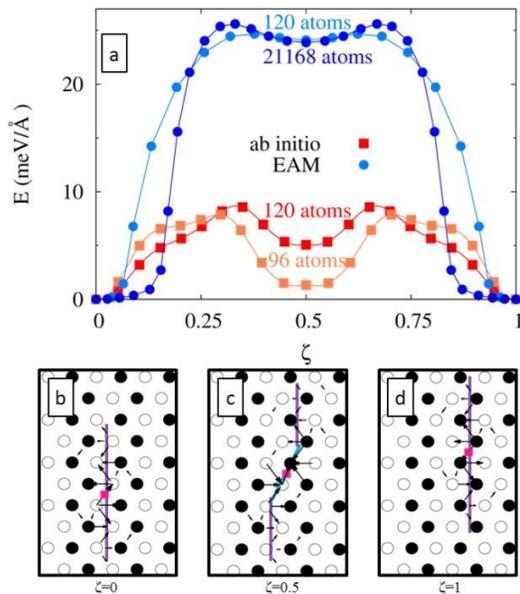
## Ab initio modeling of secondary slip in zirconium

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Both experiments [1] and simulations [2] have demonstrated that, in zirconium, the prism plane is the favored slip plane, where screw dislocations dissociate spontaneously and have a small lattice friction. However, screw dislocations can also deviate from the prism plane to glide either in the first order pyramidal plane or in the basal plane. This cross-slip phenomenon has been evidenced with Transmission Electron Microscopy [3], but a detailed understanding is still lacking. Here we investigate dislocation glide in both pyramidal and basal planes using atomic-scale simulations based on a combination of ab initio calculations and empirical potential calculations with the Mendelev potential [4]. We show that surprisingly, both slip systems share the same energy barrier, which is explained by the fact that, in both cases, the dislocation passes through the same metastable configuration with a complex core structure.



**Figure 1:** (a) Peierls barrier for pyramidal slip. Differential displacement maps show the dislocation core structure at its initial (b), intermediate (c) and final position (d).

We used the NEB method to determine the Peierls barrier of a screw dislocation initially spread in the prismatic plane and gliding either in a pyramidal plane (fig.1a) or in a basal plane [5]. In both cases, the minimum energy path passes through the same intermediate metastable configuration where the dislocation spreads in the pyramidal plane (Fig.1c). This spreading is rationalized by a metastable stacking fault in the pyramidal plane which corresponds to an elementary twin with a thickness of 2-atomic layers.

The metastable core may thus be described as two partial dislocations spread in two neighbor prismatic planes joined to a nano-twin by a dipole of disconnections.

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## **MD simulations of defect accumulation and the early stage of crack nucleation in titanium alloys during fatigue**

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It was recognized more than 50 years ago that for metals and alloys, defects start to accumulate from the very early stage during fatigue, even at the first cycle of fatigue deformation. However, due to the lack of method to observe the *in situ* defect behavior during fatigue at the atomic scale, it is not very clear up to now how defects produced and accumulated, what is the nature of such defects and how they lead to crack formation. The situation becomes worse for titanium alloys used as the rotation components in jet engines, where crack nucleation period constitutes the major part of the component life. Deeper understanding of the defect accumulation and crack nucleation mechanisms is crucial for the design of new materials and components. In the last a few years, large scale molecular dynamics simulations have been carried out to investigate the deformation of titanium alloys, such as dislocation nucleation, interaction and point defect formation by their reaction under various conditions. It was found that dipolar dislocation reaction is an effective way of reducing the number of mobile dislocations, resulting in the hardening of the slip system due to the exhaustion of mobile dislocations. At the same time, the defects formed can be sites for further dislocation nucleation upon continuous fatigue deformation, resulting in deformation localization in the slip bands, and point defects accumulate as deformation proceeds. The strength of the crystals becomes substantially reduced with the presence of large amount of dislocations and other defects, and the strength decreases continuously as the density of defects increases. The factors influencing defect nucleation and accumulation upon dislocation reaction and implications to fatigue failure are discussed.