



# First-principles investigation of hydrogen trapping and diffusion at grain boundaries in nickel



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## ABSTRACT

In this work, the interaction of hydrogen with high-angle GBs in nickel has been investigated by means of density functional theory simulations. Two distinct types of GBs have been considered: the  $\Sigma 3(111)[110]$  with a close-packed interface structure and the  $\Sigma 5(210)[001]$  with a less dense interface structure consisting of open structural units. Our calculations reveal that these two GBs have a markedly different interaction behavior with atomic hydrogen. The close-packed  $\Sigma 3$  GB neither traps H nor enhances its diffusion, but instead acts as a two-dimensional diffusion barrier. In contrast, the  $\Sigma 5$  GB provides numerous trapping sites for H within the open structural units as well as easy migration pathways for H diffusion along the GB plane that can enhance the H diffusivity by about two orders of magnitude compared to bulk Ni. The obtained results are analysed in detail and compared with available experimental and other theoretical data.

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## 1. Introduction

Hydrogen is known to have a deleterious effect on mechanical properties of many metals and alloys. This phenomenon, known as hydrogen embrittlement (HE), has been studied intensively over decades but its underlying microscopic mechanisms are still debated and not fully understood (for reviews see [1–6]). For structural materials, which do not form hydrides, such as Ni, several mechanisms responsible for HE have been proposed including hydrogen enhanced decohesion (HEDE), hydrogen enhanced local plasticity (HELP), adsorption-induced dislocation emission, or hydrogen enhanced strain induced vacancy formation. Although all these mechanisms are of different nature, they are not mutually exclusive and are likely to occur simultaneously in many situations. The dominant damage mechanism will then depend on a particular material, its microstructure and external conditions (H concentration, type of loading, strain rate, temperature, etc.).

It has been shown by Bechtle et al. [7] that the fracture mode of polycrystalline Ni changes sharply from intragranular and ductile to intergranular and brittle when the material is charged with H. However, the transition depends sensitively on the Ni microstructure and the presence and fraction of special grain boundaries (GBs). These observations clearly indicate that hydrogen affects

the cohesive strength of grain boundaries, as proposed in the HEDE mechanism, and that the sensitivity of a GB to HE likely depends on its interface structure [7,8]. Nevertheless, in a follow-up work Martin et al. [9] concluded that plasticity always plays an important role in hydrogen-induced embrittlement in Ni, even when the macroscopic fracture appears to be brittle. The HELP mechanism, considering the variations of dislocation mobility due to hydrogen, can therefore be a contributing factor as well. In addition, a possible formation of a Ni nanohydride phase in the vicinity of crack tips, dislocations and GBs has been proposed recently based on results of atomistic simulations [10,11].

A key element common to all HE mechanisms is the need for a critical local concentration of hydrogen in the metal. In the case of the HEDE mechanism, this critical concentration needs to be achieved in the vicinity of the failing GBs at an accumulation rate comparable with the propagation rate of a crack [12,13]. In order to fulfill this requirement, it is necessary for the H atoms to be both able to diffuse fast towards the GBs and become efficiently trapped there. Whereas most reports in the literature [14–19] agree on favorable trapping properties of GBs, it is still rather controversial whether the GBs can also enhance H diffusion [3,14,16,18,20–22]. This controversy stems from a complicated interplay between intrinsic material properties, microstructure, and external conditions, but it is also partly due to a lack of systematic atomic-scale information regarding the diffusion of H along GBs. So far, only a few experimental studies [16,23,24] have considered, for example, the dependence of the H diffusivity at GBs on their interface

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character. Moreover, in experimental studies it is often difficult to exclude effects of other structural imperfections, such as point defects, dislocations, or impurities, which can all influence the diffusion measurements. In computational studies, the major difficulty lies in the massive amount of work required to identify and investigate representative cases from the virtually infinite variety of possible GBs in materials.

In order to shed some light on this problem, we have investigated the trapping and diffusion of H across and along GBs in Ni using first-principles calculations. Two symmetric tilt grain boundaries (STGBs) have been selected for our study: the  $\Sigma 5(210)[001]$  STGB and the  $\Sigma 3(111)[\bar{1}10]$  STGB. These GBs (denoted briefly as  $\Sigma 5$  and  $\Sigma 3$  in the following) have very distinct interface structures and, as discussed in detail below, can be considered as representative cases for a broader variety of GB types.

The paper is organized as follows: In Section 2, we describe our computational approach. In Section 3, our results regarding the interface structures, the H segregation and the H diffusion for both GBs are presented. In Section 4, we discuss the results and provide a detailed comparison with available experimental and other theoretical results. In Section 5, the main findings and conclusions of the work are summarized.

## 2. Computational approach

Atomistic supercell models of the two GBs were investigated by means of density functional theory simulations using the Vienna ab initio simulation package (VASP) [25–27]. A generalized gradient approximation (GGA) in the form given by Perdew, Burke and Ernzerhof [28] was employed for exchange–correlation and ultrasoft pseudopotentials [29] were used for the core–valence interactions. All calculations were carried out as spin-polarized. For the Brillouin-zone integrations, Monkhorst–Pack k-point meshes of  $6 \times 10 \times 1$  for the  $\Sigma 3$  and  $4 \times 8 \times 2$  for the  $\Sigma 5$  were used. For supercells without H, both ionic positions and cell vectors were relaxed. In supercells containing H atom, the dimensions were kept fixed (identical to the corresponding supercells without H) and only the ionic positions were relaxed.

The investigated GBs are characterized by the GB energy calculated as

$$\gamma_{GB} = \frac{E_{GB} - E_{bulk}}{2A}, \quad (1)$$

where  $E_{GB}$  is the total energy of the supercell containing the GB,  $E_{bulk}$  is the total energy of bulk Ni crystal with the same number of atoms, and  $A$  is the interface area of one GB in the supercell (the factor of two in the denominator takes into account that there are two identical GBs in the supercell). Lower values of  $\gamma_{GB}$  generally indicate a stronger cohesive bonding between the two grains in contact. Another useful parameter characterizing the GBs is the associated excess volume per one GB in the supercell defined as

$$\Delta V = \frac{V_{GB} - NV_{Ni}}{2}, \quad (2)$$

where  $V_{GB}$  is the total volume of the supercell containing the GB,  $N$  is the number of atoms in the supercell, and  $V_{Ni}$  is the volume per atom of bulk Ni. Larger values of  $\Delta V$  indicate a more open GB structure, while smaller values indicate a more compact GB structure.

The efficiency of a GB to trap H atoms is quantified by the segregation energy,  $E^{seg}$ , defined as

$$E^{seg} = E_{GB}^{sol} - E_{bulk}^{sol}, \quad (3)$$

where the  $E_{GB}^{sol}$  and  $E_{bulk}^{sol}$  are the solution energies of H segregated at the GB and in the middle of the grain (in the same supercell), respectively. The solution energy for an H atom at a site  $x$  is defined as

$$E_x^{sol} = E_{x+H} - E_x - \frac{1}{2}E_{H_2}, \quad (4)$$

where  $E_{x+H}$  is the total energy of supercell containing H,  $E_x$  is the total energy of the same supercell without H, and  $E_{H_2}$  is the energy of an isolated  $H_2$  molecule. With these definitions, negative values of the solution energies indicate that it is energetically more favorable for H to be dissociated and absorbed in Ni, while negative values of the segregation energies imply a preferable segregation of H at the GB.

## 3. Results

### 3.1. H in bulk Ni

As a reference, we first computed properties of bulk Ni in its face-centered cubic (fcc) equilibrium structure as well as H solution energies and migration barriers in a large bulk supercell containing 32 Ni atoms. The equilibrium lattice parameter of 3.53 Å for fcc Ni is in good agreement with other theoretical and experimental data [17,11]. The calculated solution energy for H occupying an octahedral interstitial site in the large supercell amounts to 0.084 eV, similar to values obtained in other computational studies [11,30,31]. The migration of an H atom between two neighboring octahedral sites proceeds via an intermediate metastable tetrahedral site (see Fig. 4(a)). The calculated energy barrier associated with the jump was found to be 0.37 eV without mechanical effects [32,33]. This result closely agrees with results of previous calculations [34,35]. We investigated in detail the influence of quantum corrections [2,32,34–36] using the semi-classically corrected transition state theory [37,38] and found that these corrections are relatively small for Ni and do not affect the results presented here. This investigation will be reported elsewhere [39].

### 3.2. Structure of the $\Sigma 3(111)[\bar{1}10]$ GB

The  $\Sigma 3$  GB supercell consists of an orthorhombic cell with 24 Ni atoms and contains two GBs separated by five atomic (111) layers. The relaxed GB structure is shown in Fig. 1, the corresponding supercell dimensions and the GB energy are given in Table 1. The first-nearest-neighbor distances between Ni atoms in the vicinity of the GB deviate less than a half percent from the bulk value of 2.50 Å indicating that the atomic arrangement at the interface is only slightly distorted. This is not surprising, since the presence of this twin interface only alters the stacking of the close-packed (111) planes. As a result, the  $\Sigma 3$  GB has a negligible excess volume (see Table 1), and the calculated GB energy of 0.18 J/m<sup>2</sup> is very small in comparison with typical GB energies values [40].

### 3.3. Structure of the $\Sigma 5(210)[001]$ GB

The orthorhombic supercell of the  $\Sigma 5$  GB contains 40 Ni atoms distributed on 10 atomic (210) layers. Previous studies [15,17,41] have shown that this supercell is sufficiently large to avoid spurious interactions between two GBs. The relaxed GB structure is shown in Fig. 1, additional characteristic data are listed in Table 1.

In contrast to the  $\Sigma 3$  GB, the local atomic and electronic structure of the  $\Sigma 5$  GB is significantly different with respect to the bulk interior. In order to visualize these differences, we plot several cross sections showing the valence electron densities in the  $\Sigma 5$  supercell in Fig. 2. In the central (bulk) part of the supercell (see the cross section in Fig. 2b), the regions of the lowest electron density are located at the ordinary octahedral interstitial sites in bulk Ni. In contrast, much larger regions of low electron density are present along the GB plane (see Fig. 2a and c). We refer to these

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