Hydrogen migration modeling in a symmetric tilt boundary of the Iron-Chromium system

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ABSTRACT

Previous experimental studies of H permeation in 9%Cr-Fe alloys have found a permeation coefficient 10 times lower and a diffusion coefficient 200 times lower than in pure annealed Fe. In an effort to shed some light on the microscopic origin of these findings, we perform an extensive study of Fe, Cr, and H migration in a high-angle symmetric tilt grain boundary in bcc Fe, both via vacancy and interstitial mechanism. This is undertaken in the framework of transition state theory with the relevant energies obtained from classical interatomic potentials, and partially from Density Functional Theory calculations, in order to check the consistency of structures. Trapping sites for H and possible migration paths are explored. We find that the presence of Cr and its migration via vacancy and interstitials creates the conditions in produce stable preferential trapping sites for H in the grain boundary, that delay the H migration, thereby explaining the experimental results.

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1. Introduction

9Cr steels such as T9 are mainly used in tubes of steam generators for conventional thermal power plants. This is due to their excellent mechanical properties at operating temperatures, particularly creep resistance and corrosion resistance in water and steam systems. The material does not suffer H damage under normal operating conditions, however, it may be susceptible to H embrittlement when cooled to room temperature during plant stops.

Also, T91 has been (and partly still is) candidate material for core-components in GenIV reactors, while Eurofer and other reduced-activation Ferritic/Martensitic (F/M) steels (also containing 9%Cr) are the candidate structural materials for future fusion reactors.

Besides the H problem, also of concern for the nuclear applications envisaged for these steels, is the radiation-induced segregation (RIS) phenomena at GBs, exhibited by steels while in-service. Little is known about the mechanism behind RIS in F/M steels. The current understanding of RIS in F/M steels consists of a mechanism where point defects migrate to GBs acting as perfect sinks.

The properties and applications of the 9−12%Cr steel family have been the subject of numerous reviews [1−3]. The usual heat treatment at temperatures between 1050 and 1060 °C, followed by air cooling, results in a martensitic structure of slats. Subsequent tempering between 750 and 780 °C (i.e. substantially higher than the operating temperature) [4,5], strengthens the material against H attack; it has been found that such a treatment produces abundant traps for H. From the microscopic point of view, 9Cr steels are expected to show conventional H trapping, ascribed to microstructural defects (grain boundaries, dislocations, carbides, etc), as well as effects from Cr, the main minority component of the metallic matrix.

In previous works [6,7] we have studied the diffusion and trapping of H in T9 steel membranes. The H permeation method with gas phase charging and electrochemical detection was employed, at temperatures ranging from 30 to 70 °C. The steel was studied in three different metallurgical conditions: as received (quenched and tempered), annealed (775 °C, 4 h), and quenched (950 °C, 40 min, air cooling), and the respective microstructures were assessed by means of optical and scanning electron microscopy. The nature of the H traps was discussed in Refs. [6,8−10], and their density was inferred from the temperature variation of the apparent diffusion coefficient given by the permeation tests. In particular, a permeation coefficient 10 times lower and a diffusion

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coefficient 200 times lower than in pure, annealed Fe, were found [6]. Also, it was observed that the trap density first increases as the annealing temperature increases from standard metallurgical state, reaching a maximum for a tempering temperature of 500 °C; further temperature increase results in trap density decrease [6]. Against the expectations, the density of traps does not correlate with either the hardness of the material or the width of X-ray diffraction peaks, suggesting that the role of dislocations as traps is secondary [6]. Apparently, the presence of substitutional Cr causes a change in the matrix, making dislocation trapping less important. Electron microscopy reveals that the different thermal treatments obtain carbonitrides in the form of submicron, coherent, second phase particles [11,12], which are likely candidates to behave as H traps. The latter hypothesis is also supported by ab-initio calculations [7].

Concerning grain boundaries, Du et al. [13], have performed a recent study of H diffusion in idealized grain boundaries of bcc Fe, as well as in the Σ5 grain boundary that is also the focus of this work. These authors have shown that the overall diffusion is a result of a complex jumping network, whose outcome depends on temperature, direction, and H concentration. A partial aim of the present investigation is thus a careful examination of the microscopic processes involved and a comparison with the results of that work.

Concerning the bulk of bcc Fe, Hayward and Fu [14] studied the behavior and interactions of hydrogen and vacancies in body centered cubic (bcc) iron, using both ab initio and classical molecular dynamics methods, considering corrections for Hydrogen zero-point energy (ZPE). They have studied the role of Hydrogen materials damage in terms of embrittlement, hardening, and swelling; investigating the role of vacancies in these processes, as well. Hydrogen, which normally diffuses with a very small barrier, is strongly trapped at monovacancies and vacancy clusters that typically form under irradiation, resulting in changes to its electronic structure.

All the above considerations motivate our present study of the Σ5 GB structure, taken as a prototype, starting point, to model H trapping in Fe. The final goal is to provide some qualitative results concerning H migration mechanisms in the Σ5 GB that also contains Cr. However, before dealing with such a complex system, we must understand first Fe and Cr migration, as well as H migration in this GB, separately from the mechanisms that delay H diffusion; to such a task is devoted the current contribution. In particular, we outline a simple model of H trapping and study possible migration paths in the above GB, deemed to be pertinent to the experimental observations.

The work is organized as follows. In Section 2 the details of the calculation methodology are given. From Section 3 on, the results of an extensive study of Fe, Cr, and H, migration in the $\Sigma = 5(310)[001]$ grain boundary are reported; Section 3 itself is Section 4 to H. In Section 5, the binding energies of mixed defects including H and Cr simultaneously, are reported. Finally, in the closing Section 6 some conclusions are advanced. One Appendix is devoted to the study of H and Cr in the bulk of bcc Fe.

2. Calculation methodology

Most calculations are performed with the molecular statics technique (MS), implemented in an in-house code, provided with suitable interatomic potentials for the Fe-Cr [15] and Fe-H [16] systems. Both local energy minima and energy barriers are obtained, the latter via the Monomer method developed in Ref. [17]. Electronic structure Density Functional Theory (DFT) calculations are also performed, but only for energy minima; besides, due to the lack of interatomic potentials for the ternary Fe-Cr-H, this is the

only kind of calculations carried out in section 5, where such a system is considered. The reason behind this parallel approach is to use the relatively cheap MS technique to probe for possible non trivial defect structures that may develop in the GB, while checking their consistency with the more fundamental DFT technique. We use DFT as implemented in the freely available code SIESTA [18], which is based on pseudopotentials and numerical, atomic-like, basis functions.

The pseudopotential and basis for Fe are according to Ref. [19]. Pseudopotentials for Cr and H were downloaded from SIESTA's home page, and the corresponding bases were automatically generated using the code itself; a few tests indicated that no significant differences in results appeared when varying parameters for basis generation within reasonable ranges. In this context, a note regarding H is in order, namely, several bases were tried and we found that the so called TZDP with a split norm parameter of 0.5 is the accurate one that most efficiently relaxes the GB containing H.

The basic Σ5 GB structure is build in a slab-type geometry, with the GB parallel to the (x, y) plane defined by axis $\hat{x} = [301]$, and the tilt axis $\hat{y} = [010]$; moreover, enough atomic planes are stacked along axis $\hat{z} = [10\bar{3}]$ such as to minimize the effects of the free surfaces. Strictly, this description refers to the top half-grain, $z > 0$, the bottom one being its mirror image. Besides, the simulation crystallite includes some empty space along axis $\hat{z}$ in order to avoid interaction between z-periodic images. In summary, the GB is characterized by the number of in-plane periodic images, $(N_x \times N_y)$, and the number of planes N_z, above and below (but excluding) the contact plane. Fig. 1 depicts a schematic view along the tilt axis of the Σ5 GB for the case $N_x = N_y = 1, N_z = 2$.

Classical MS simulations are carried out only for a single size GB, whereas two, fairly smaller, sizes are tried with the costlier DFT. Table 1 summarizes the geometric parameters used, also reported is the GB formation energy obtained in each case, E_f^{GB}. The latter is calculated as,

$$E_f^{GB} = [E_3 - E'_3] \frac{1}{S_3} - [E_2 - E'_2] \frac{1}{S_2} \,, \tag{1}$$

where E_3 (E_2) refers to the energy of a slab with (without) a GB in the middle, containing N_3 (N_2) atoms in total, and exposed surface area S_3 (S_2). E'_3 (E'_2) stands for the same concept but referred to the perfect lattice; the purpose of the second term is to cancel the contribution of the (double) free surface. In the case where the GB has not any exposed free surface, Eq. (1) reduces to the first term, and E_f^{GB} is calculated as usually.

A last detail worth of note is that MS and DFT calculations employ their respective equilibrium lattice parameters, namely, 2.855 Å and 2.885 Å.

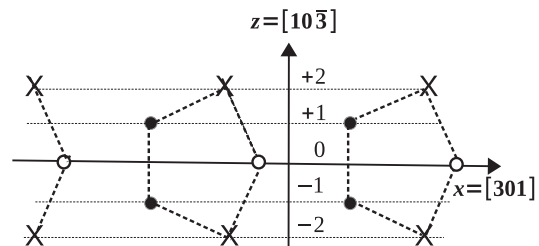For the bulk, we use a $7 \times 7 \times 7$k-points mesh (which

Fig. 1. Schematic cross section perpendicular to the tilt axis, $y = [010]$. Symbols ●, ○ and ×, denote atoms at planes n with n = 0, 1 and 2, respectively. Only the GB core is shown; y heights of symbols differ in half lattice parameter; so called structural units are remarked for purposes of later reference.