Computational Materials Science 97 (2015) 276–284

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Effects of grain-boundary networks on the macroscopic diffusivity of hydrogen in polycrystalline materials

B. Osman Hoch *, A. Metsue, J. Bouhattate, X. Feaugas

Laboratoire des Sciences de l'Ingénieur pour l'Environnement, LaSIE UMR CNRS 7356, Bat. Marie Curie, Av. Michel Crepeau, 17042 La Rochelle, France

ARTICLE INFO

Article history:
Received 31 July 2014
Received in revised form 9 October 2014
Accepted 25 October 2014
Available online 18 November 2014

Keywords:
Hydrogen
Grain-boundary network
Effective diffusivity
Clustering
Connectivity

ABSTRACT

The diffusion heterogeneities of grain boundaries are known to affect the effective diffusivity in polycrystalline materials. However, the correlation between both has not been clearly established. In this work, the influence of the grain boundary topology and connectivity on hydrogen effective diffusivity was investigated, for membranes with different grain sizes. We modeled a polycrystal in two dimensions, as a composite containing three phases, one for the grains and the others for grain boundaries. These phases are characterized by their diffusion coefficient, with a contrast of six orders of magnitude between grain boundaries of different character and three between grains and grain boundaries. The path length and correlation length of high diffusivity boundaries were statistically characterized. We found three different behaviors of the effective diffusivity depending on the grain-boundary networks structure. We observed two linear regimes between the connectivity parameters and the effective diffusivity, and a percolated regime. We quantitatively analyzed the impact of the grain-boundary network structure on the variation of the effective diffusivity, in the two first regimes.

1. Introduction

Hydrogen embrittlement (HE) is a serious problem affecting the durability of structures materials and can cause catastrophic failures such as in offshore structures and pipelines. This phenomenon has been studied for several decades, but it is still difficult to formulate a general theory of HE due to its complexity and the lack of consistent and comprehensive studies on the interaction between hydrogen and metals. It was pointed out that the kinetics of HE are controlled by the hydrogen diffusion mechanisms [1,2]. In polycrystalline materials, grain boundaries (GB) have a strong influence on the transport and segregation of hydrogen and are therefore critical in the mechanisms of fracture [3–8].

The acceleration of hydrogen diffusion along grain boundaries has been highlighted in several studies [9–12]. However, it has been suggested that only some boundaries represent fast diffusivities paths, depending on their configuration and energy [11,13–17]. GBs are generally classified using their coincidence index Σ which is defined as the reciprocal density of coincidence sites between the two lattices at the boundary plane. Random boundaries, with $\Sigma > 29$, are generally considered to contribute to GB diffusion acceleration. Several studies pointed out that the macroscopic effect of this acceleration can be compensated by the trapping phenomenon in dislocations cores that are present in some grain boundaries [11,15]. Indeed, special GBs (with $\Sigma < 29$) may represent source of trapping effect for hydrogen [11]. In a recent experimental study on pure nickel, conducted by Oudriss et al. [11] it has been shown that a high proportion of special boundaries leads to an increase in the density of trapping sites. Pedersen and Jónsson [15] confirmed, in a numerical analysis at the atomic scale, that because of trapping, the hydrogen diffusion at GBs is reduced by more than one order of magnitude compared in the crystal. This dual effect of GBs may explain controversial interpretations and conclusions found in the literature on the grain boundary influence on hydrogen diffusion. In term of GB fracture, it has been shown by Bechtle et al. [18] that the increase of fracture sensitivity depends on the different fractions of special boundaries.

For a better analysis of the grain boundary effect, another important parameter is the grain-boundary character distribution (GBCD) [3]. The control of GBCD, which is achieved by increasing the population of special boundaries, is generally used in order to improve the mechanical properties of polycrystalline materials [5,19–21]. However, most of these studies only focused on measuring the relative area of different types of boundaries. Few of them tried to correlate grain boundary connectivity with the properties of materials [22–26]. Mathematical percolation tools have been frequently used to quantify GB connectivity by using binary classification of boundaries [25–29]. Chen and Schuh [23] proposed a

* Corresponding author.

http://dx.doi.org/10.1016/j.commatsci.2014.10.048
0927-0256/

composite model, with two types of boundaries, that predict effective GB diffusivity in connection with GB network structure. Their approach, by neglecting lattice diffusion, is limited to Harrison type-C kinetics diffusion [30]. However, in real materials, it is rarely possible to separate the GB diffusion from lattice diffusion [31].

The purpose of this paper is to examine the influence of GB networks on the macroscopic diffusion coefficient, obtained by permeation tests [32]. To do so, we have developed a composite model that contains a grain phase and two types of boundaries (special boundaries with low diffusivity and "random" boundaries with high diffusivity). We characterized the structure of the GB networks, by determining the topology and connectivity parameters. Then the effective diffusivity was correlated with these parameters.

2. Methodology

2.1. Simulation procedures

To study hydrogen diffusion through a metallic membrane, electrochemical permeations tests were simulated, using the FEM software Comsol Multiphysics©. This experimental procedure was first introduced by Devanathan and Stachurski in 1962 [32]. The device used in electrochemical permeations experiments is mainly composed of two cells: the charging cell (source of hydrogen) and the detection cell, separated by a metallic membrane. The goal is to measure the hydrogen flux at the exit side of the membrane and deduce its effective diffusivity. The details of hydrogen permeation tests can be found in the literature [11,32,33]. A 2D polycrystalline microstructure was modeled with a periodic hexagonal lattice. The modeled microstructure is composed of grains surrounded by grain boundary phases (Fig. 1). For computational convenience, it was considered necessary to define a representative volume element (RVE) of the macroscopic heterogeneous microstructure. Fig. 1 illustrates the heterogeneous macroscopic composite with clusters of random GB and the microstructural RVE. The defined RVE is characterized by the self-similarity of GB clusters at different scales. Secondly the microstructural RVE has the same effective diffusivity as the macroscopic membrane. According to our previous work [34], the ratio between the RVE membrane size e_m and the grain size λ, is taken high enough to avoid the membrane size effects. In the literature, there is not a unique value for the grain boundaries thickness (e_{gb}) because it is closely connected to the crystallographic properties of the boundary such as the misorientation [35,36]. The commonly used value is 1 nm or less [9,37,38]. This value is purely geometric. However, it has been shown the existence of chemically altered zone around the GB, in relation with short-and long-range elastic strain fields and solid segregation gradients [39,40]. This strained/distorted region around the structural grain boundary corresponds to the zone of enhanced diffusion rate or the "segregational" zone. It was found that the thickness of this effective zone could reach values up 5 nm [41]. According to this definition and for computing convenience, we assume a thickness of grain boundary e_{gb}, of 5 nm in our model. The grains phase was meshed by triangle elements and the GB phase by a quadrilateral elements. The mesh was refined near the GB phase and a minimum of two elements has been imposed on the thickness of every GB. The total number of elements varies with the considered grain size. For the highest contrast between GB thickness and the grain size, a total number of 4.245.000 elements was reached.

The grain boundary character, i.e., the grain boundary diffusivity, is randomly distributed. Each GB was assigned either a high diffusion coefficient D_R, with a given probability f_R, or low diffusion coefficient D_Σ, otherwise. The subscripts R and Σ are associated respectively with random and special boundaries. The Mersenne twister algorithm implemented in Matlab has been used as a random number generator [42]. For simplicity, we consider that the diffusivity of a triple junction is determined by the types of GBs surrounding it. For instance, a triple junction surrounded by at least two random GBs, is assigned a high diffusivity D_R. To simulate hydrogen permeation tests, we impose a constant hydrogen concentration C_0 at the entry side of the membrane, and zero at the exit side. A non-flux boundary condition is applied on the lateral sides. The classical Fick's equations (Eq. (1)) are implemented in each node of the meshing, with a diffusion coefficient D_i, depending on the phase:

$$\frac{\partial C}{\partial t} = \nabla(D_i \nabla C) \tag{1}$$

As we are considering 2D model, the concentration gradient in the third direction is null. Using the analytical solutions of Fick's equations, the effective diffusion coefficient D_{eff} can be determined from the flux curve, by Eq. (2) [32,43]:

$$D_{eff} = \frac{J_{\max} \times e_m}{15.12 \times t_B} \tag{2}$$

where $J_{\max}$ is the steady state flux and t_B is the breack-through-time which is the time required for the flux to reach 10% of the steady state flux $J_{\max}$.

The computations are performed on a membrane containing 40×20 grains which is equivalent to 2400 GBs. The length scale of the model is defined by the grain size, which varies from 20 nm to 500 nm. The parameters of the model are summarized in Table 1. Values of diffusion coefficients D_L and D_R are taken from Ref [10]. D_Σ value was deduced from experimental effective

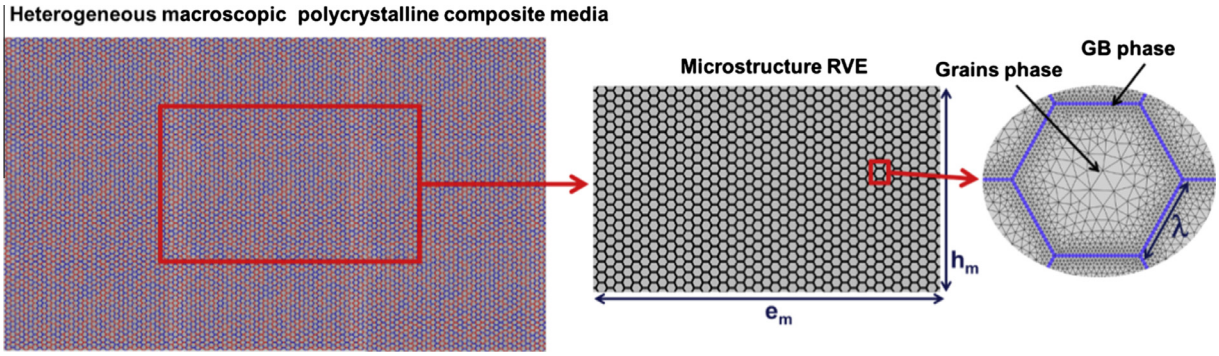

Fig. 1. Heterogenous polycrystalline composite media (random GB in red and Special GB in blue) and the microstructure RVE, e_m and h_m are the thickness and height of the microstructure RVE and λ the grain size. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)