

## ДЕФЕКТЫ КРИСТАЛЛИЧЕСКОЙ РЕШЁТКИ

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### Hydrogen Grain Boundary Segregation and Migration in the Alpha-Iron

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Based on the difference in diffusion mechanisms of substitutional and interstitial atoms and using molecular dynamics simulation of hydrogen migration, it is shown that accelerated hydrogen flux in the polycrystalline iron observed during cathodic charging cannot originate from the enhanced hydrogen grain-boundary diffusion. A possible role of grain-boundary cracking is supposed.

**Key words:** hydrogen diffusion, grain boundaries, molecular dynamics simulation.

Ґрунтуючись на відмінностях механізмів дифузії атомів заміщення та втілення і використовуючи молекулярно-динамічні розрахунки міграції атомів Гідрогену, показано, що прискорений потік водню в полікристалічному залізі, який спостерігається в процесі катодного наводнення, не може бути наслідком прискореної зерномежової дифузії водню. Розглядається можлива роль зерномежового розтріскування.

**Ключові слова:** дифузія водню, межі зерен, молекулярна динаміка.

Основываясь на отличиях механизмов диффузии атомов замещения и внедрения и используя моделирование методом молекулярной динамики миграции водорода, показано, что ускоренный поток водорода в поликристаллическом железе, который наблюдается в процессе катодного наводнения, не может быть следствием ускоренной зернограницной диффузии водорода. Рассмотрена возможная роль зернограницного растрескивания.

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**Ключевые слова:** диффузия водорода, границы зёрен, молекулярная динамика.

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## 1. INTRODUCTION

The enhanced grain boundary hydrogen permeation has been a topic of many experimental studies since the eighties, *e.g.* [1–6]. A feature of those studies was a huge scattering of the enhancement ratio in relation to bulk permeation, *e.g.*, in the experiments with hydrogen-charged nickel, it was constituted as 2 [5], 2 to 7 [6], 8 to 17 [4], 60 to 100 [3]. At the same time, the enhanced hydrogen migration along the grain boundaries was not confirmed in [7, 8], and moreover, the opposite results were obtained in [9, 10].

Recently, Koyama *et al.* [11] have studied hydrogen location throughout the surface of a hydrogen-charged polycrystalline iron using a technique of silver decoration earlier developed in [12–16]. In contrast to previous studies, silver decoration was used directly in the course of hydrogen permeation. Hydrogen visualization was needed to correlate the cracking events with presence of local hydrogen because, as it is claimed by the authors [11], ‘the factors causing the cracking are preferential diffusion and the segregation of hydrogen on or in the vicinity of the grain boundaries’.

Three main results were obtained using hydrogen visualization by means of silver decoration of hydrogen atoms:

- (i) a significant delay, 30 min against 20 s, in comparison with the calculated time for hydrogen permeation through the full thickness of the specimen;
- (ii) the difference in hydrogen diffusivity between grain boundary and grain interior is claimed to be small compared to the absolute value of bulk diffusivity;
- (iii) the permeated hydrogen atoms are located preferentially at the grain boundaries, and, based on this observation, it is claimed that grain boundaries are the sites with maximum hydrogen flux, which is in consistency with experimental data in [1–6] and at variance with the data in [7–10].

The aim of this paper is to discuss the interpretation of the above-mentioned experimental data about the hydrogen grain-boundary migration in comparison with a computer modelling using molecular dynamics.

## 2. MODELLING

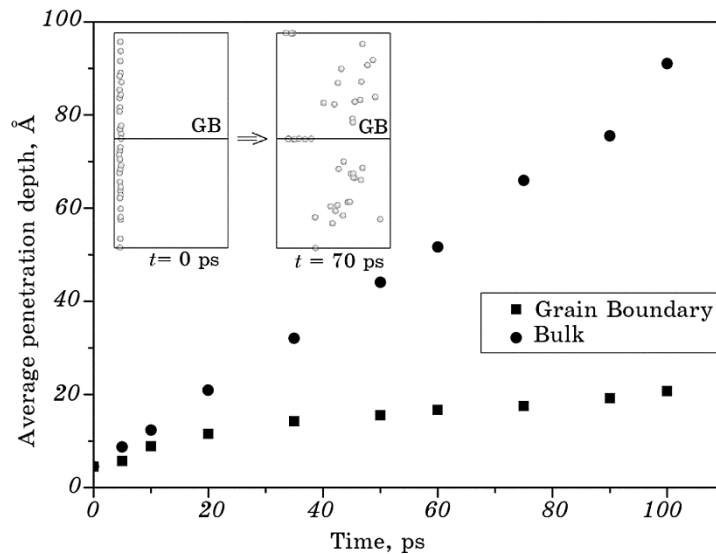
To simulate the hydrogen permeation process, a single crystal of pure

iron having the b.c.c. structure and dimensions of about  $90 \times 180 \times 85 \text{ \AA}^3$  was constructed with crystallographic orientations  $\langle 100 \rangle$ ,  $\langle 010 \rangle$  and  $\langle 001 \rangle$  (see about details [17, 18]).

The symmetric tilt grain boundary  $\Sigma 5(310)[001]$  was generated within the framework of the coincidence site lattice (CSL) theory [19, 20]. The grain boundary plane was created orthogonal to the surface along  $\langle 100 \rangle$  crystal orientation. Initially, the hydrogen atoms were homogeneously distributed on the crystal surface along  $\langle 010 \rangle$  crystallographic axis, *i.e.* orthogonal to the grain boundary plane.

In the course of experimental measurements of hydrogen permeation, the electric potential is always applied to create a hydrogen flux in a sample. To realize the same condition for simulations, an additional force was applied to all hydrogen atoms along the  $\langle 100 \rangle$  axis. The value of this force should satisfy two requirements: (i) it should provide the movement of hydrogen atoms along the force direction, instead of random walk; (ii) the energy created by this additional force component should not significantly exceed the activation enthalpy of hydrogen migration, otherwise the difference between the hydrogen movement in the bulk and in the grain boundary will be hidden. The temperature of simulation was equal to 300 K.

The result of simulation of hydrogen permeation in the iron crystal containing the grain boundary  $\Sigma 5(310)[001]$  is presented in Fig. 1. Starting from the homogeneous distribution of hydrogen atoms on the



**Fig. 1.** Molecular dynamics simulation of hydrogen penetration in the  $\alpha$ -iron crystal with  $\Sigma 5(310)[001]$  special grain boundary. Initially, the hydrogen atoms were homogeneously distributed on the surface of the simulated crystal. A representation of hydrogen atoms redistribution is given in the insert.

one side of the crystal, the concentration profile is being significantly modified with time. As it is seen, the average penetration distance of hydrogen atoms in the grain boundary is smaller than in the bulk, which is the evidence of retarded hydrogen migration along the grain boundaries.

At the same time, separate calculations of activation enthalpy of hydrogen migration have been carried out for three grain boundaries,  $\Sigma 5(310)[001]$ ,  $\Sigma 17(410)[001]$  and  $\Sigma 25(710)[001]$ . The obtained results are presented in Table 1. The data for the enthalpy of bulk hydrogen diffusion are in a perfect consistency with the experimental activation enthalpy obtained in [21, 22], whereas the activation enthalpy for hydrogen diffusion along the grain boundaries is always higher in comparison with that of bulk diffusion.

### 3. DISCUSSION

First, it is worth noting that the calculations of the expected hydrogen permeation in their experiment were performed by the authors of [11] for the bulk migration of hydrogen atoms, which ignores the existence of grain boundaries. Therefore, the delay in hydrogen visualization observed in [11] can be interpreted as an indirect evidence for retarded hydrogen diffusion due to grain boundaries.

Second, in their statements concerning hydrogen diffusivity at grain boundaries and in the grain interior, the authors [11] proceed from the data by Hagi *et al.* [16] where the bulk diffusivity of hydrogen in the pure iron is claimed to be independent of the existence of grain boundaries at ambient temperature.

However, the rate of hydrogen permeation through a membrane of certain thickness is obtained in [16] as a solution of the diffusion equation given by Fick's second law. The diffusion coefficient is then derived due to application of theoretical results to experimental measurements of hydrogen permeation. Such an approach could be correctly applied only to the case of hydrogen diffusion in single crystals, which

**TABLE 1.** Characteristics of grain boundaries and their contribution to hydrogen migration, according to molecular dynamics calculations.

Type of grain boundary	Misorientation angle, $\Theta^\circ$	Energy, $\text{mJ/m}^2$	Activation enthalpy for hydrogen migration, eV
Bulk			$0.037 \pm 0.004$
$\Sigma 5(310)[001]$	36.87	1073	$0.314 \pm 0.017$
$\Sigma 17(410)[001]$	28.07	1102	$0.341 \pm 0.011$
$\Sigma 25(710)[001]$	16.26	1023	$0.244 \pm 0.001$

is confirmed by a reasonable agreement with the experimental data. The application of the same model to polycrystalline samples needs to take into account the segregation factor because of the well-known affinity of hydrogen atoms with the grain boundaries. Such a correction has not been done in [16]. With this correction, the diffusion coefficient in the polycrystalline iron should be smaller than in the single crystal.

Furthermore, the Arrhenius curve  $D$  vs.  $1000/T$  for hydrogen in the polycrystalline iron is obtained to be nonlinear in [16] and such behaviour has been attributed to a trapping effect of grain boundaries at temperatures below 298 K. This interpretation is not convincing because the segregation factor is temperature dependent and the nonlinear behaviour of the Arrhenius curve, as observed by the authors, results from the absence of the above mentioned segregation parameter in the determination of the diffusion coefficient in polycrystalline iron.

Third, the existing models for the analysis of experimental data on the grain boundary migration of solute atoms are traditionally based on the concept that grain boundaries are the fast diffusion path (see *e.g.*, [23–25]). The theory used in these models was developed for the case of vacancy migration, which is applicable only for the substitutional atoms.

In addition, it is obvious that this mechanism can be hardly operative for the interstitial atoms in the solid solutions. Furthermore, the hydrogen atoms form complexes with vacancies, see *e.g.* [26] for carbon and [27] for hydrogen in the  $\alpha$ -iron, which reduces their mobility because the binding energy in the hydrogen–vacancy complexes should be added to the migration enthalpy.

On the other hand, because of a strong hydrogen affinity with the grain boundaries, the observed increased concentration of hydrogen at grain boundaries, *i.e.* that of silver dots in [11], cannot depend on the difference between the rates of hydrogen migration in the bulk and along the grain boundaries.

Indeed, after reaching the grain boundary, the hydrogen atom can leave it only if some additional energy can be spent to overcome the enthalpy of its binding to the grain boundary. For this reason, whatever hydrogen migration is accelerated or retarded at the grain boundaries, each hydrogen atom migrating in the bulk and intersecting the grain boundary will further preferentially migrate along it and the hydrogen content at grain boundaries is expected to increase with increasing distance from the bottom surface of the charged sample, as well as with decreasing grain size.

Therefore, the experimentally observed increase in the number of silver dots at the grain boundaries, *i.e.* the higher fraction of hydrogen atoms migrating along them, has no relation to accelerated as well as to

retarded hydrogen diffusion in the vicinity of grain boundaries.

Moreover, be captured by the grain boundaries, the hydrogen atoms are expected to possess a limited diffusivity because of smaller distortions in the crystal lattice and corresponding disappearance of the elastic term in the gradient of chemical potential as a driving force for diffusion.

One can suppose the following reason for the enhanced hydrogen flux along the grain boundaries observed in the above quoted studies [1–6]: all of them are carried out using electrolytic hydrogen charging. The point is that electrolytic charging is accompanied by a significant plastic deformation, which is confirmed, *e.g.*, by a strong crystallographic texture in the hydrogen-charged austenitic steels [28]. In the course of this deformation, due to hydrogen segregation at the grain boundaries and the corresponding large local stresses, they are expected to be the most probable sites for opening of cracks. If so, molecular hydrogen recombination in these cracks with alternating repeated dissociation and subsequent migration along the grain boundaries is expected to result in the enhanced hydrogen transport, which, in fact, is observed in the experiment.

The cracking along the grain boundaries in the electrolytically charged austenitic steels was demonstrated, *e.g.* in [29]. At the same time, the observations of the cracks opening during electrolytic charging and its absence in case of the gaseous hydrogenation are rather old. In the sixties, they have given a critical argument against the pressure-expansion hypothesis for hydrogen embrittlement of which the essence was the precipitation of gaseous hydrogen in pre-existing microvoids and their growth under increased internal hydrogen pressure (see, *e.g.* [30, 31]. However, as was shown in [32], despite on the absence of cracks, the gaseous hydrogen of 1 bar pressure caused a greater embrittlement of high strength steels in comparison with electrolytic charging.

Therefore, one can give a noncontradictory interpretation of the apparent increased hydrogen flux along the grain boundaries, which is consistent with fundamental ideas for diffusion mechanisms of interstitial atoms in the metal solid solutions.

#### 4. CONCLUSIONS

1. Using molecular dynamics simulation of hydrogen permeation in the  $\alpha$ -iron having a grain boundary and based on the calculated values of enthalpy of hydrogen diffusion along grain boundaries, it is shown that migration of hydrogen atoms along the grain boundaries is retarded in comparison with that in the bulk.
2. The accelerated hydrogen flux through the polycrystalline iron, as observed in the experiments with electrolytic hydrogen charging, can

be related with the hydrogen-caused cracking at the grain boundaries.

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