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Grain boundary carbides as hydrogen diffusion barrier in a Fe-Ni alloy: A thermal desorption and modelling study



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HIGHLIGHTS

- Grain boundary carbides significantly reduce hydrogen absorption in a Fe-Ni allov.
- A diffusion model accounting for grain boundary diffusion was developed.
- The model was used to predict and interpret the absorption behaviour in experiments.
- Carbides act as obstacles for otherwise fast diffusion along grain boundaries
- It was shown that the model can be applied more generally to diffusion in Ni alloys.

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GRAPHICAL ABSTRACT



ABSTRACT

A significant decrease in hydrogen absorption in the presence of grain boundary carbides compared to the carbide-free microstructure in the Ni-based HR6W alloy was measured by thermal desorption analysis (TDA). This novel observation is at odds with numerous existing reports - precipitate-rich microstructures generally absorb more hydrogen due to trapping effects. This discrepancy can only be explained by grain boundary diffusion which is known to be fast in Ni-based alloys. It is proposed that grain boundary diffusion is hindered by carbides, resulting in decreased hydrogen absorption. Further experimental evidence corroborates the hypothesis. In addition, a diffusion model was developed to quantify the experimental results, incorporating trapping, grain boundary diffusion and temperature effects. It was successfully applied to the reported TDA data as well as additional diffusion data from the literature. A parametric analysis showed that hydrogen absorption scales strongly with grain size and grain boundary diffusivity while grain boundary segregation energy has a much lower impact. The results of the study point at grain boundary precipitation as a possible means of hydrogen embrittlement mitigation in Ni alloys and austenitic stainless steels.

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1. Introduction

Hydrogen is known to cause a range of issues in high hydrogen fugacity service conditions in thermal power plant components made of Ni alloys such as boilers, pipes for high-pressure steam and nuclear reactors [1]. Reported effects include embrittlement, intergranular cracking, increased creep rates and decreased fatigue life [2-4]. Some of them, particularly hydrogen embrittlement, are strongly tied to grain boundary (GB) effects, such as locally accelerated diffusion and segregation as GBs are often fracture sites. Experimental work has shown that hydrogen diffusion along some types of GBs in Ni is at least two orders of magnitude faster compared to the bulk [5-9]. Similar evidence exists for austenitic steels, although the subject is less well documented [10-12]. However, the origin of the observed increase in the measured H diffusivity in polycrystals appears guite complicated as the diffusivity varies with GB geometry. Despite the large differences between different GB geometries, the net effect seems to be an increase in the effective hydrogen diffusivity [9], although its magnitude may vary (compare [9] to e.g. [5,6]). This difference is likely related to varying grain structure and the varying fractions of particular GB types.

Diffusion in Ni and Fe-Ni alloys is also significantly affected by the presence of precipitates, which act as trapping sites for hydrogen, reducing the rate of diffusion until the traps saturate or steady-state diffusion is reached. Electrochemical permeation has been broadly used to study trapping effects and the results invariably show a decrease in effective hydrogen diffusivity with increasing precipitate density as a result of trapping [13,14]. What is also evident from the data, however, is that the steady-state hydrogen flux is consistently higher in microstructures without GB precipitates. This cannot be explained by trapping effects as they do not play a role in steady-state diffusion. It can, however, be explained by a decrease in hydrogen diffusivity along GBs occluded by GB precipitates.

In this work we focus on this overlooked effect. The impact of GB carbides is studied with a combination of thermal desorption experiments and diffusion modelling. We present experimental data showing that the presence of GB carbides reduces hydrogen absorption in the studied Ni-based HR6W alloy. The effect cannot be explained using conventional diffusion models, in which the presence of hydrogen traps such as carbides invariably results in increased hydrogen absorption. Because of this, a new model incorporating the effect of GB diffusion is derived and successfully used to corroborate our hypothesis by reproducing the experimental results. Furthermore, to demonstrate its robustness, the model is successfully applied to the existing literature data to capture the effect of grain size on hydrogen permeation in pure nickel.

2. Material and experimental methods

The material used in this study was a Ni-Fe-Cr alloy, HR6W, with a high creep and oxidation resistance beyond 650 °C designed for use in ultra-supercritical conventional power plants. An FCC matrix which generally has higher barriers for the diffusion of substitutional atoms reduces their segregation at GBs and excessive growth of some types of brittle precipitates. The chemical composition of as received alloy is listed in Table 1. In comparison to common Nialloys, HR6W contains less nickel and more chromium. Tungsten is used for additional solid solution strengthening and is also involved in the precipitation of MC and Cr-based $M_{23}C_6$ carbides.

Samples were machined from a tube with an outside diameter of 38 mm and wall thickness of 8.8 m. To simulate the microstructures expected in HR6W components after different service times, the corresponding microstructures were prepared, studied previously in [15]. The aging treatments performed at 900 °C for 1 h and 10 h correspond to equivalent service times of 1820 and 18 200 h, respectively (see [15] for justification). To minimise surface oxidation, samples were sealed in quartz tubes filled with argon prior to aging.

2.1. Microscopy

The aged microstructures and the as-received microstructure were characterised using optical, transmission electron (TEM) and scanning electron (SEM) microscopy.

For optical microscopy and SEM, samples were mounted and then ground using standard metallographic techniques and electrochemically polished, followed by etching in a mixture of 10 ml HNO₃, 15 ml HCl and 15 ml ethanol. Optical microscopy was conducted on a Zeiss Axio Imager.M1m, while SEM examinations were carried out on a Zeiss Neon 40EsB CrossBeam microscope.

Thin discs for TEM imaging were manually ground to a thickness of approximately 100 μ m followed by electropolising in a Struers TenuPol-5 in a solution of 300 ml of HClO₄ and 1200 ml of ethanol. TEM was conducted with FEI Tecnai G20 TWIN microscope operated in the bright-field mode to acquire images of carbides and GBs.

2.2. Hydrogen charging and thermal desorption analysis

Cylindrical samples 8 mm in diameter and 20 mm in height were used for thermal desorption experiments. Prior to hydrogen charging, the samples were ground with a 1200 grit paper to remove oxides, spark-welded onto a stainless wire holder and ultrasonically cleaned in acetone for 1 min. The top and bottom of the cylinders and the wire holder were coated with non-conducting varnish to restrict hydrogen diffusion to the circumference of the sample to simplify the subsequent numerical simulations. The charging solution was a mixture of 21 of deionised water, 70 g of NaCl and 6 g of NH₄SCN as a hydrogen recombination inhibitor. A Gamry Interface 1000E galvanostat was used to charge the samples under a constant current density of 100 Am^{-2} for 96 h with a platinum coil used as a counterelectrode. After charging, the specimens were washed in deionised water, dried and stored in liquid nitrogen to prevent hydrogen effusion.

A thermal desorption rig connected to an Agilent 7890B gas chromatograph was used to perform thermal desorption analysis on hydrogen charged samples. The following procedure was used for all the tests: the test sample was removed from the liquid nitrogen container and ultrasonically cleaned in acetone for 1 min to heat the sample to room temperature. It was then transferred to the thermal desorption rig furnace, which underwent a purging cycle of 30 min before the start of the desorption experiment. During this time, some hydrogen was lost due to effusion which was accounted for during simulations.

Table 1	
Nominal chemical composition of HR6W.	

С	Si	Mn	Р	S	Cr	W	Ti	Nb	Fe	Ni
<0.1	<1.0	<1.5	< 0.03	<0.015	21.5-24.5	6.0-8.0	< 0.2	< 0.35	20-30	bal.



Fig. 1. The three microstructures investigated: a), d) and g) – as received, b), e) and h) – aged for 1 h, c), f) and i) – aged for 10 h.

3. Experimental results

The as-received microstructure consisted of a twinned, supersaturated FCC matrix with large primary MX precipitates with dimensions of up to $5\,\mu$ m in diameter which precipitated at GBs. The two aged conditions contained, apart from the MX precipitates, a large number of $M_{23}C_6$ carbides concentrated on grain and twin boundaries as well as on previous dislocations. They appeared more numerous near GBs, likely as a consequence of previous dislocation pile-ups there. The carbides on GBs were significantly coarser and slightly elongated, forming a continuous network. Very little precipitation occurred elsewhere in the microstructure. Fe₂W Laves phase precipitates, which may also form in this alloy, were not observed [15]. Secondary electron SEM images and TEM micrographs of the investigated microstructures are depicted in Fig. 1. It can be seen that both aged conditions are nearly identical.

The results of the quantitative analysis of the three conditions are shown in Table 2. Grain size was stable, with insignificant variations in grain diameter among the three conditions, which were

Table 2

Properties of the three microstructures of HR6W. Note that GB carbides are excluded from carbide measurements.

	As-received	1 h aging	10 h aging
Grain diameter	205 μm	199μm	196μm
Grain carbide diameter	_	190μm	165μm
Grain carbide density	_	5.16 × 10 ¹² m ⁻²	6.64 × 10 ¹² m ⁻²

measured at around 200 µm. The grain diameter was calculated using the Jeffries method. The inverse value was taken as the average grain cross-section which was then approximated as a circle to derive the equivalent grain diameter. There was a slight increase in $M_{23}C_6$ area density from 5.2 × 10^{12} m⁻² to 6.6 × 10^{12} m⁻² with longer aging time. During prolonged aging the average size of precipitates decreased slightly, pointing to ongoing, albeit slow, precipitation of new $M_{23}C_6$ carbides.

Thermal desorption results at a heating rate of $50 \circ Ch^{-1}$ are shown in Fig. 2. The curves have a large primary peak at around $90 \circ C$ and a smaller secondary peak around $500 \circ C$, which is likely a result of back-diffusion. Because of the low H diffusivity, the charging time was insufficient to reach a flat concentration profile and H was mostly concentrated near the surface. This results in H redistribution during desorption which is an effect that has also been observed elsewhere [16]. The high-temperature peak is therefore very unlikely to be a result of the large MX carbides present in all three conditions as their volume fraction is negligible.

The peaks reveal that the aged microstructure with a relatively high precipitate density absorbs much less hydrogen than the precipitate-free one. This is the opposite of what is normally observed in most alloys – high precipitate densities are associated with higher hydrogen absorption as a result of trapping effects. The experimental evidence for trapping is strong and here we only list a few examples e.g. [14,17,18]. To eliminate potential experimental errors the experiments were conducted two more times but yielded the same trends – the results can be found in the supplementary



Fig. 2. Experimental thermal desorption curves using a heating rate of $50 \,^{\circ}$ Ch⁻¹. The two aged samples (yellow and orange markers) absorb the same amount of hydrogen, while the as-received sample (blue markers) absorbs nearly a third more.

material. The two preliminary series were performed under the same charging conditions but were charged for only 48 h and tested to 300 °C, one set of samples directly after charging while the other was left to degas at room temperature for 96 h. The degassing was conducted in order to rule out potential trapping effects – if carbides acted as traps, the two aged samples would be expected to retain more H after degassing compared to the solutionised reference sample. This, however was not the case. To the authors' knowledge this is the first work reporting reduced hydrogen absorption in microstructures with carbides and suggests that carbides in aged HR6W hinder H diffusion.

3.1. Proposed mechanism of H absorption

Let us first examine the effect of intragranular carbides, which could in principle act as 'repellents' rather than traps. However, their dispersed nature and small volume fraction cannot make them effective obstacles to bulk diffusion. It was shown that dispersed defects could only slow down the overall diffusion rate if their volume fraction was high [19], which is clearly not the case for the microstructures discussed here. It is also likely that whatever trapping might occur at intragranular carbides is negligible. First, it was demonstrated recently [20] that the trapping density scales with the carbide radius as $N_t \propto r^{-1}$. The carbides in HR6W are relatively coarse (~150 nm compared to ~15 nm in [20]) leading to a much lower trap

density. The second reason is that the hydrogen lattice concentration during electrochemical charging in nickel alloys is orders of magnitude higher compared to ferritic steels. This means that the trapped hydrogen concentration will be almost negligible relative to the lattice concentration.

A more plausible reason for our unexpected results may be the presence of GB carbides. GBs are densely populated with precipitates in both aged conditions (Fig. 1) and it is therefore likely that they might alter the hydrogen diffusivity locally. This could be either via trapping effects, obstruction (similar to the concept of a tortuosity factor [21], which accounts for the fact that atoms must travel a longer effective distance), or a change in GB chemistry and thus activation energies for GB diffusion.

In the as-received carbide-free samples, GB diffusion is likely to contribute significantly to the overall diffusion rate. Oudriss et al. [22] showed that polycrystalline Ni samples can be almost an order of magnitude more permeable to H than single crystal Ni. In the carbide-free condition, hydrogen is therefore free to diffuse along boundaries while the carbides in the aged microstructure hinder GB diffusion, reducing the hydrogen absorption rate as schematically shown in Fig. 3.

This occlusion mechanism is corroborated by previous reports on H permeation experiments. Jebaraj et al. [13] studied Inconel 718 and found that the precipitation hardened condition with GB precipitates [23] exhibits a much lower steady-state permeation flux J_{SS} . Similarly, Zagal et al. [24] found a much higher J_{SS} value in solutionised compared to aged Inconel 690. Both microstructures were very similar to that of HR6W reported here – the solutionised condition was almost completely carbide-free while the aged one contained a dense network of $M_{23}C_6$ carbides. Fig. 4a displays the ratios of J_{SS} between the solutionised and GB carbide-containing microstructures from the two reports. Despite the scatter it is clear that $J_{SS}^{sol}/J_{SS}^{Garab} > 1$ – solutionised microstructures are therefore much more permeable to H.

This matters because J_{SS} is a measure of the intrinsic diffusivity of the alloy, unaffected by trapping: $J_{SS} = D(c_{1,L} - c_{1,R})/L$ where *L* is the sample thickness, $c_{1,L}$ and $c_{1,R}$ the H lattice concentrations on the left and right side of the sample, respectively, and *D* the intrinsic diffusivity of the sample. The equation is derived from Fick's first law by noting that the concentration gradient is linear throughout the sample. Therefore, as there is no physical reason for the change in the boundary conditions $c_{1,L}$ and $c_{1,R}$ or in the sample thickness *L* between the experiments, the reduction in J_{SS} for the aged microstructures can only be ascribed to the reduction in *D*. The effective diffusion coefficient D_{eff} , on the other hand, is a function of trapping effects [25] as $D_{\text{eff}} = D_1(1 + (N_tN_iK)/(N_1 + Kc_1)^2)^{-1}$ where D_1 is the lattice diffusivity (the diffusivity in a single crystal), N_1 the number of interstitial



Fig. 3. Proposed mechanism for decreased hydrogen absorption for the aged HR6W microstructure. a) GBs act as fast diffusion pathways in the as-received, carbide-free condition and increase the hydrogen absorption rate aided by the boundary segregation energy which leads to a locally increased H concentration. b) GB carbides act as obstacles to hydrogen diffusion along GBs in both aged conditions, effectively decreasing hydrogen absorption.



Fig. 4. a) Ratios of steady-state H flux in Ni alloys in solutionised versus aged conditions. b) Permeation curve schematic, illustrating the difference between J_{SS} and D_{eff} . The blue curve represents a trap-free sample while the red one is affected by trapping. Breakthrough times t_{t1} and t_{t2} differ while J_{SS} stays constant.

lattice sites, c_1 the hydrogen lattice concentration, N_t the number of trapping sites and K the trap equilibrium constant based on its binding energy ΔE_t . D_{eff} can be experimentally determined from the breakthrough time t_t [26] as shown in Fig. 4b. The figure also demonstrates the difference between J_{SS} and D_{eff} . The red and blue curves are schematic permeation curves of two different microstructures under the same permeation conditions. J_{SS} is the same in both cases while D_{eff} values, as measured by the different breakthrough times t_{t1} and t_{t2} , are different as a result of different trapping properties.

Note that permeation literature on Ni-based alloys and austenitic steels in the presence of GB carbides is scarce. An extensive literature search revealed only one other work that can be used in this discussion. Turnbull et al. [14] conducted permeation experiments on Ni alloys 600 and X-750 in different aging conditions, some of which also contained GB precipitates. J_{SS} in alloy 600, which is strengthened by Cr-rich carbide precipitation, followed the trends above, with the solutionised condition exhibiting a significantly higher value. In X-750, which is strengthened both by the γ ' phase and GB carbides, the trends were less consistent. The double aged condition which appears to have a dense network of GB carbides is less permeable, while the direct aged condition is more permeable to H than the solutionised X-750. Note that the GB carbides in the latter are much coarser - possibly too coarse to fully occlude GBs, which could explain why there is no reduction in J_{SS} . It cannot, however, explain the observed increase in J_{SS} from the solutionised to the single aged condition. Since the J_{SS} values reported in the work show notable scatter they should be viewed with some caution.

In the next sections we present a diffusion model able to describe this anomalous behaviour, which takes into account GB diffusion, trapping and the effect of non-isothermal conditions. Because direct quantitative measurement of hydrogen on GBs is beyond the reach of current techniques, using diffusion modelling is particularly valuable.

4. Grain boundary diffusion modelling

4.1. Existing grain boundary diffusion models

Existing GB diffusion models have various drawbacks that make them unsuitable for the study of thermal desorption. All apply only to the isothermal case and do not account for the trapping effects of defects. Those that do incorporate the effect of GB segregation use the Boltzmann approximation which may introduce large errors when hydrogen concentrations in the lattice are high and GBs approach saturation. Nevertheless, it is worth conducting a short review.

A number of GB diffusion models were proposed in the fifties and sixties. Whipple [27] derived analytical solutions for the behaviour of a 2D rectangle of a high-diffusivity material embedded in a lowdiffusivity matrix with a constant concentration boundary condition at the edge of the composite. A similar model was derived by Suzuoka [28] but for a surface concentration that depletes in time such as a sputtered layer of some diffusing species. Both models use the assumptions of a constant concentration and equal mass fluxes at the interface between the matrix (grain) and the rectangle (GB), which is not always applicable. GBs are often energetically more favourable for diffusants to occupy and have thus higher local concentrations. This characteristic was first implemented by Bernardini and Martin [29] and features in other later models [30,31]. It is relevant in nickel where GBs can have segregation energies in excess of -26 kJ mol⁻¹ [32]. Abraham et al. [6] focused on GB diffusion almost exclusively, with grains acting as infinite sinks. Several authors provided analytical expressions which were later used for experimental measurements of GB diffusion coefficients, e.g. [27,28]. The limitations of the model used for fitting the diffusion data when evaluating GB diffusion coefficients are worth bearing in mind. Depending on the choice of the model, GB diffusivities are reported to be between 1 and 10^3 times larger than that of the lattice [33,34].

A recent GB diffusion model for hydrogen in nickel was developed by Ilin [35], starting from the assumptions of concentration and flux continuity but incorporating the effect of segregation. No analytical solutions were provided – instead, the work focuses on the effect of GB orientation relative to hydrogen diffusion direction and local stress gradients. To the authors' knowledge this is the first work that incorporates both the effects of segregation and orientation. Other recent work, notably by Legrand et al. [36], explored the effects of geometry, although assuming no segregation at the GB. Likewise, Jothi et al. [37] explored GB diffusion using the assumption of no segregation. Instead, they treated GBs as trapping sites and calculated hydrogen segregated there *a posteriori*. However, they incorporated two other important effects: trapping at geometrically necessary dislocations in a layer close to the GB using the McNabb-Foster model and grain geometry.

Considering that none of the existing models can be directly applied to this case, we propose a different approach to study thermal desorption in HR6W with the primary aim of studying the effect of GB diffusivity, segregation energy and volume fraction and their effect on the overall diffusion behaviour. It must include the effect of segregation at GBs where hydrogen concentration can be appreciably higher than in the lattice and must incorporate the effect of changing temperature. Note that hydrogen concentration at GBs and other defects is a function of temperature – the model must therefore include the (de)trapping H flux as the temperature changes. Finally, the model must be relatively simple as a two-dimensional explicit description of GBs would be computationally infeasible. We therefore propose to treat the GB network as a homogeneous medium embedded in a nickel matrix in which hydrogen concentration can be expressed as an analytical function of the hydrogen concentration in the lattice.

With the last condition the effects of GB anisotropy, connectivity and texture are lost. However, in our thermal desorption experiments several factors render this less significant: the simulated domain is on the order of several mm and thus much larger than the average grain size, the texture is random and the grain shape is isotropic.

4.2. Proposed grain boundary diffusion model

To arrive at our formulation we start with the approach introduced by Fischer et al. [38], which builds upon an earlier formulation by Oriani [25]. It is based on the assumption of local equilibrium between the hydrogen in the lattice and multiple trapping sites. More importantly, unlike a number of early models based on the local equilibrium assumption, e.g. [25], it does not assume low lattice occupancy, i.e. $\theta_1 \approx 0$. This enables it to treat systems where hydrogen lattice concentrations are high, which is generally the case in austenitic steels and nickel. However, we extend the formulation to incorporate the effect of linearly changing temperature in order to arrive at a description that is able to simulate thermal desorption experiments.

In the original formulation, the expression for the Gibbs free energy of a system in the presence of an arbitrary number of trapping sites is given as

$$G = G_0 + RT \bigg(\left(\theta_l \ln \theta_l + (1 - \theta_l) \ln(1 - \theta_l) \right) N_l \\ + \sum_{k=1}^m \bigg(\left(\theta_{tk} \ln \theta_{tk} + (1 - \theta_{tk}) \ln(1 - \theta_{tk}) \right) N_{tk} - \frac{\Delta E_{tk}}{RT} \theta_{tk} N_{tk} \bigg) \bigg)$$
(1)

where *G* is the Gibbs free energy function, *G*₀ is the Gibbs free energy of the system under standard conditions without the presence of traps and the sum term with the index *k* differentiates different kinds of traps (*m* is the total number of traps present in the system). Indices *l* and *t* denote lattice and trap sites, respectively, θ is site occupancy, *N* is the total number of sites (lattice or trap) per unit volume and ΔE_t the trap binding/segregation energy. *R* and *T* are the gas constant and temperature, respectively. Note that site occupancy is defined as $\theta_t = c_t/N_t$ for traps and $\theta_l = c_l/N_l$ for the lattice. For convenience, the use of *N* is omitted and instead their inverses *V*₁ and *V*_t are used, defined as

$$V_{\rm l} = N_{\rm l}^{-1}; \quad V_{\rm tk} = N_{\rm tk}^{-1}$$
 (2)

Minimising the Gibbs free energy function *G* by means of Lagrange multipliers leads to the following expression for the equilibrium between an individual trapping site and lattice site occupancy

$$\frac{\theta_{l}(1-\theta_{tk})}{\theta_{tk}(1-\theta_{l})} = \exp\left(\frac{-\Delta E_{tk}}{RT}\right) = K_{k}$$
(3)

Eq. (3) can also be expressed in terms of lattice and trap concentrations c_l and c_t , as well as the number of lattice and trap sites as

$$c_{tk} = \frac{V_l}{V_{tk}} \frac{1}{K_k + c_l V_l (1 - K_k)} c_l$$
(4)

The implicit idea behind describing diffusion in terms of c_1 and c_t terms is that the total concentration *c* can be expressed as the sum of

the lattice and trapped hydrogen

$$c = c_{\rm l} + \sum_{k=1}^{m} c_{tk} \tag{5}$$

The next step is the definition of mass flux **J**. In [38] it is defined as a sum of contributions from the lattice diffusion and diffusion through interconnected trapping sites, such as GBs and dislocations

$$\mathbf{J} = -D_{\mathrm{I}} \nabla c_{\mathrm{I}} - \sum_{k=1}^{m} D_{tk} \nabla c_{tk}$$
(6)

In [38], only the case of isolated traps was considered, which is a valid approach in many cases, particularly in ferritic steels where the diffusivity along GBs and dislocations has been shown to be at most equal to that in the lattice [39]. As this is not the case in nickel alloys and austenitic steels, the second term in Eq. (6) needs to be defined. To do this, the use of the local equilibrium assumption from Eq. (3) again proves useful.

The local equilibrium hypothesis is worth elaborating on here. Eqs. (3) and 4 are equivalent to the Langmuir model in surface science, which is in turn based on the Fermi-Dirac distribution in statistical mechanics. In both cases the model system is a collection of particles distributed among two energy states. A few key characteristics of the Langmuir model, which will be useful to our discussion, are the following:

- 1. There is a finite number of available segregation sites, which is in our case the GB.
- 2. The boundary has only one type of site characterised by a constant segregation energy which can be occupied by a single hydrogen atom.
- 3. The system is only characterised by the difference in the two energy states – the model does not say anything about the time needed to reach equilibrium if such a closed system is initially out of equilibrium.

It is important to evaluate these characteristics in relation to GBs in nickel to see whether c_t on GBs and c_l in the neighbouring grains can be expressed as time-independent functions of one another. The first characteristic holds true – in the absence of voids, there is a limited number of interstitial sites on the GB where hydrogen can be found. The second one does not strictly hold – DiStefano et al. [32] have studied hydrogen potential energy landscapes near GBs in nickel and found that they possess multiple sites whose segregation energy depends quite strongly on the structure of the boundary. However, all the boundaries with the same character will have the same potential energy landscape and we can assume that there will be some segregation energy representing the global average. This can be used as a substitute for a collection of accurate contributions of a number of individual types of boundaries.

The third feature is the most crucial. The time needed for the equilibration of the system must be shorter than the time needed for the concentration of hydrogen in one of the states to change appreciably via diffusion, which again perturbs the system out of equilibrium. This was the idea behind the early papers discussing local equilibrium [25,40] and we apply a similar analysis in this paper, described in the appendix. Our results suggest that the local equilibrium assumption holds true in nickel, meaning that Eq. (6) can be rearranged, limiting the sum term to only one site, GBs, and using Eq. (4) to substitute c_{tk} . Because GBs are the only diffusion path beside the lattice we use the index GB. Limiting the problem to one dimension and applying the chain rule $\partial c_{\text{CB}}/\partial c_1 \times \partial c_1/\partial x$ on the

second term on the right-hand side the equation for flux *J* becomes

$$J = -D_{\rm l} \frac{\partial c_{\rm l}}{\partial x} - D_{\rm GB} \frac{V_{\rm l}}{V_{\rm GB}} \frac{1}{\left(K_{\rm GB} + c_{\rm l} V_{\rm l} \left(1 - K_{\rm GB}\right)\right)^2} \frac{\partial c_{\rm l}}{\partial x}$$
(7)

The next step is to apply the mass conservation law $\partial c/\partial t = \partial J/\partial x$ substituting the total concentration c on the lefthand side according to $c = c_1 + c_{GB}$. We currently disregard other potential trapping sites, although an arbitrary number thereof can be incorporated using Eq. (5) and the procedure described below. As we want to capture the effects of changing temperature, the partial derivative of c_{GB} on the left hand side of the mass conservation law must be adjusted as some of the parameters in Eq. (4) are no longer constant in time. Considering that $c_{GB} = f(K_{GB}(T(t)), c_1(t))$ and applying the chain rule where necessary, the expression becomes

$$\frac{dc_{\rm GB}}{dt} = \frac{\partial c_{\rm GB}}{\partial K_{\rm GB}} \frac{\partial K_{\rm GB}}{\partial T} \frac{\partial T}{\partial t} + \frac{\partial c_{\rm GB}}{\partial c_{\rm I}} \frac{\partial c_{\rm I}}{\partial t}$$
(8)

Knowing that the temperature in thermal desorption is a linear function of the heating rate ϕ and the starting temperature T_0 and can be written as $T = T_0 + \phi t$, the partial derivatives in Eq. (8) can be found using previous definitions. Inserting all the corresponding expressions for partial derivatives and leaving only the $\partial c_l / \partial t$ term on the left hand side the final diffusion equation accounting for GBs as diffusion pathways and traps is

$$\frac{\partial c_{\rm l}}{\partial t} = \left(1 + \frac{V_{\rm l}}{V_{\rm GB}} \frac{1}{(K_{\rm GB} + V_{\rm l}c_{\rm l}(1 - K_{\rm GB}))^2}\right)^{-1} \\
\left(\frac{\partial}{\partial x} \left(\frac{\partial c_{\rm l}}{\partial x} \left(D_{\rm l} + D_{\rm GB} \frac{V_{\rm l}}{V_{\rm GB}} \frac{1}{(K_{\rm GB} + V_{\rm l}c_{\rm l}(1 - K_{\rm GB}))^2}\right)\right) \\
- \left(\frac{1}{V_{\rm GB}} \frac{c_{\rm l}^2 V_{\rm l}^2 - c_{\rm l} V_{\rm l}}{(K_{\rm GB} + V_{\rm l}c_{\rm l}(1 - K_{\rm GB}))^2} \frac{K_{\rm GB} \Delta E_{\rm GB} \phi}{RT^2}\right)\right) \tag{9}$$

The right-hand term on the first line in Eq. (9) comes from $1 + \partial c_{GB}/\partial c_1$ in Eq. (8), while the source term on the third line is the first right-hand term in the same equation. The above derivation is similar to those recently used by Kirchheim [41] and Raina et al. [16]. In the following sections, the only trap type considered is the GB for reasons discussed in Section 3, but the model can be easily extended to include an arbitrary number of traps.

4.3. Numerical methods

Eq. (9) was solved using the finite differences method as implemented in Matlab's pdepe solver. The model parameters used were the same as in Table 3 unless stated otherwise. The domain represented the radius of the cylindrical samples, 4 mm in length starting from the centre. There, a zero-flux boundary condition was applied because of symmetry reasons. Initially, a uniform grid with a step size of 5 µm was tested but proved to be inadequately fine. Instead, a 200-point grid with spacing defined in terms of an exponential function was used. The resulting step size was uneven – large in the middle of the sample and progressively finer near the edge. This was

Table 3

necessary to minimise numerical errors as most of the hydrogen was concentrated there. The simulations were performed in three stages, following our experiments. A simulation of the four-day charging step $(3.456 \times 10^5 \text{ s})$ under a constant-concentration boundary condition at the outer edge was followed by a short degassing step (1800 s) with the boundary condition set to zero concentration. The thermal desorption step also had the zero-concentration boundary condition and lasted for $5 \times 10^4 \text{ s}$. The starting temperature T_0 was $27 \,^\circ\text{C}$ and the heating rate $\phi 50 \,^\circ\text{C} \,\text{s}^{-1}$.

4.4. Model parameters

For the simulations, no trapping sites other than GBs were assumed despite the presence of precipitates. This is because the hydrogen content in the as-received metal, which was precipitate-free, was much higher compared to the aged samples. We can therefore conclude that whatever trapping effect these precipitates might have is negligible compared to GB diffusion effects. As GBs were considered as both diffusion paths and traps at the same time, the last term in Eq. (9) only contains the term for GBs. In the simulations of charging and thermal desorption, the parameters used are listed in Table 3.

To obtain the GB volume fraction v_f^{GB} it was assumed that grains are roughly cubic in shape of size d_g and are surrounded by GBs of thickness $d_{GB}/2$. The dependence of v_f^{GB} on grain size then becomes

$$v_{\rm f}^{\rm GB} = \frac{(d_{\rm g} + d_{\rm GB})^3 - d_{\rm g}^3}{(d_{\rm g} + d_{\rm GB})^3} = 1 - \frac{d_{\rm g}^3}{(d_{\rm g} + d_{\rm GB})^3}$$
(10)

The volume fraction of GBs is related to the density of GB sites as

$$N_{\rm GB} = v_{\rm f}^{\rm GB} N_{\rm l} \tag{11}$$

where the assumption is that the GBs possess the same site density as the lattice.

No information is available on the relationship between hydrogen concentration at the surface and current density during hydrogen charging in NaCl solution which could serve as a boundary condition for the simulations. For this reason an estimate of 1.5×10^4 mol m⁻³ was chosen, based on the subsurface hydrogen concentrations resulting from similar current densities [42]. It should be noted however, that the solution in [42] is different and the values are thus likely not very accurate. A literature search revealed that the scatter in hydrogen subsurface concentrations can be an order of magnitude even when using identical charging conditions [42,43], and it was thus concluded that our choice of boundary condition is reasonable. The initial condition of $c_1 = 0$ was chosen for the charging step. For degassing and thermal desorption, the initial condition corresponded to the concentration profile resulting from charging. The boundary condition was then changed to 0 under the commonly applied assumption that surface desorption kinetics is rapid enough to remove all the effusing hydrogen before it starts to build up.

Despite the effort to fully describe the system with physical parameters available from the literature, some of them, particularly

Diffusion parameters used in numerical simulations

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	Value	Ref.	Comments	
D ₁	$1.07 \times 10^{-6} \exp(-49800/(RT))$	[67]	In m ² s ⁻¹	
D_{GB}	$10^{3}D_{1}$		Default value	
Vl	$4.9 \times 10^{-6} \text{m}^3 \text{mol}^{-1}$	[38]		
ΔE_{GB}	-6 kJ mol ⁻¹	[48,52]	Default value, slightly lower than in refs.	
d_{GB}	10 nm	[48,47]		
N _{GB}	$17.3 \text{mol} \text{m}^{-3}$		Default value, from Eq. (11)	
C _{l,BC}	$1.5 \times 10^4 \text{mol} \text{m}^{-3}$	[42]		

GB width d_{GB} , GB diffusivity D_{GB} and lattice diffusivity D_{I} are uncertain to various degrees. The boundary condition for charging $c_{I,BC}$ can be calculated under potentiostatic charging conditions in the case of pure bulk diffusion and known final average concentration. This was achieved using the right analytical solution to the regular diffusion equation by Yagodzinskyy et al. [44]. However, in our case this is not possible due to the assumption that the intrinsic diffusivity changes between the as-received and aged samples because of GB effects whose contribution is not known. With these limitations in mind let us examine our modelling results.

5. Modelling results

In this section an attempt to reproduce the experimental TDA curves is described. Based on the effect of different model parameters, the most convincing explanation for the experimentally observed decrease in hydrogen absorption for the two aged microstructures is that N_{GB} decreases because of the presence of GB carbides. It is plausible that because of the carbide occlusion the effective GB width decreases significantly, restricting hydrogen diffusion. Of course, the actual changes might be much more complicated than that. The GBs hosting carbides will likely have a different potential energy landscape because of geometric reasons, the presence of carbide-matrix interfaces, possible differences in the local chemical composition (potential Cr depletion) and the presence of dislocations. These considerations are of interest but can only be addressed in small, idealised volumes via density functional theory calculations which are outside the scope of this paper.

Experimental and theoretical thermal desorption curves are displayed in Fig. 5. The as-received state was modelled using the parameters listed in Table 3. For the aged condition N_{CB} was taken as 0 assuming complete occlusion of the GBs. There is some discrepancy between the first peaks between the model and the experimental data. The model predicts a slight shift towards higher temperatures not observed experimentally and it somewhat underestimates the difference in desorbed hydrogen. However, as the model is fairly sensitive to changes in D_{CB} and N_{CB} , choosing a slightly higher value of either would have yielded a more accurate agreement. As these parameters show some scatter it seems reasonable to apply these changes.

The secondary peak is less prominent than expected and also exhibits a small shift, although towards lower temperature, particularly for the case where GB diffusion has a significant effect. This peak is the result of the hydrogen that penetrates further into the sample during the initial stages of thermal desorption and cannot effuse until much later in the process. The peak shift implies that the model somewhat overestimates the diffusivity at high temperatures



Fig. 5. Comparison of experimental and modelled thermal desorption curves.

which may be due to a number of parameters. A possible explanation is that because the expression for bulk diffusivity D_1 used here was based on measurements on a different nickel-based alloy, its value is inaccurate.

5.1. Comparison to literature: effect of grain size on hydrogen permeation

To further support the argument of GB-enhanced bulk diffusion, we applied the model to simulate hydrogen permeation in pure nickel [22]. The simulation is somewhat simpler, as the temperature is constant and the terms containing ϕ in Eq. (9) are null. In permeation simulations it proved sufficient to use a relatively coarse 50-point grid unlike in the thermal desorption simulations. The boundary condition on the ingress side was a constant concentration as described below and zero concentration on the exit side.

Oudriss et al. [9,22] conducted extensive permeation experiments on thin nickel foils with varying grain size and focused on the analysis of the effective diffusivity D_{eff} . D_{eff} is a function of the H breakthrough time calculated from the slope of the rise in permeation flux and its intersection with the time axis. It is a metric that is very sensitive to trapping effects although it does also depend on lattice and GB diffusivity. As argued in Section 3.1, this makes the steady-state flux i_{SS} a better measure of the GB contribution to diffusion. It is not influenced by trapping, because in steady-state diffusion, trapping and detrapping processes reach equilibrium and no longer contribute to the overall diffusion process. It should be emphasised that in [22] the i_{SS} increases with decreasing grain size, demonstrating that a higher GB volume fraction increases the intrinsic H diffusivity.

We therefore simulated the permeation curves in [22] at 25 °C with parameters listed in Table 4. Let us point out that while most of the simulation parameters were the same as for the thermal desorption case, the GB width d_{GB} had to be altered in order to reproduce the permeation data. Regardless, the value used for permeation is still within the range of values reported in the literature and the difference between the thermal desorption and permeation cases is probably related to the difference in composition of the material which can have a profound impact on GB geometry and H potential landscape. The choice of D_{I} and $c_{I,BC}$ was based on the reported value for a nickel single crystal sample, as both should stay constant regardless of the grain size of the samples.

Fig. 6 compares the experimental data to our simulations and the agreement between them is quite good. Somewhat unexpectedly, the experimental data indicate that the single crystal and 168 μ m cases have the same steady-state flux which would suggest a very low contribution of GB diffusion. However, it must be pointed out that steady-state flux values are sensitive to a number of parameters. This includes sample thickness, reported to be $180 \pm 20 \mu$ m, and boundary conditions which are notoriously fickle in electrochemical experiments. Some experimental scatter is thus inevitable and may explain the coincidence of the two curves. Furthermore, it appears that the 168 μ m sample has a lower steady-state flux value which should not be the case even if GB diffusion were completely suppressed.

In the $18 \,\mu\text{m}$ case (and to a lesser degree in the $168 \,\mu\text{m}$ one), it is apparent that the modelled curve saturates much faster than the experimental one. This is a result of additional trapping effects that

Diffusion parameters used in permeation simulations.

Table 4

	Value	Comment
d _{GB} D _l c _{l,BC}	$\begin{array}{l} 1 \text{ nm} \\ 9.0 \ \times \ 10^{-14} \text{ m}^2 \text{ s}^{-1} \\ 83 \text{ mol } \text{m}^{-3} \end{array}$	In range of GB cavity width [32] Based on single crystal value [22] Based on <i>D</i> ₁ and steady-state current on single crystal Ni [22]
x	$1.8 \times 10^{-4} \mathrm{m}$	Sample thickness [22]



Fig. 6. Comparison of experimental [22] and modelled permeation curves. SC denotes single crystal nickel and the numbers refer to grain sizes. a) Shows the fits assuming all GBs are fast diffusion pathways while b) shows the retarding effect of additional trapping sites (GBs that do not possess high hydrogen diffusivities). It is clear that the steady state flux stays the same but the curve saturates more slowly.

were not included in the simulation in Fig. 6a. As discussed previously, some GBs are not fast diffusion pathways and merely act as hydrogen traps. Their fraction varies depending on the grain size, which is likely why Oudriss and coworkers found the pronounced variation in $D_{\rm eff}$. If an additional trapping site density is included in the model, the initial part of the permeation curve tracks the experimental one much more closely as shown in Fig. 6b.

Let us finally discuss the role of grain size. The fraction of GBs v_f^{GB} should scale in approximate accordance to Eq. (10) and when grains are relatively large, *i.e.* $d_{GB} \ll d_g$, v_f^{GB} is inversely proportional to d_g . Decreasing the grain size by some factor will then result in an equal increase in the GB density N_{GB} , in turn increasing the GB flux term by the same factor. This means that the overall diffusivity is sensitive to grain size which may result in rapid diffusion in nanograined Ni, assuming that most boundaries are fast diffusion pathways.

6. Discussion

The reduced hydrogen absorption in HR6W in the presence of GB carbides is a novel finding and the unusual behaviour was attributed to the role of GBs. The phenomenon can only be attributed to microstructural differences between the solutionised and aged microstructures. As GBs can have a notable effect on the overall

hydrogen diffusion rate, the observed difference in hydrogen absorption is best interpreted through the occluding effect of carbides on GB diffusion. To explore these effects, a model incorporating GB diffusion and trapping was developed.

The resulting model is, to the authors' knowledge the first to incorporate GB diffusion effects and is also applicable to problems such as thermal desorption. While a handful of existing models use similar assumptions related to GB segregation and treat them in a more elaborate manner [30,45], the models are not suitable for this purpose. A major issue is that they treat GB segregation in terms of the Boltzmann distribution. This is inaccurate for high hydrogen concentrations during electrochemical charging because hydrogen concentrations at the GB can be close to complete saturation.

Below, we explore the effects of the model parameters N_{GB} , D_{GB} and ΔE_{GB} which are related to GB properties. N_{GB} is related to GB volume fraction and depends on grain size and the effective width of the GB where hydrogen diffusion is accelerated. The other two parameters are intricately linked to the GB structure. Note that all the parameters used for the simulations presented below are listed in Table 3, unless stated otherwise.

The model captures well the increase in diffusivity due to grain size reduction reported by Oudriss et al. [22] when the grain size is in the micron range. In Fig. 7a we demonstrate the effect of varying N_{CB} , which is related to grain size as illustrated in Fig. 7b. All the other



Fig. 7. a) Simulated thermal desorption curves using different N_{GB} values. b) Correlation between grain diameter and N_{GB} at two different GB width values.

simulation parameters used in this section are as listed in Table 3, unless stated otherwise in the figures. Increasing $N_{\rm CB}$ should have a complicated impact on the thermal desorption curve. It features in the GB flux term in Eq. 9 and increases the relative contribution of GBs. It also features in the trapping term $1/(1 + \partial c_{\rm GB}/\partial c_1)$ where increasing $N_{\rm CB}$ decreases the diffusion rate. An additional effect is caused by the trapping itself – the larger the $N_{\rm GB}$, the higher the concentration of trapped hydrogen. The latter is particularly significant when c_1 is low and $N_{\rm GB}$ is high, as GB hydrogen represents a large fraction of the total concentration.

The model is unable to incorporate the effect of the structure of the GB network explicitly, making it challenging to model microstructures with a significant texture where diffusion may be anisotropic or study the effect of GB connectivity. However, it is in principle possible to incorporate the contributions of different types of GBs, to explain, for example, the variations in D_{eff} in [22]. Some GBs in nickel are high-diffusivity paths while others act exclusively as traps and it was shown that the fraction of boundaries with a particular symmetry varies significantly with grain size. This means that the fraction of GBs which act as hydrogen traps to those that are fast diffusion pathways changes, which in turn causes changes in trapping in effective diffusivity. With accurate characterisation of the microstructure it is possible to obtain the fractions of the special GBs and their associated segregation energy ΔE_{GB} and diffusivity D_{GB} , which can then be plugged into the model to capture trapping and accelerated GB diffusion more accurately.

Fig. 8 shows the effect of changing ΔE_{GB} . It is clear that higher segregation energy results in both peaks shifting to lower temperatures, indicating faster overall diffusion. Examining the limits of the GB diffusion term in Eq. (9) reveals why that occurs. Very low segregation energies imply $K_{GB} \rightarrow 1$, which reduces the GB term to $D_{GB}V_1/V_{GB}$. Diffusion is thus controlled strictly by the volume fraction of the GBs, which is fairly low in the present case. Conversely, high segregation energies imply $K_{GB} \rightarrow 0$, reducing the factor to $D_{GB}V_1/V_{GB}(c_1^2V_1^2)^{-1}$. The latter is always higher than the former, unless the lattice is nearly saturated, i.e. $c_1 \approx 1/V_1$. This makes sense – when the segregation energy ΔE_{GB} is negligible, GBs are still fast diffusion pathway. However, since the concentration of hydrogen there is now the same as in the lattice, their contribution is less significant. When the segregation energy is large, however, the concentration of hydrogen at the boundaries is large relative to the lattice and so the role of GB diffusion is more important.

It is also apparent that increasing ΔE_{GB} does not have a significant effect on increased hydrogen absorption. The reason for that appears to be that because GBs contain a larger fraction of the total hydrogen, the overall diffusion rate increases significantly. This causes a large fraction of hydrogen to effuse during the room-temperature degassing stage occurring between the charging and the

thermal desorption steps, negating any net gain in absorption during charging.

Though not shown in Fig. 8 it is worth mentioning what happens when the segregation energy is negative. In this case $K_{\text{GB}} \gg 1$ and the GB flux term becomes $V_1/D_{\text{GB}}V_{\text{GB}}(K_{\text{GB}}^2(1 - V_1c_1))^{-1}$. When K_{GB} becomes sufficiently large the entire term approaches zero, effectively eliminating GB diffusion.

Fig. 9 shows the effect of changing D_{GB} . Despite the small effective volume fraction of GBs their contribution to the diffusion kinetics is significant beyond $10^2 D_1$. The low temperature peak is located at $110 \,^{\circ}$ C and does not seem to shift to lower temperatures with increasing D_{GB} . The secondary peak comes from hydrogen that keeps diffusing towards the centre of the sample during thermal desorption and is very sensitive to changes in D_{GB} . Low D_{GB} means this redistribution is slow and very little hydrogen diffuses far into the sample, leading to a weak peak at higher temperatures. When D_{GB} is high, more hydrogen is able to diffuse out of the sample, but because of higher overall diffusivity it also diffuses out of the sample faster, resulting in a stronger peak at a lower temperature. Overall, the degree of absorbed hydrogen scales strongly with $D_{GB} = 5 \times 10^3 D_1$.

Following this sensitivity analysis it should be acknowledged that some of the model parameters are inaccurate to various degrees. For example, the equivalent surface concentration during galvanostatic charging is poorly documented and shows scatter [43,42], as well as dependence on the charging solution [46]. To the authors' knowledge no information is available for the NaCl solution used here. However, boundary condition values c_{LBC} for a particular combination of solution and charging current density can be calibrated with permeation experiments on single crystal samples of the alloy in question. The effective GB width is another parameter that shows a degree of uncertainty. Recent ab initio calculations suggest it is on the order of several nanometres at most [32], while experimental observations show increased hydrogen hydrogen concentrations significantly further away from the boundary [47,48]. GB segregation energy ΔE_{GB} also shows some scatter – while it is most commonly reported to be $20-26 \text{ kJ} \text{ mol}^{-1}$ [32,49-51], some reports suggest it to be much lower, $11-12 \text{ k} \text{ mol}^{-1}$ [48,52], and some show that some GBs also possess sites with a much higher segregation energy [53]. The scatter in reported segregation energies is expected to reduce in the future however, as more density functional theory simulations of various GB structures are performed and more data becomes available. Together with the emerging automated methods of GB characterisation [54] this will yield a better understanding of GB segregation energetics. It should be noted that other modelling work on hydrogen diffusion and trapping to date is also troubled by the lack of



Fig. 8. Simulated thermal desorption curves using different ΔE_{GB} values.



Fig. 9. Simulated thermal desorption curves using different D_{GB} values.

accurate parameters and uses at least some of the assumptions discussed so far. Additionally, the implications of the choice of parameters are often not discussed, which is something we attempted to account for here.

6.1. Implications for alloy design and modelling of hydrogen embrittlement

The results of our study are relevant in low-temperature applications where HR6W or similar alloys are being considered because of their corrosion resistance. Here, choosing a microstructure containing GB precipitates may significantly decrease hydrogen uptake although it is less clear whether that will also mitigate hydrogenrelated problems. Reports indicate that in some Ni-Fe-Cr alloys the presence of GB carbides exacerbates hydrogen embrittlement [55-57], although the effect appears to be strongly compositiondependent. It is also worth mentioning that a dense network of GB precipitates has been proven to mitigate hydrogen-related issues in some aluminium alloys [58,59]. The mechanism behind this has not been identified yet but there might be at least some similarities with HR6W as Al also exhibits high hydrogen solubility and low diffusivity.

The findings of this study are fairly broadly applicable to general alloy design, not only the HR6W alloy. The evidence that GB carbides can be used as a H diffusion barrier offers a new means of designing heat treatments for components where a reduced H absorption is desirable, which may be useful in the design of corrosion-resistant Ni alloys and austenitic stainless steels where GB diffusion is also a significant factor in H embrittlement. Furthermore, the model presented here can be applied to all alloy systems where GB diffusion of H is rapid. The ability to accurately model H diffusion as a function of the alloy microstructure allows for improved component design as H concentration, which is often critical to component safety, can be tracked as a function of the service conditions (temperature variations and gradients, boundary conditions). The model can also be easily extended to take into account additional effects such as stress gradients and microstructural evolution [60,38].

The model could also complement the existing work on intergranular failure. There is increasing attention to the effect of grain distribution, GB structure and GB connectivity in light of H diffusion. In the studies of intergranular failure due to H, diffusion has so far been modelled under the assumption that H leakage into the grains is negligible and diffusion therefore only takes place in the GB network [61,62]. This is a good approximation in some cases and the studies cited here have been able to reproduce the appearance of multiple cracks along the gauge length of a tensile sample, which is characteristic of H-assisted intergranular fracture. Because it takes into account the H flux from the GBs into grains, our model can provide a means of cross-validation for these fracture models by tracking the overall diffusion rate and the H concentration at GBs.

Some recent work also tackles the problem of extracting bulk properties that depend on the topology of the GB aggregate, such as the effective diffusivity. It paves the way towards a better understanding of some microstrucutral effects such as the fraction of particular GB orientations/symmetries and grain morphology and their effect on the net H diffusion properties [63-65]. The model presented in this work could be further refined with insights from such studies in the future.

7. Conclusions

To summarise, the highlights of this work are as follows:

• The presence of dense grain boundary (GB) carbides results in decreased hydrogen absorption in the HR6W alloy studied by means of thermal desorption. This behaviour was attributed to

GB carbides suppressing diffusion along GBs which is rapid in Ni-based alloys. Literature data corroborates this conclusion.

- A diffusion model was developed that includes GB diffusion, trapping and heating effects and is able to elucidate the complex effects of GB properties. It was successfully used to predict the experimental thermal desorption curves as well as hydrogen permeation curves in pure nickel from the literature.
- The effects of grain boundary properties, namely grain size/GB fraction, GB diffusivity and GB segregation energy were elucidated. It was found that the hydrogen absorption rate under severe charging conditions only weakly depends on the segregation energy of GBs. It is, however, very sensitive to GB volume fraction and diffusivity, which are controlled by the grain size and GB type.
- The experimental results indicate that GB precipitation can be used to reduce H absorption in Ni alloys and austenitic steels, potentially improving their hydrogen embrittlement resistance. The model is transferrable to a variety of alloys as it is microstructurally sensitive and can be used for microstructural design against H embrittlement.

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Appendix A. Local equilibrium at grain boundaries during hydrogen charging

To evaluate whether local equilibrium can be assumed we adapt the original approach by Oriani [25]. We want to answer the following question: if we consider hydrogen ingress along GBs and the lattice as two independent diffusion processes, are the resulting concentrations at the beginning of electrochemical charging, when concentration gradients are the highest, far from the values predicted by the local equilibrium estimate? If they are, are the kinetics of redistribution rapid enough to re-establish the equilibrium during this time?

To answer this we use the following procedure. First, the diffusion equation must be solved for the lattice and the GB, separately. Then the average concentration in both the lattice and the boundaries in a thin layer close to the surface must be calculated. The average concentration in the lattice is used to calculate the equilibrium GB concentration. Next, the difference between this theoretical equilibrium and the average GB concentration from solving the diffusion equation is calculated. If the latter is higher than the former GBs contain an excess of hydrogen that needs to diffuse into the neighbouring grains for the local equilibrium assumption to hold. Finally, we estimate whether this redistribution is rapid enough.

For simplicity, we limit the case to one dimension and use the geometry of a semi-infinite slab of some thickness *L*, for which analytical solutions of the standard diffusion equation are available. The initial concentration is taken to be zero and the boundary condition for lattice hydrogen is a constant concentration c_{LBC} . For GB concentration, the boundary condition $c_{GB,BC}$ is derived from local equilibrium (Eq. (4)) which must hold at the very surface of the slab. The thickness coordinate is labelled as *x* and is zero in the centre of the slab. We then evaluate hydrogen concentrations in GBs and in the lattice after a short time δt - we choose 10⁵ s taking $D_{\rm I}$ and $D_{\rm GB}$

to be $10^{-16} \text{ m}^2 \text{ s}^{-1}$ and $10^{-13} \text{ m}^2 \text{ s}^{-1}$, respectively. To calculate $c_{\text{GB,BC}}$, we shall assume $\Delta E_{\text{GB}} = 26 \text{ kJ mol}^{-1}$, $V_{\text{I}} = 4.9 \times 10^{-6} \text{ mol} \text{ m}^{-3}$ and $V_{\text{GB}} = 10^4 V_{\text{I}}$.

We can use analytical solutions for the diffusion equation for the slab geometry (Crank [66], pages 47 and 48), to get the hydrogen concentration profiles and penetration depths. The latter is defined as the depth where the hydrogen concentration becomes less than 1% of the boundary condition value. Penetration depths are 11 µm and 360 µm for GB and lattice diffusion, respectively. We now consider what happens in the outer layer affected by GB diffusion (360µm thick). The average lattice and GB concentrations in this layer based on analytical solutions mentioned above are $\bar{c}_{GB} = 0.3121c_{GBBC}$ and $\bar{c}_1 = 9.918 \times 10^{-3} c_{1 BC}$. If we use the obtained \bar{c}_1 value and plug it into Eq. (4) using the same GB parameters as before, it is clear that the \bar{c}_{GB} resulting from diffusion along GBs is higher than that based on the equilibrium with the lattice. This means there is excess hydrogen in the GBs that needs to redistribute into the lattice in time δt for the equilibrium assumption to hold. The concentration difference between the two, labelled δc_{GB} , is 3.12 mol m⁻³. The above process is illustrated in Fig. A.1a.

We next need to examine whether $\delta c_{\rm GB}$ can redistribute into the lattice in time δt . Following Oriani's formulation, the concentration of hydrogen atoms released $\delta' c_{\rm GB}$ can be related to the rate of successful jumps per unit time

$$p = \nu \exp\left(\frac{-(\Delta E_{\rm GB} + \Delta E_{\rm a})}{RT}\right) \tag{A.1}$$

where ΔE_a is the activation energy for lattice diffusion and ν is the atomic jump frequency, and the concentration of hydrogen in traps as

$$\delta' c_{\rm GB} = p c_{\rm GB} \delta t \tag{A.2}$$

The values ΔE_{GB} and ΔE_a refer to the potential differences indicated in Fig. A.1b.

Next, for the local equilibrium to hold we account for the fact that hydrogen released from GBs into the surrounding lattice as calculated based on atomic jump rates must be greater than the hydrogen concentration difference $\delta c_{\rm GB}$ derived earlier, yielding the condition

$$\delta c_{\rm GB} \le p c_{\rm GB} \delta t \tag{A.3}$$

From the above we can get the maximum barrier energy for atomic jumps from GB into the lattice which still allows the equilibrium assumption to hold

$$\Delta E_{\rm GB} + \Delta E_{\rm a} \le -RT \ln \left(\frac{\delta c_{\rm GB}}{\nu c_{\rm GB} \delta t} \right) \tag{A.4}$$

We now look at the potential energy landscape near the $\Sigma 5$ GB in nickel in Fig. A.1c. This particular boundary is chosen as an example for convenience as it is well documented. As discussed before different GBs can have quite different potential energy landscapes, although most documented segregation energies are reported to be close to the values in Fig. A.1b. $\Delta E_{\rm CB}$ between the lattice site $T_{\rm GB}$ and GB site S_6 is 0.20 eV and the additional barrier energy is decidedly lower (0.07 eV for the $\Sigma 5$ GB) Eq. (A.4) can now be used to estimate the equilibrium condition. We use the values listed in Table 3 and $\delta c_{\rm CB}$ of 3.12 mol m⁻³, giving the condition $\Delta E_{\rm GB} + \Delta E_{\rm a} \le 105$ kJ mol⁻¹ which is much lower than the total barrier energy of -0.27 eV (-26 kJ mol⁻¹. This means local equilibrium can be assumed for virtually all GB transitions in nickel, even when assuming more extreme conditions, e.g. higher $D_{\rm GB}$, shorter δt and lower ν (sometimes reported to be 10¹² s⁻¹ instead [25]).

For the degassing of an initially fully saturated sample the analysis is similar as the analytical solutions of the diffusion equation are identical. The only difference is that there is now excess hydrogen in the lattice so the transition rate that needs to be examined is the one from the lattice into GBs. As this energy is only 0.07 eV



Fig. A.1. Illustration of local equilibrium analysis during hydrogen charging. a) Lattice and GB diffusion are analysed independently in a layer close to the surface in time δt bounded by the penetration depth of the faster diffusion process (GBs). b) Hydrogen potential energy landscape at the idealised matrix-boundary interface. E_{GB} is the energy level at the GB and E_g is the energy level in the grain. c) Hydrogen potential energy landscape normal to the Σ 5 boundary in Ni. Adapted from [32].

the transition rate is significantly higher than the one in the analysis above and local equilibrium clearly holds. The equilibrium is also easier to achieve at higher $c_{l,BC}$ values. Beyond a certain point δc_l becomes negative, meaning that hydrogen concentration on boundaries resulting from GB diffusion is actually smaller than the one given by the equilibrium with the lattice. This also leads to the above scenario where hydrogen will redistribute from the lattice into the boundaries for which the required energy barrier is much lower.

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matdes.2018.10.012.

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