



## Impurity effects on He diffusion in $\alpha$ -Fe

C.J. Ortiz <sup>a,\*</sup>, M.J. Caturla <sup>a</sup>, C.C. Fu <sup>b</sup>, F. Willaime <sup>b</sup>

<sup>a</sup> Departamento de Física Aplicada, Universidad de Alicante, Alicante E-03690, Spain

<sup>b</sup> Service de Recherches de Métallurgie Physique, CEA/Saclay, 91191 Gif-sur-Yvette, France

### A B S T R A C T

The diffusion of He in  $\alpha$ -Fe in the presence of defects produced by irradiation (vacancies and self-interstitials) is studied using rate theory models with input from *ab initio* calculations. Comparison between the model based on He in pure Fe and experimental data of He desorption obtained in different conditions shows discrepancies. This disagreement is attributed to the presence of carbon in the experimental samples. An extended model for the kinetics of He in  $\alpha$ -Fe including carbon is presented. Results obtained with this model are in good agreement with experimental He desorption data.

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### 1. Introduction

High levels of He are produced by transmutation under neutron irradiation in materials under fission and fusion conditions. This element strongly interacts with vacancies created during irradiation into stable He–V complexes that can deteriorate mechanical properties of the material. Therefore, understanding the kinetics of He in metals has become crucial for the development of materials resistant to radiation in nuclear power plants. Although the basic He migration mechanisms are well known [1], there are still many unknowns regarding He clustering in the presence of defects and impurities [2].

In a recent work [3], the authors have presented an *ab initio*-based rate theory model to account for the agglomeration of He–vacancy complexes in Fe. Using recent *ab initio* data on the stability and mobility of defects and He–vacancy complexes in Fe [4,5], the authors simulated the desorption experiments carried out by Vasen et al. [6]. Results obtained with this kinetic model showed discrepancies with the experimental data. On the other hand, it was shown that a good agreement between calculations and experimental results could be obtained by using effective values for the migration energy of the vacancy and V–He<sub>i</sub> and V–HeV binding energies. These results were explained by invoking the presence of impurities in the experimental samples, which were not taken into account in the initial model. Since carbon is a common impurity in Fe and since it strongly interacts with vacancies, as confirmed by *ab initio* calculations [7,8], carbon was proposed as the most likely candidate for the effect observed. This work showed that although good results could be obtained by reevaluating some of the *ab initio* parameters, in a more rigorous approach one should explicitly include the formation of He–V–C complexes in the ki-

netic model. In this work we present a first extension of the initial kinetic model presented in Ref. [3] that includes the presence of carbon.

### 2. Rate theory model including carbon impurity

Following the conclusions of our previous work, we extended our initial model in order to include reactions between vacancies and carbon as well as the interaction between carbon and He. As in our previous work [3], in this investigation we consider that single self-interstitials, single vacancies, interstitial helium and di-interstitial clusters are mobile. Following *ab initio* calculations [7,8], the interstitial carbon atom is also assumed to be mobile. All other defects are considered immobile. Migration energies of 0.06, 0.67, 0.34 and 0.42 eV obtained by *ab initio* calculations [4,9] for He<sub>i</sub>, V, I and I<sub>2</sub> were used in this model. For interstitial carbon a migration energy of 0.92 eV was used, according to *ab initio* investigations [7]. According to this new model, the mechanisms governing He clustering in the presence of carbon in irradiated Fe are summarized below:



\* Corresponding author.

E-mail address: [christophe.ortiz@ciemat.es](mailto:christophe.ortiz@ciemat.es) (C.J. Ortiz).

Eqs. (1) and (2) represent the Frank–Turnbull and Kick-Out mechanism, respectively. Eqs. (3) and (4) describe the agglomeration of monovacancies and mobile helium into He-vacancy clusters. Reactions (5) and (6) represent the formation of interstitial clusters by agglomeration of self-interstitials and di-interstitials. Eqs. (7) and (8) describe the recombination of vacancies at self-interstitials and interstitial clusters, respectively. Self-interstitials can also recombine at He-vacancy clusters according to reaction (9). Eqs. (1)–(9) correspond to the mechanisms of the initial model presented in Ref. [3]. As in our previous work, the vacancy mechanism by which the  $\text{HeV}_2$  complex migrates in Fe was neglected. Since carbon has a strong interaction with vacancies, as predicted by *ab initio* calculations [7,8], it is expected that a significant amount of vacancies will be trapped by carbon. Thus, the amount of vacancies that will be able to form  $\text{HeV}_2$  complexes will be significantly reduced. Therefore, the vacancy mechanism can also be neglected in the conditions considered here. In Fig. 1 the results obtained with this model are compared to experimental desorption data obtained by Vassen et al. [6]. As one can see, the model cannot reproduce helium desorption measured experimentally. With this model of He clustering in pure Fe, He desorption is highly underestimated in all conditions. Eqs. (10) and (11) correspond to the new mechanisms introduced to extend the model in order to

account for the trapping of a vacancy by an interstitial carbon atom and the trapping of a mobile He atom by a CV cluster, respectively. Using this kinetic model and the *ab initio* data given in Refs. [4,9] we simulated the desorption experiments carried out by Vassen et al. [6]. The only free parameters of this model are the concentration of carbon and the binding energies of Eqs. (10) and (11). These parameters were modified until a good agreement between simulation and experimental desorption data was reached for all conditions described in Ref. [6]. A good fit to the experimental data was obtained for concentrations of carbon ranging between 50 and 150 appm, and binding energies of  $0.69 \pm 0.08$  eV and  $1.78 \pm 0.08$  eV for  $\text{C}_i\text{-V}$  and  $\text{CV-He}_i$ , respectively. As can be seen in Fig. 2, with these fitted values the model including carbon impurity reproduces well the different phases of He desorption for the very different conditions of temperature, He concentration and sample thickness.

### 3. Discussion

The fitted value found in this work for the binding energy of  $\text{C}_i\text{-V}$  is in relatively good agreement with these values of 0.47 and 0.64 eV found theoretically by *ab initio* calculations in Refs. [7] and [8], respectively. This result supports thus the mechanism introduced in Eq. (10) according to which a vacancy can be temporarily trapped by interacting with an interstitial carbon atom. On the other hand, this trapping mechanism could explain the high value for the effective migration energy of the vacancy found in our previous work, which indicates that vacancy diffusion is delayed in the experimental conditions considered here. The binding energy found for  $\text{CV-He}_i$  clusters is the same as the effective binding energy of  $\text{He}_i\text{-V}$  found in Ref. [3], i.e. 1.78 eV. This suggests that the effective binding energy found for  $\text{He}_i\text{-V}$  in our previous work corresponds in fact to the binding energy of  $\text{CV-He}_i$  complexes. Thus, the results found with the model presented here support the assumption that carbon likely affects He kinetics by forming  $\text{He-V-C}$  complexes. It is important to note that although the simulation results obtained here are in agreement with experimental observations, the authors are aware that other reactions with carbon than the ones introduced here (Eqs. (10) and (11)) should be taken into account. At the moment, *ab initio* calculations are being conducted and a more extended kinetic model is being developed in order to include reactions of higher order between He, vacancies and carbon.

In the following we analyse in detail with the model including carbon impurity the different mechanisms responsible for the experimental He desorption. In Fig. 3 we reported the temporal evolution of the dominant species during annealing at  $T = 577$  K.

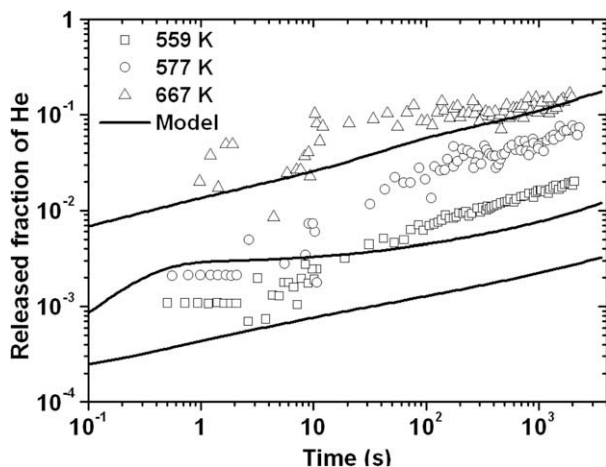


Fig. 1. Comparison between the experimental desorption data (open symbols) of Ref. [6] and simulations (solid lines) with the model of He clustering in pure Fe (without carbon) for temperatures of 559, 577 and 667 K.

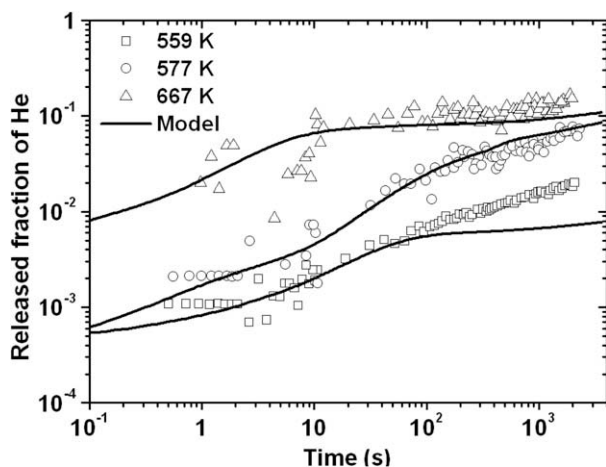


Fig. 2. Comparison between the experimental desorption data (open symbols) of Ref. [6] and simulations (solid lines) performed with the model including carbon for temperatures of 559, 577 and 667 K.

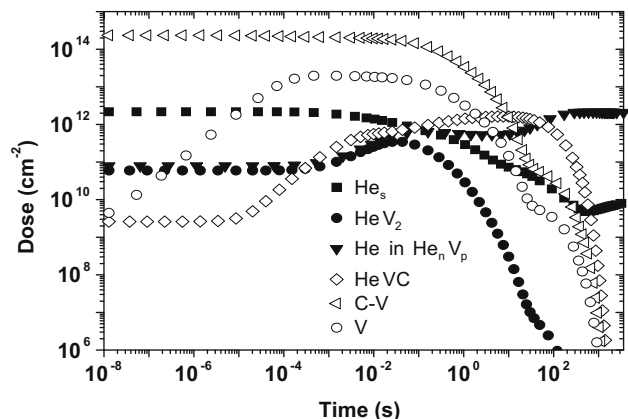


Fig. 3. Temporal evolution of the dominant He–V–C species at 577 K, according to the model including carbon.

Fig. 3 shows that at the beginning of annealing most He atoms are in substitutional sites. Simulation results show that a small amount of He is also trapped in small He<sub>2</sub>V and HeV<sub>2</sub> complexes. We can also see that most vacancies have recombined either with interstitial He or interstitial C at room temperature, which explains the high concentrations of HeV and CV complexes. According to these simulations, during the first 10<sup>-1</sup> s at 577 K, the concentration of HeV slowly decreases while the concentration of HeVC increases. This indicates that HeV dissociates, releasing an interstitial He that may migrate and react with C–V clusters present in high concentration, to form HeVC complexes (Eq. (11)). We can see that at the same time, the concentration of HeV<sub>2</sub> increases. A detailed analysis showed that this is due to the reaction between HeV and mobile vacancies. Fig. 3 shows that between 10<sup>-1</sup> s and up to  $t \approx 100$  s, most of He atoms are now trapped in HeVC clusters. Finally, after this stage, the concentration of HeVC drops while the concentration of He contained in larger He–V clusters increases. This occurs by dissociation of HeVC clusters, which release mobile He<sub>i</sub> that migrate and agglomerate into more stable He–V complexes. With these results we are now able to explain why the model predicts a faster – and in agreement with experiments – He desorption when carbon is present in the samples. At the beginning of annealing, a large amount of vacancies reacts with interstitial carbon according to Eq. (10). This trapping of the vacancies is crucial since it inhibits the formation of stable He–V complexes that form at the beginning of annealing when carbon is not present. At the same time, the formation of C–V clusters at high concentration by means of this trapping mechanism, promotes the formation of HeVC clusters following reaction (11) when HeV dissociates and releases mobile He<sub>i</sub>. Since HeVC is present at high concentration during the first 100 s of annealing and has a dissociation energy substantially smaller than stable He–V clusters, we observe thus a faster desorption than in pure Fe (see Figs. 1 and 2). These results evidence the essential role of carbon in the He desorption.

#### 4. Conclusions

In the present work we studied the effects of carbon on He kinetics. We introduced in our model two mechanisms to ac-

count for the influence of carbon on experimental desorption of He, namely, the formation of C–V and HeVC complexes. A good agreement could be found between the model and experimental data for binding energies of 0.69 eV and 1.78 eV for C<sub>i</sub>–V and He<sub>i</sub>–CV, respectively. The binding energy for C<sub>i</sub>–V was compared to *ab initio* calculations and was found to be in good agreement, which supports the role of these complexes in the model. The binding energy for He<sub>i</sub>–CV was found to be exactly the same as the one found in a recent work of the authors for the effective binding energy of He<sub>i</sub>–V. This strongly suggests that the effective energy we found in our previous work – which did not include carbon – corresponds in fact to the binding energy of He<sub>i</sub>–CV. A detailed study of the mechanisms responsible for He desorption was made using the model including carbon. This analysis showed that CV and HeVC complexes play an important role in the He kinetics. This model is a first approach to including the effect of C in Fe. This simplified model only includes two new types of clusters, CV and HeCV, and therefore the values obtained for binding energies of these clusters can only be taken as effective values. Other, more complex clusters, could be formed, such as the V–C<sub>2</sub> complex, which has a strong binding energy of 0.71 eV according to *ab initio* data [7]. The introduction of this complex could explain the higher binding energy value that we obtain for the CV cluster compared to the *ab initio* results. A full model based on *ab initio* data for different C–V and He–C–V clusters sizes is now in progress.

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