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Radiation Effects

PERFORM 60 - <u>Prediction of the Effects of Radiation FOr Reactor</u> pressure vessel and in-vessel <u>Materials using multi-scale modelling</u> – <u>60</u> years foreseen plant lifetime

<u>A. Al Mazouzi¹</u>, D. Lidbury², M. Konstantinovic³, D. Moinereau¹, A. Alamo⁴,

¹EDF R&D, Avenue les Renardières, Ecuelles, 77818 Moret sur Loing Cedex, France ²SERCO assurance, Walton House, Warrington Cheshire WA3 6GA, UK ³SCK.CEN, Boeretang 200, 2400 Mol, Belgium ⁴CEA, Saclay 91 191 Gif-sur-Yvette cedex, France

In nuclear power plants, materials may undergo degradation due to severe irradiation conditions that may limit their operational life. Utilities that operate these reactors need to quantify the ageing and the potential degradations of some essential structures of the plant to ensure its safe and reliable operation. So far, to take into account these degradations in the design and safe operation of the installations, the utilities and consequently the safety authorities rely mainly on infield experience and on the experimental testing of surveillance materials in specialized hot cells.

Continuous progress in the physical understanding of the phenomena involved in irradiation damage and environmental effects, and in computer sciences encouraged the development of multi-scale numerical tools able to simulate the material behavior in nuclear field. Thus, recently, the FP7 Collaborative Project PERFORM 60 [1], has been launched to pursue the improvement of the developed tools under the previous FP6 PERFECT project [2], for reactor pressure vessel (RPV) steels and to initiate the development of similar multi-scale modeling tools to simulate the combined effects of irradiation and corrosion on the RPV internals.

To reach these objectives, twenty European organizations involved in the nuclear field are engaged to develop the necessary computer tools and their integration in a user friendly platform with the main concern to produce experimentally validated physical models to predict the lifetime of these components.

In this lecture, in addition to an overview of the project, the work that is being performed will be illustrated by examples to demonstrate the robustness and the complexity of the multi-scale modeling approach when applied to nuclear materials.

[1] <u>www.perform60.net</u>

[2] <u>www.fp6-perfect.net</u>

Contact: Abderrahim AL MAZOUZI, E-mail : abderrahim.al-mazouzi@edf.fr Tél. : 01 60 73 62 19

Thermodynamics of nanoclusters in bcc-Fe containing copper, nickel and vacancies

<u>A.T. Al-Motasem¹</u>, M. Posselt², M. Talati¹, F. Bergner¹

Forschungszentrum Dresden-Rossendorf, ¹Institute of Safety Research, ²Institute of Ion Beam Physics and Materials Research, P.O.Box 510119, D-01314 Dresden,

Germany

E-Mail: a.almotasem@fzd.de

Reactor pressure vessel (RPV) steels consist of polycrystalline bcc-Fe with different alloying elements, e.g. Ni, and different impurities, e.g. Cu. The continuous irradiation by fast neutrons leads to a supersaturation of vacancies and self-interstitials which enhances the diffusion of the foreign atoms and causes the formation of nanosized clusters. The interaction of dislocations with these precipitates is considered to be the main cause of hardening and embrittlement of RPV steels. In order to model the evolution of the nanoclusters under irradiation at typical temperatures by rate theory, the dependence of their nucleation free energy on cluster size and composition must be known. In the present work atomic-level computer simulations are employed to determine these data since they are hardly obtainable by experimental investigations. The ternary Fe-Cu-Ni interatomic potential by Bonny et al. [1] is used in order to consider the thermodynamics of nanoclusters which may consist of the two foreign species and vacancies. In particular the influence of Ni on the formation of clusters containing Cu and vacancies is investigated since previous theoretical [1] and experimental [2,3] studies indicated synergistic effects. The nucleation free energy of the clusters is determined by the energy and the entropy change due to precipitation using isolated (diluted) Cu and Ni atoms as well as vacancies as the reference. In agreement with experimental observations the nanoclusters are assumed to have the bcc structure of the iron matrix. The energy and entropy contributions are calculated using combinations of on-lattice Monte Carlo simulations and off-lattice molecular dynamics calculations.

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In Situ TEM Study of Dynamic Behaviors of Nanoscale Defects: Similarities and Differences between Experiments and Simulations

Kazuto Arakawa^{1,2}, Takafumi Amino¹ and Hirotaro Mori¹

¹ Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan (arakawak@uhvem.osaka-u.ac.jp)
² JST, CREST, 5, Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

It is believed that dynamic behaviors of nanoscale and subnanoscale defects, such as prismatic dislocation loops, in metals play key roles in microstructural evolution under irradiation. Molecular dynamics (MD) simulations have revealed various dynamic processes of loops. In particular, it was shown that loops can undergo one-dimensional glide diffusion. On the other hand, we have been applying in-situ transmission electron microscopy (TEM) technique to actual dynamic behaviors of loops in body-centered cubic iron and tungsten after and under high-energy electron irradiation. In this talk, we will provide some examples of our TEM experimental results, and show the similarities and differences between the results obtained by MD simulations and our experiments.

The examples shown will be as follows: (1) Diffusivity and activation energy of one-dimensional glide diffusion and three-dimensional diffusion of 1/2<111> loops and <100> loops: Here, the effects of even small amounts of impurity and solute atoms will be emphasized. (2) Interaction among loops: Elastic interaction among loops modifies the loop diffusion, and often causes the collision among loops. (3) Effects of high-energy particle irradiation on the loop motion.

Diffusion studies on the Al₃U ordered compound applying Artificial Intelligence tools

N.Barrios¹, N.Castin^{2,3}, <u>M.I.Pascuet</u>^{4,5}, J.R.Fernandez^{1,5,6}

 ¹Instituto Sabato,Univ. Nac. de Gral. San Martin / CNEA, 1499 Gral. Paz Av., B1650KNA, Buenos Aires, Argentina.
 ²Phys. de Solides Irradiés et des Nanostruct. (PSIN), Univ. Libre de Bruxelles (UBL), Blvd. du Triomphe CP234, 1050 Brussels, Belgium.
 ³SCK-CEN, Nucl. Mat. Sci.Inst., Boeretang 200, B-2400 Mol, Belgium.
 ⁴Ciclo Básico Común, Univ. de Buenos Aires, R.Cantilo Av. s/n, Buenos Aires, Argentina.
 ⁵Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), 1917 Rivadavia Av., C1033AAJ Buenos Aires, Argentina.
 ⁶Dept. de Materiales, CAC, Com. Nac. de Energía Atóm. (CNEA), 1499 Gral. Paz Av., B1650KNA, Buenos Aires, Argentina Corresponding author e-mail: pascuet@cnea.gov.ar

The U-Mo alloy dispersed in AI matrix has been proposed as a prototype for new fuel elements of experimental nuclear reactors. The diffusion products stability in the U-Mo/AI interface is of fundamental importance to avoid material degradation. Such stability can be achieved by promoting the formation of Al₃U intermetallic against those of higher AI concentration [1].

In this work, we study the mobility of species in the AI_3U ordered compound (struktubericht L1₂). An artificial neural network (ANN) based approach [2] is used to introduce relaxation and long-range chemical effects into the prediction of activation energy barriers, assuming a vacancy diffusion mechanism. A moderately large number of vacancy migration energies are tabulated as a function of the local atomic environment in order to train the ANN. Each migration energy is calculated by means of suitable EAM potentials for the AI-U system [3,4] using molecular statics (T=0K). After training, the ANN succeeds in providing accurate predictions of the migration energies, at a reasonable CPU cost.

Finally, the obtained synapsis is used to calculate the diffusion coefficients of both species by performing atomistic kinetic Monte Carlo simulations at different temperatures.

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Phase Stability of Metallic Nuclear Fuels: a Multi-scale Coupling of Phase-field Modeling with CALPHAD and First-Principles¹

James F Belak^a, Jean-Luc Fattebert^b, Gerard L. Hofman^c, Yeon S. Kim^c, Alexander I. Landa^a, Vincenzo Lordi^a, Per A. Söderlind^a, Patrice E.A. Turchi^a and Abdellatif M. Yacout^c

^aCondensed Matter and Materials Division ^bCenter for Applied Scientific Computing Lawrence Livermore National Laboratory PO Box 808, L-45 Livermore CA 94550 USA ^cNuclear Engineering Argonne National Laboratory 970 South Cass Avenue Argonne IL 60439 USA belak1@llnl.gov

An analysis of the performance of UZr-based metallic fuels for fast reactor applications requires the knowledge of alloy composition and phase stability everywhere in the fuel during the entire in-reactor history. A multi-scale model was developed for describing concurrent phase content. composition. and microstructure evolution in metallic fuels based on the phase-field framework. The elements of this model include: a representation of the alloy thermodynamic driving force; the mobility of alloy elements and defects; and a spatially resolved phase-field evolution model. Here, we extend our phase-field code² to include the physics of UZr metallic fuels through the thermodynamic approach that forms the core of our phase diagram modeling. The Gibbs energy of individual phases is represented, and the model parameters are collected in a thermodynamic database from the assessment of available experimental data supplemented with first-principles calculations. These methods have been developed to the point where reliable ground-state properties can be predicted for metallic alloys and actinides mixtures.³ The Gibbs energy of individual phases and the coupling of phase diagram and thermo-chemistry is represented using the CALPHAD methodology. This CALPHAD representation feeds directly into our phase-field modeling as the thermodynamic driving force. This modeling is then used to examine the influence of irradiation on the relative change of phase stability and inter-diffusion.

1. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

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Kinetic lattice Monte Carlo simulations of solute atom cluster formations based on ab initio calculations

Kiyoshi Betsuyaku¹, Toshiharu Ohnuma¹ and Naoki Soneda¹

¹Material Science Research Laboratory, Central Research Institute of Electric Power Industry, 2-11-1 Iwado Kita, Komae, Tokyo 201-511, Japan E-mail: betuyaku@criepi.denken.or.jp

An accurate prediction of embrittlement of neutron-irradiated reactor pressure vessel steel is very important for the long-term operation of light water reactors. Although solute atom clusters formed in the steel have been observed by using several techniques such as three-dimensional atom probe tomography, an understanding of the elementary mechanisms of the formation of the clusters has not been established. It is difficult to carry out fully ab initio calculation for formation of solute atom clusters which sizes are over 2nm. The combination of ab initio calculation and kinetic lattice Monte Carlo simulation is powerful tool to describe formation process of solute atom clusters.

We have carried out ab initio calculations to determine the interactions among solvent, solute atoms and vacancies, and migration barriers in Fe based alloys and built the database used to parameterize pair energies for kinetic lattice Monte Carlo simulations. The result of the simulations for Fe-Cu-Ni-Si alloy with plural vacancies shows that each vacancy acts as a nucleus of small Cu-main cluster and is trapped by the cluster (Fig. 1). This indicates the importance of surplus vacancies in the alloys caused by irradiations for the initial process of the formation of solute atom clusters.



Fig. 1 Spatial distribution of atoms for Fe-Cu-Ni-Si alloy on 32768 lattice points with 5 vacancies. (001) plane is parallel to the sheet. Green, blue, yellow, red balls indicate Cu, Ni, Si, vacancy, respectively. Solute atom clusters with vacancies are encircled by red circles.

Mobility of self-interstitial defects and small dislocation loops in Fe-Cu-Ni alloys: model alloy for RPV steels

<u>G. Bonny¹ and D. Terentyev¹</u>

¹Nuclear Materials Science Institute, SCK•CEN, Boeretang 200, B-2400 Mol, Belgiumum Gbonny@sckcen.be

Reactor pressure vessel (RPV) steels are known to undergo hardening and embrittlement under neutron irradiation. This is attributed to the formation of nanometric precipitates, dislocation loops and voids. In recent years, atomistic simulations have shown to be a helpful tool to better understand the mechanisms leading to the material's degradation and to be a good supplementary tool to rationalize experiments. In particular, atomic-scale simulations allow to consider tiny details of the interaction between point defects and impurities, which are very well to known to affect significantly the evolution of microstructure. Here, we consider ternary Fe-Cu-Ni alloy as a first approximation to a model RPV steel.

In this work, we characterize the interaction of small 1D-mobile selfinterstitial atom (SIA) clusters, as observed to form cascades, with Cu and Ni solutes. On the one hand, we use static simulations to characterize the energetics of interaction between SIA clusters and solutes. On the other hand, we use a recently developed "loop-drag" model, formulated by Rong et al., to estimate the mobility of dislocation loops at finite temperature. The latter model allows one to correlate the drag coefficient for the dislocation dragging the loop to the loop diffusion coefficient. Thus, we apply this model to calculate the effective mobility of SIA clusters as a function of alloy composition and temperature. The obtained results can serve as input parameters for object kinetic Monte Carlo and mean field theory models which treat 1D-migrating dislocation loops.

On the atomic-scale design of metal-metal heterointerfaces for radiation resistance

M. J. Demkowicz¹, K. Kolluri² and A. J. Vattré²

¹Department of Materials Science and Engineering, MIT room 4-142, Cambridge MA, 02139, USA | demkowicz@mit.edu ²Department of Materials Science and Engineering, MIT room 4-053, Cambridge MA, 02139, USA

We present a multiscale modeling effort to understand and control the effect of heterointerfaces on the radiation response of metal-metal nanocomposites. For selected model interfaces, atomistic simulations are used to characterize interface structure and to determine the mechanisms of interface-point defects interactions, including trapping, diffusion, and defect reactions. This information is then incorporated into mesoscale dislocation-based and continuum approaches to investigate the steady-state interface response to radiation-induced defect fluxes. With insights gained from studying this "forward" problem of predicting radiation response of selected model interfaces, we attempt to solve the "inverse" problem of determining what interfaces will yield desired radiation response. Quantification of uncertainty and validation through comparison with experiments are discussed.

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Modeling of helium bubble growth in neutron irradiated boron doped RAFM steels

C. Dethloff^{1,a}, E. Gaganidze¹, V. Svetukhin², M. Tikhonchev², O. Weiß¹, J. Aktaa¹

¹Karlsruhe Institute of Technology (KIT), Institute for Materials Research II, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany ²Ulyanovsk State University, 432970, Leo Tolstoy Str. 42, Ulyanovsk, Russian Federation ^aEmail address: christian.dethloff@kit.edu

ABSTRACT

Upcoming fusion technology requires advanced structural materials that are capable to withstand high temperatures and neutron irradiation on years scales typical for reactor lifetimes. Reduced activation ferritic-martensitic (RAFM) steels are main candidates for this purpose, also providing low activation to ease radioactive waste recycling. Besides other microstructural defects 14.1 MeV fusion neutrons will generate transmutation helium in the steel matrix, whose negative influences on the mechanical properties need to be investigated. Helium generation in irradiation experiments taking place in conventional fission reactors is quite low, therefore doping with boron isotope ¹⁰B is used to simulate helium production.

A phenomenological model is developed to describe homogeneous nucleation and growth of helium bubbles in irradiated boron doped RAFM steels. The model is based on kinetic rate equations for helium clustering, which are numerically solved by using a Fortran code. The calculations, which are performed for a fixed helium-to-vacancy ratio and with an effective helium diffusivity as a fit parameter, yield the time dependent size distributions of helium bubbles. Peak bubble diameters were obtained for different boron doped steels in the range of 3 to 10 nm with bubble densities depending on the helium content. Quantitative microstructural investigations of unirradiated and irradiated specimens will be used to support and verify the model.

1. Introduction

Due to their advanced irradiation resistance compared to conventional austenitic steels reduced activation ferritic-martensitic (RAFM) steels are considered as primary candidate structural materials for in-vessel components of future fusion power plants. Severe microstructural changes under neutron irradiation lead to strong low temperature hardening and embrittlement, and therefore limit their application at temperatures below 350 °C. Furthermore, transmutation helium to be generated in the RAFM steels due to 14 MeV fusion neutrons is believed to strongly influence the materials mechanical properties [1].

Lacking an appropriate irradiation facility capable of providing a neutron spectrum close to fusion conditions experimental fission reactors are used to assess irradiation damage. Unfortunately, transmutation reactions in particular depend highly on neutron spectra, and are therefore underestimated by irradiation experiments. One of the methods to simulate helium production in a spectrum of conventional fission reactor is alloying with the boron isotope ¹⁰B, which is contained in natural boron to a fraction of 20 %. Due to its high transmutation cross section ¹⁰B can be used to generate helium in fission irradiation experiments [2]. Furthermore, by varying the ratio of ¹⁰B and ¹¹B the amount of transmuted helium can be

adjusted while the steel composition remains unchanged, eliminating microstructural influences.

A phenomenological model based on kinetic rate equations is developed to describe homogeneous nucleation and growth of helium bubbles in irradiated boron doped RAFM steels. Simulation parameters are adapted to irradiation conditions in two different irradiation experiments, namely HFR IIb (SPICE) [3] performed in the Petten High Flux Reactor at 250 °C and ARBOR1 [4] performed in the Bor-60 reactor, Dimitrovgrad at 338 °C. Taking into account different helium generation rates due to the different irradiation conditions (neutron spectra, dose) the time evolution of the helium bubble size distributions is calculated and compared.

2. Model description & numerics

In this paragraph a short description of the developed model is presented, for a more comprehensive view the reader is referred to [5].

The model is based on homogeneous nucleation theory [6]. Unlike larger helium clusters only helium monomers (M) are considered mobile in the matrix. They may join each other and form dimers or may be caught by larger clusters of size i according to the following scheme

$$M + M_i \xrightarrow{k_i} M_{i+1}.$$
(1)

The probabilities of capturing and emitting of a monomer with concentration C_1 by a cluster are expressed by kinetic rate coefficients k_i and g_{i+1} , respectively. The evolution of cluster concentrations C_i with time is described by the Master equation

$$\frac{\partial C_i(t)}{\partial t} = -[k_i C_1(t) + g_i] \cdot C_i(t) + g_{i+1} \cdot C_{i+1}(t) + k_{i-1} C_1(t) \cdot C_{i-1}(t).$$
(2)

The kinetic rate coefficients are given by the following equations

$$k_{i} = 4\pi \cdot D_{He}^{eff} \cdot R_{i} \quad \text{and} \quad g_{i+1} = k_{i} \cdot C_{He}^{eq} \cdot \exp\left[\frac{2 \cdot \Omega \cdot \gamma}{k_{B}T \cdot R_{i}}\right], \quad (3), (4)$$

with D_{He}^{eff} - the effective helium diffusivity, R_i - the cluster radius, C_{He}^{eq} - the helium solubility, Ω - the atomic volume of host lattice, γ - the surface energy, k_B - the Boltzmann constant and T the absolute temperature [7]. Due to the size-dependent emission rate constant a coarsening mechanism is introduced similar to [8], where smaller clusters have a higher probability of emitting a monomer than larger bubbles leading towards an enhanced bubble growth.

Within the model the helium-to-vacancy ratio in a cluster is assumed to be unity. This simplification is supported by [9] where a helium-to-vacancy ratio close to one was shown to correspond to the lowest helium-vacancy cluster formation energy. The helium diffusion mechanism is not explicitly specified in the model. We rather assume the dominance of only one mobile defect type, without explicit specification of vacancies. The effective diffusivity of helium is taken as a fit parameter close to calculated values for a helium-divacancy diffusion mechanism from [10].

A developed Fortran code numerically solves the rate equations. Explicit Euler's method is used to calculate the cluster size distribution after a chosen step size Δt . An automatic step

size control [11] is implemented to optimize the calculation. While initial condition $C_i(t_0)$ and right boundary condition $C_{imax}(t)$ are set to zero, the left boundary condition is given by the concentration of single helium atoms C_1 , calculated at each time step by

$$C_{1}(t) = C^{He}(t) - \sum_{i=2}^{i\max} iC_{i}(t), \qquad (5)$$

where C^{He} is the produced cumulative helium concentration (described in the next section). The sum expresses all helium bound to clusters with a size of $i \ge 2$.

4. Simulations and discussion

The model is adapted to EUROFER97 based RAFM steels ADS2 and ADS3 (compositions are shown in [1]), which were doped with 0.0082 wt% natural boron and 0.0083 wt% ¹⁰B, respectively. Simulations were performed for both SPICE and ARBOR1 irradiation experiments. The produced characteristic cumulative helium concentration C^{He} is described by

$$C^{He}(t) = C_{10B}^{\max} \cdot \left(1 - \exp\left[-\frac{G_{dpa} \cdot t}{G_{dpa}^{0}}\right]\right) + G_{Fe-matrix}G_{dpa} \cdot t.$$
(6)

While the first term gives the helium concentration due to boron-to-helium transmutation [12], the second one provides additional helium produced by alloyed elements and their natural isotopes [13]. Within this equation, C_{10B}^{max} is the maximum helium content available after transmutation of all ¹⁰B, G_{dpa} is the damage rate, G_{dpa}^{0} is the transmutation time constant and $G_{Fe-matrix}$ is the helium generation rate due to matrix isotope transmutation. Calculation parameters for irradiation experiment SPICE are taken from [12,13], ARBOR1 parameters from [14]. Final cumulative helium concentrations C^{He} in SPICE (ARBOR1) yield 91 (13) appm for ADS2 and 439 (50) appm for ADS3.

Simulations were performed with characteristic irradiation parameters and helium diffusivities as fit parameters of 8.0×10^{-11} and 2.4×10^{-10} cm²/s for SPICE and ARBOR1, respectively. The resulting helium bubble size distributions in both boron doped steels ADS2 and ADS3 are shown in Fig 1.



Figure 1: Simulated helium bubble size distributions in ADS2 and ADS3 for SPICE and ARBOR1 irradiation experiments

In the case of SPICE irradiation the final bubble size distributions peak after 6.67×10^7 s at bubble diameters of 3.8 and 4.6 nm for ADS2 and ADS3, respectively. The peak concentrations are two orders of magnitude higher than those for the ARBOR1 experiment due to the different helium generation rates and helium contents. The peak bubble diameters for the ARBOR1 calculations yield 5.4 and 6.2 nm for ADS2 and ADS3, respectively, already after 1×10^7 s, which are larger than the diameters in SPICE and can be attributed to a higher neutron flux and higher irradiation temperature influencing the material parameters. The temperature was taken into account by estimating the helium diffusivity to a higher value in the simulation parameters [10]. While the helium generation by boron transmutation already ceases after 1×10^7 s for the SPICE experiment, only about 2 percent of the boron in ARBOR1 specimens is burnt up after that time. This circumstance is also observable in Fig 1: while for the SPICE specimens the concentrations drop at small bubble sizes the ARBOR 1 specimens show increase of concentrations at small bubble sizes due to continuous boron burn up. Almost constant transmutation rates during the whole ARBOR1 irradiation experiment of 3.98x10⁷s yield estimated final peak bubble diameters of 8.5 and 9.6 nm for ADS2 and ADS3, respectively. Calculated final helium bubble size distributions will be used for comparison with the results of ongoing quantitative TEM investigations on irradiated specimens and for estimating the influence of helium bubbles on the mechanical properties.

Acknowledgements

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The early evolution of damage in the Fe-Cr system

D. Diaz¹, M. Hernández-Mayoral², M.-J. Caturla³, M. Victoria¹, M. Perlado¹

¹Instituto de Fusión Nuclear, Universidad Politecnica de Madrid, Madrid, Spain

²CIEMAT, Madrid, Spain ³Dept. Física Aplicada, Facultad de Ciencias, Fase II, Universidad de Alicante, Alicante, E-03690, Spain mi.caturla@ua.es

The accumulation of damage in the Fe-Cr system has been studied by both experiments and modeling. The presence of difference concentration of both 1/2<111> and <100> interstitial loops are being observed under transmission electron microscopy (TEM) in these alloys at different doses and temperatures.

Molecular dynamics simulations of cascade evolution have been performed in pure Fe and Fe-Cr alloys to determine the origin of the different types of loops. This information is used as an input of a kinetic Monte Carlo code that correctly predicts the densities of the cluster types observed. It also provides information on the density of nanovoids that are being observed by positron annihilation spectroscopy.

Effect of P and C in model dilute Fe alloys under irradiation by atomic kinetic Monte Carlo

R. Ngayam-Happy^{1,2}, C. Domain^{1,2} and C.S. Becquart²

 ¹ EDF-R&D Département MMC, Les Renardières, F-77818 Moret sur Loing Cedex, France
 ² Laboratoire UMET, UMR 8207, Université de Lille 1, ENSCL, F-59655 Villeneuve d'Ascq Cedex, France

Raoul.ngayam-happy@edf.fr

The cohesive model used to simulate the evolution of the microstructure of dilute Fe alloys (Fe-CuNiMnNiSi) under irradiation has been extended to take into account C and P atoms. In this multiscale approach based on *ab initio* and atomistic kinetic Monte Carlo simulations solute atoms can diffuse either by a vacancy mechanism or via the formation of mixed dumbbells when these dumbbells are stable, as is the case for phosphorous and manganese. The carbon atoms diffuse by atomic jumps on their own interstitial lattice on octahedral sites.

The model has been used to simulate the medium term evolution of different Fe dilute alloys under electron or neutron irradiations. These irradiations are modeled by introducing cascade debris of MD cascades as well as a flux of Frenkel pairs. The results obtained will be presented and discussed. Because of its non negligible attraction to the vacancies, the presence of carbon atoms modifies the other solute diffusion and thus the formation of solute clusters. The influence of phosphorus atoms whose mixed dumbbells are trapped by other phosphorous atoms will also be examined.

Coupled microstructure and microchemical evolution in irradiated alloys

Santosh Dubey¹, Anter El Azab^{1,3}, Dieter Wolf²

¹ Department of Scientific computing, Florida State University, Tallahassee, FL, USA ² Idaho National Laboratory, Idaho Falls, ID, USA ³ Email: aelazab@fsu.edu

ABSTRACT

We present a reaction-diffusion model for element redistribution in a concentrated binary alloy under irradiation. The model tracks the space and time evolution of the concentration fields of vacancies, interstitial dumbbells and atomic species A and B, under cascade conditions. With this model, we have studied redistribution of alloying elements as a result of irradiation.

1. Introduction

The interaction of energetic particles with a multi-component material results in localized atomic displacement bursts and atomic mixing. Following these displacement bursts, diffusion tends to flatten out the resulting perturbations in defect concentrations and species composition. The competition between the continual perturbation of the lattice by external particles and the continuous recovery by diffusion brings about interesting types of microstructural and microchemical changes. For example, irradiation can bring about species redistribution, precipitation of thermally unstable phases, dissolution of thermally stable phases, disordering of ordered precipitates, irreversible segregation near lattice inhomogeneities, self-organized compositional patterns, etc. All of these irradiation-driven changes in the state of the material have been studied under one heading: *Phase Stability under Irradiation*^{1.2}.

In this short communication, we shed light on one related aspect, phase stability due to inverse Kirkendall effect^{1,6}, a process of irreversible segregation of solute atoms under irradiation. This process was first observed experimentally by Anthony³ and verified later by Wiedersich⁴ with a successful model based on the random alloy theory^{5,6}. In his model, Wiedersich considered the interstitial flux to be identical to the vacancy flux, and that interstitials jumps occur by an interstitial mechanism. This treatment is inadequate in alloys where interstitials exist in dumbbell configuration because the migration and conversion of a dumbbell happens through interstitialcy mechanism⁷. In this process, one of the atoms of the dumbbell jumps to a nearest neighbor to form a new dumbbell and the atom left behind becomes a regular lattice atom. Explicit calculation of dumbbell fluxes using interstitialcy mechanism and its effect on radiation-induced material redistribution has been conducted by Hashimoto and co-workers⁸. Murphy⁹ has also studied the contribution of interstitial flux to radiation-induced segregation in concentrated alloys by considering interstitialcy migration. In the latter work⁸, the authors considered the diffusion of dumbbells and derived expressions for their fluxes; these expressions have terms corresponding to conversion of one dumbbell to another, which may not be a proper way to treat dumbbell fluxes. In fact, in a dumbbell, one of the two atoms sharing the lattice site diffuses, while the other becomes a regular atom. So, instead of defining flux of the dumbbell, we need to define flux of the diffusing atom, which brings about changes in concentration of dumbbells and also regular atoms. Keeping this in mind, we have re-derived the flux of interstitial atoms in the dumbbells and consequent changes in concentration of all species accordingly.

2. Basic Model

We consider a random solid solution with components A and B. Due to irradiation, Frenkel pairs are produced in concentrations much higher than the equilibrium values. A and B atoms in interstitial state form dumbbells of configurations AA, BB and AB. So, in total, we have six species to deal with: A, B, AA, BB, AB and vacancies, and material under irradiation may be viewed as reaction-diffusion system maintained away from equilibrium by point defect sources. The species concentrations evolve according to

$$\frac{\partial C_j}{\partial t} = -\nabla \cdot J_j + R + S,\tag{1}$$

where C_j is the site fraction of species j (j = A, B, V, AA, BB and AB), J_j is flux of j^{th} species, which is equal to $-\sum_{k=1}^{n} D_{jk} \nabla C_k$, with D_{jk} being $n \times n$ matrix of diffusion coefficients and n is number of species. In the above, R and S are reaction and source terms. Here, the fluxes of A and B depend on the defects fluxes and have been derived using standard Fick's law approach, and mass transport is assumed to be carried out by vacancy and interstitialcy mechanism. In the latter mechanism, the interstitial sharing the lattice site with a regular atom may jump to nearby site to form a new dumbbell. In this process, the interstitial jump brings about change in the concentration of regular lattice atoms and the dumbbells. For example, an A^{int} jump may change the concentration of AA and AB dumbbells and regular A atoms. Similarly, B^{int} diffusion may bring about changes in BB, AB and B concentration. In addition to these mechanisms, regular A and B atoms diffuse by vacancy mechanism. Thus, the flux of regular A atoms can be written as:

$$J_A = J_A^v + J_A^I,\tag{2}$$

where J_A^v is due to vacancy mechanism and $J_A^I = -[J_{A^{int}}^{AA} + J_{B^{int}}^{AB}]$ is due to interstitialcy mechanism; $J_{A^{int}}^{AA}$ is a part of A^{int} flux that changes the AA concentration. Similarly, $J_{B^{int}}^{AB}$ is a part of B^{int} flux that changes the AB concentration. The flux of regular B atoms is given by

$$J_B = J_B^v + J_B^I,\tag{3}$$

in which J_B^v is the flux due to vacancy mechanism and $J_B^I = -[J_{Bint}^{BB} + J_{Aint}^{AB}]$ is due to interstitialcy mechanism.

With the above details in hand, we write a system of reaction-diffusion equations describing species redistribution in concentrated binary alloys as follows:

$$\frac{\partial C_{AA}}{\partial t} = -\nabla \cdot J_{A^{int}}^{AA} - R_{AA} + R_{AA}^{conv} + S_{AA}, \tag{4}$$

$$\frac{\partial C_{BB}}{\partial t} = -\nabla \cdot J_{Bint}^{BB} - R_{BB} + R_{BB}^{conv} + S_{BB}, \qquad (5)$$

$$\frac{\partial C_{AB}}{\partial t} = -\nabla \cdot \left[J_{A^{int}}^{AB} + J_{B^{int}}^{AB}\right] - R_{AB} + R_{AB}^{conv} + S_{AB},\tag{6}$$

$$\frac{\partial C_v}{\partial t} = -\nabla \cdot J_v - R_{AA} - R_{BB} - R_{AB} + S_v, \tag{7}$$

$$\frac{\partial C_A}{\partial t} = -\nabla \cdot J_A + 2R_{AA} + R_{AB} + R_A^{conv} + S_{AA}, \tag{8}$$

$$\frac{\partial C_B}{\partial t} = -\nabla \cdot J_B + 2R_{BB} + R_{AB} + R_B^{conv} + S_B.$$
(9)

In these equations, R_{ij} terms are due to vacancy-dumbbell recombination, R^{conv} are due to dumbbell conversion, and S are the cascade-induced source, which can be positive or negative for various species. These sources are taken here to have a core-shell distribution ¹.

3. Simulation and Results

The reaction-diffusion equations are non-dimensionalized and solved numerically on a 2D square domain of size 250×250 , $\Delta x = \Delta y = 1.0$ (non-dimensional units). Simulation has been performed at 800K for FCC Cu-Au alloy (see details in Ref. [10]). The initial concentration of alloying elements are $C_a = 0.6$ and $C_b = 0.4$. A centered difference scheme and a forward Euler method has been used. Figure 1 shows snapshots of evolution of concentration of various species: From Figure 1, we see a significant change in concentration of alloying elements



Figure 1: Concentration of various species after 1.48×10^6 time steps.

after irradiating the material for some time. We can characterize this redistribution in reciprocal space by studying the Fourier transform of fluctuations of C_a and C_b fields (Figure 2). From



Figure 2: A snapshot of Fourier transform of fluctuations in C_a (left) and C_b (right) fields.

Figure 2, we see that in the case of C_a , higher Fourier modes are concentrated symmetrically near the center (low $k \rightarrow$ large wavelength), whereas in case of C_b this is not the case (high $k \rightarrow$ short wavelength). This is attributed to the fact that A is a fast diffuser, hence it can diffuse to large distances and bring about changes in concentration farther into the domain, but B being a slow diffuser, the change in concentration is more or less localized (short wavelength). This behavior can be thought to indicate segregation of the alloying elements in the sense of inverse Kirkendall effect. We also see that, in both the cases, various modes are symmetrically placed, which means that at this stage of irradiation, there is no preferred mode/direction for the system to evolve to (patterning).

4. Concluding Remarks

We have developed a reaction-diffusion model which is able to predict microchemical changes (species redistribution and irreversible segregation) in concentrated binary alloy in the sense of an inverse Kirkendall effect. The model has been used to study species redistribution and its characterization in Fourier space. Preliminary results show significant changes in composition of material components due to irradiation. A natural extension of this work, to study segregation of alloying elements at the surfaces and how segregation can affect void nucleation and growth, is in progress. Integration of this model into a phase field approach, to study concurrent microstructure and compositional changes, is also underway.

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A stochastic algorithm for simulating real-time dynamics of interacting nano-defects in irradiated bcc metals

<u>S.L. Dudarev^{a1}</u>, M.R. Gilbert^a, K. Arakawa^{b,c,d}, H. Mori^b, **Z. Yao^e**, M.L. Jenkins^f, P.M. Derlet^g

^aEURATOM/CCFE Fusion Association, Culham Centre for Fusion Energy, Abingdon, Oxfordshire OX14 3DB, UK.

^bResearch Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.

^cOkinawa Institute of Science and Technology, Kunigami, Okinawa 904-0411, Japan. ^dJST, CREST, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan.

^eDepartment of Mechanical and Materials Engineering, Queen's University, Nicol Hall, 60 Union Street, Kingston K7L 3N6, Ontario, Canada.

^fDepartment of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK. ^gCondensed Matter Theory Group, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.

ABSTRACT

In-situ real-time electron microscope observations of metals irradiated with ultra-high-energy electrons or energetic ions show that the stochastic dynamics of microstructural evolution is visibly influenced by long-range elastic interactions between mobile nano-scale radiation defects. Treating elastic interactions is also necessary for modelling defect and dislocation microstructures formed in *ex-situ* high-dose-rate ion-beam irradiation experiments, and for interpolating the ion-beam irradiation data to the low-dose-rate limit characterizing the neutron irradiation environments of fission and fusion power plants. In this paper, based on Refs. (1; 2), we show that simulations, performed using an algorithm where nano-scale radiation defects are treated as interacting Langevin particles, are able to match and explain the key features of real-time dynamics of nano-defects observed in *in-situ* electron microscope experiments.

Diffusion of defects biased by elastic interactions gives rise to the new modes of microstructural evolution, involving trapping and correlated motion of defects, which in turn strongly influence the rates of reaction and coalescence between the defects. The Langevin dynamics approach described in this paper is able to model the dynamics of motion of radiation defects on timescales comparable to those of experimental observations (10 to 1000 s), as opposed to molecular dynamics simulations that are only able to address timescales many orders of magnitude shorter. The stochastic Langevin dynamics model appears particularly suitable for treating large ensembles of interacting defects, offering advantages related to the computational implementation and parallelization of the algorithm.

1. Introduction

Elastic fields bias thermally activated motion and the rates of coalescence and annihilation of radiation defects, and in this way drive microstructural evolution of materials in a nuclear environment. Evolution of an ensemble of non-interacting defects in an external potential field

¹corresponding author, email: sergei.dudarev@ccfe.ac.uk

 $U(\mathbf{r})$ is described by the diffusion equation of the form

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = D \frac{\partial}{\partial \mathbf{r}} \left[\frac{\partial P(\mathbf{r},t)}{\partial \mathbf{r}} + \frac{P(\mathbf{r},t)}{k_B T} \frac{\partial U(\mathbf{r})}{\partial \mathbf{r}} \right],\tag{1}$$

where $P(\mathbf{r}, t)$ is the single-particle ensemble-averaged probability density for migrating defects, T is the absolute temperature, and D is the diffusion coefficient.

In the above equation, the external elastic interaction field $U(\mathbf{r})$ is a factor responsible for the higher rate of absorption (by dislocations) of self-interstitial atom defects in comparison with vacancies. The difference between the rates of absorption of self-interstitial atoms and vacancies by dislocations, following from equation 1, forms the basis for the Rate Theory treatment of radiation swelling of materials (3; 4). Solutions of diffusion equations, required for defining the parameters of the Rate Theory model, were investigated by Bullough and Newman (5) in the isotropic, and by Skinner and Woo (6) in the anisotropic diffusion approximations.

One fundamental assumption associated with the treatment of diffusion based on equation 1 is related to the fact that this equation describes the evolution of a statistical ensemble of defects, and not the evolution of a *particular configuration* of defects and dislocations. Furthermore, the use of equation 1 implies that (i) the single-particle distribution function fully characterizes the evolving microstructure, making the evaluation of the two-particle and higher-order correlation functions not necessary, and that (ii) radiation defects do not interact, or the density of the defects is sufficiently low. Assumption (ii) suggests that equation 1 applies only in the limit of low irradiation dose rate. Provided that assumptions (i), (ii) are satisfied, the full many-particle diffusion equation

$$\frac{\partial P(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, t)}{\partial t} = \sum_{i=1}^N D_i \frac{\partial}{\partial \mathbf{r}_i} \left(\frac{\partial P}{\partial \mathbf{r}_i} + \frac{P}{k_B T} \frac{\partial U}{\partial \mathbf{r}_i} \right), \tag{2}$$

where $U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \sum_i U^{(1)}(\mathbf{r}_i) + (1/2) \sum_{i,j} U^{(2)}(\mathbf{r}_i, \mathbf{r}_j) + ...$ can, by neglecting the $U^{(2)}$ and higher-order terms, be reduced to a set of independent diffusion equations similar to equation 1.

In-situ electron microscope observations show that the above assumptions (i), (ii) about the twoparticle and higher-order correlation functions, and effects of interaction between the defects, being negligible under the conditions characterizing ultra-high-energy electron and/or ion-beam irradiation experiments, are not satisfied.

In-situ electron microscope observations, providing real-time visualization of diffusion of defects produced by ultra-high-energy electron irradiation (7; 8; 9), or showing microstructural evolution occurring under ion beam (10; 11; 12) irradiation, have revolutionized our understanding of how properties of metals and alloys change in the extreme radiation and thermal environments of a fission or a fusion power plant. The key feature of *in-situ* electron microscopy is its ability to exhibit the time-dependent dynamics of migration, interaction, and transformation of radiation defects, and to visualize the entire complexity of evolving defect and dislocation microstructures.

Interpreting *in-situ* real-time electron microscope observations remains genuinely problematic. The ten orders of magnitude mismatch between the nanosecond $(10^{-9}s)$ timescale accessible to a molecular dynamics simulation, and the 10 to 1000 seconds timescale of a typical *in-situ* electron microscope observation, impedes meaningful quantitative analysis. *In-situ* electron microscope observations show that simultaneous, as opposed to sequential, production of mobile



Figure 1: A sequence of *in-situ* electron microscope snapshots recorded for $\mathbf{g} = 002$ diffraction conditions at a 200 kV accelerating voltage, and showing the evolution of a system of two prismatic $a/2[11\overline{1}]$ dislocation loops formed in nominally pure iron by ultra-high voltage electron irradiation prior to the *in-situ* experiment. The loops perform one-dimensional thermally activated Brownian motion in the direction parallel to their Burgers vector at T = 673K.

defects at high irradiation dose rates results in microstructural evolution that is influenced by the 'collective' dynamical events involving correlated motion of several defects, leading to the formation of defect rafts, coalescence of defects, and the eventual self-organization and spatial ordering of defects. All these phenomena are routinely seen in *in-situ* electron microscope experiments, suggesting that interaction between radiation defects does play a significant part in the dynamics of microstructural evolution, at least in the high irradiation dose rate limit.

The fact that elastic interactions between defects might affect microstructural evolution of a material under irradiation was noted by Hudson *et al.* (1) who investigated, using kinetic Monte Carlo simulations, the evolution of ensembles of interacting defects. The kinetic Monte Carlo model developed by Hudson *et al.* (1) treated the effect of elastic forces through the use of hopping probabilities biased by the spatially-dependent elastic fields. Hudson *et al.* (1) showed that while the effect of elastic forces on the evolution of ensembles of one-dimensionally migrating dislocation loops was indeed significant, in agreement with earlier predictions showing that vacancies pin the motion of glissile dislocation loops (13), the elastic interactions between three-dimensionally migrating defects did not appear to have an appreciable effect on microstructural evolution. For the treatment of a general case of long-term microstructural evolution, further work was clearly needed to elucidate the role of elastic interactions between the defects.

Recent implementations of accelerated kinetic Monte Carlo algorithms for simulating the accumulation of radiation damage (14; 15) are however based on the assumption that defects perform unbiased (by internal elastic fields) three-dimensional migration in the material, and interactions between defects are described effectively as short-range inelastic 'collisions'. These new simulation algorithms do not include the treatment of long-range elastic forces acting between the defects, and between defects and dislocations, and moreover do not take into account



Figure 2: A series of frames showing loop growth and coalescence in pure iron irradiated with 150 keV Fe⁺ ions at 300°C over a dose range from about 10^{19} ions m⁻² (~6.5 dpa) to about 1.6×10^{19} ions m⁻² (~10 dpa). Weak-beam micrographs were taken with $\mathbf{g} = 1\overline{10}$.

the effects of one-dimensional Brownian motion of prismatic dislocation loops often observed experimentally (7; 8; 9; 10; 11; 12).

In this paper we describe a possible alternative (to kinetic Monte Carlo) approach to simulating the long timescale evolution of radiation-induced microstructures. The development of this approach was stimulated by the realization of the fact that understanding the microscopic mechanisms driving microstructural evolution, and matching simulations to experiment, requires modelling *particular* microscopic realizations of evolving defect structures, like those observed by *in-situ* electron microscopy. Indeed, certain properties of an irradiated material, for example its fracture toughness or thermal conductivity, depend on the statistical characteristics of irradiation-induced microstructure involving many defects and dislocations, and likely represent self-averaging single-particle quantities. At the same time, validating a microstructural evolution model requires understanding the dynamics of interaction between radiation defects, and comparing the results of simulations with *local* experimental observations, often involving only a few (e.g. two or three) interacting defects, where no statistical ensemble averaging is possible.

Bearing this in mind, in the approach described below we treat defects as interacting objects satisfying a set of coupled Langevin equations of motion. It is known that in terms of ensemble averaged quantities, solutions of coupled Langevin equations in the strong friction (overdamped) limit are equivalent to the solutions of a multi-dimensional diffusion equation 2, and hence they are equivalent to solutions found using kinetic Monte Carlo simulations (1). The advantage offered by the Langevin equations-based treatment is that integrating stochastic differential equations for an ensemble of interacting objects is computationally no more difficult than integrating them for an ensemble of non-interacting particles.

There are further obvious computational advantages offered by the similarity between the Langevin and molecular dynamics integration algorithms, like the ease of parallelizing the method. Also, by solving the Langevin equations we explicitly follow the trajectories of migrating defects corresponding to the initial conditions defined by experimental observations, whereas kinetic Monte Carlo algorithm operates on the logarithmic timescale, which speeds up calculations but makes it more difficult to compare simulations with observations. Hence, the modes of microstructural evolution predicted by the Langevin dynamics model can be matched and verified explicitly against real-time *in-situ* electron microscope experiments. Furthermore, the speed of the integration algorithm for Langevin dynamics is entirely independent of whether the defects migrate three- or one-dimensionally. One can easily apply the method to the treatment of either limit, with the potential for generalization to modeling reactions between the defects,



Figure 3: (LEFT) Experimentally observed trajectories of motion for two interacting d = 16nm and d = 15nm prismatic $a/2\langle 111 \rangle$ dislocation loops migrating in pure iron foil at T = 650K. The thickness of the foil is approximately 250nm and the glide cylinders of the loops are 37 nm apart, as measured using stereo microscopy. The loops were formed by ultra-high energy electron irradiation followed by specimen annealing. (RIGHT) Experimentally observed trajectories of migration for two prismatic $\mathbf{b} = a/2[111]$ dislocation loops, both of similar size $d \approx 4$ nm, performing thermally activated Brownian motion in pure iron after the specimen was irradiated with 150 keV Fe⁺ ions to a dose of ~0.65 dpa. The projected distance between the glide cylinders of the loops is 12nm. The temperature of the specimen is 673K.

and between dislocations and the defects.

2. In-situ electron microscope observations

In-situ electron microscope observations show two distinctly different modes of microstructural evolution, and two different types of defect dynamics, the occurrence of which depend on the type of particles irradiating the material. The ultra-high-energy electron irradiation (7; 8; 9) produces individual Frenkel pairs of vacancies and self-interstitial atoms, and the resulting super-saturation of defects gives rise to the nucleation and growth of small self-interstitial dislocation loops and vacancy clusters. Ion-beam irradiation (10; 11; 12) generates collision cascades, in which self-interstitial and vacancy defects form clusters as cascades cool down and re-solidify.

In the case of ultra-high-energy electron irradiation, 99.998 wt.% pure bcc Fe (the metal most extensively studied by *in-situ* microscopy so far) was used for making specimens. The impurity content characterizing the specimens is fully described in the supporting on-line material for Ref. (8). The specimens were rolled into 0.08mm-thick sheets, which were pre-annealed at 1073K for 2 hours in a hydrogen atmosphere, and electrochemically polished. The orientation of the specimen surfaces was set close to $(1\overline{10})$ to minimize the image force acting on loops whose Burgers vectors b, defining the directions in which the loops migrate, were 1/2[111] or $1/2[11\overline{1}]$. High-energy electron irradiation was performed in an ultra-high-voltage electron microscope H-3000(Hitachi) operated at an acceleration voltage of 2000 kV. The dynamics of formation and migration of small dislocation loops was observed under electron irradiation. In another set of experiments, the dynamics of thermal Brownian motion of nano-scale dislocation loops initially produced by electron irradiation was observed using sample heating in an analytical H-800 (Hitachi) microscope operated at a relatively low acceleration voltage of 200 kV, at which no further radiation damage is produced.

In-situ electron microscope observations of defects in specimens irradiated with high-energy electrons show that the dynamics of motion of loops is *visibly* affected by elastic interactions



Figure 4: (LEFT) Experimentally observed trajectory of motion of a 4.5nm $1/2\langle 111 \rangle$ dislocation loop moving in a Fe crystalline foil irradiated with 150 keV Fe⁺ ions at 673K. (RIGHT) Simulated trajectory of motion of a 6nm $1/2\langle 111 \rangle$ dislocation loop interacting with a vacancy cluster. Simulation was performed assuming that the strength of interaction with the vacancy cluster is described by the potential shown in Figure 5. Parameter γ entering the Langevin equation equals $3.1 \cdot 10^{-7}$ eV·s/Å², and T = 675K.

between the loops. For example, Figure 1 shows that two mobile prismatic dislocation loops formed in pure iron under ultra-high voltage electron irradiation, and initially separated by large distances, perform Brownian motion along their glide cylinders, and eventually approach each other closely enough so that the dynamics of loops becomes correlated due to elastic interaction between the loops. The loops eventually form a raft that migrates as a single entity, then grows and gradually coalesces into a single loop.

Other examples found by *in-situ* electron microscope examination of specimens irradiated by ultra-high-energy electrons show processes of capture of a mobile loop by the elastic field of another loop, followed by the coalescence of the loops. In general, the trend seen in *in-situ* electron microscope observations of defects migrating in high purity iron, and illustrated in Figure 1, is that the motion of the defects is highly correlated, and the typical Brownian trajectories of defects follow each other on a ~ 0.1 s timescale.

For ion-beam irradiation experiments, high purity Fe was used (containing ~ 1 ppm carbon, <5 ppm nitrogen, <10 ppm silicon, and very small quantities of other impurities, which is not dissimilar to the impurity content of the specimens used for ultra-high-energy electron irradiation experiments). Thin foils were prepared by electropolishing and irradiated with 100 or 150 keV Fe⁺ and Xe⁺ ions at room temperature (RT), and at 573K and 773K in the Argonne IVEM-Tandem Facility. The microscope was operated at 200 keV, below the threshold for knock-on radiation damage in Fe. Dynamic observations followed the evolution of damage over doses up to 13 dpa, according to a SRIM calculation with a displacement energy of 24 eV. Irradiations were paused from time to time to allow detailed characterization of microstructures using a number of diffraction-contrast techniques (10; 11; 12). Similar detailed characterization was performed at the end of the irradiation, after the specimens irradiated at elevated temperatures had cooled to room temperature.

The pattern of migration of nano-dislocation loops in *ion*-irradiated high-purity iron is surprisingly different from that of loops migrating in high-purity iron irradiated with ultra-high-energy electrons (see Figure 1).

The right panel of Figure 3 shows trajectories of migration for two nano-dislocation loops in ionirradiated iron. The trajectories exhibit a significant degree of correlation. However, as opposed to the case of electron-irradiated iron, the trajectories of loops migrating in ion-irradiated iron do not look like the characteristic random Brownian trajectories shown in the left panel of Figure 3, or like the trajectories predicted by molecular dynamics simulations. The trajectories showed in the right panel of Figure 3 show that the motion of loops consists of a series of relatively infrequent long-range 'instantaneous' jumps, separated by extended intervals of time, during which the loops are pinned at certain points in the specimen and remain effectively immobile.

3. Langevin dynamics of interacting defects

Free stochastic motion of a defect can be described by the Langevin equation of the form

$$m^* \frac{d^2 \mathbf{r}}{dt^2} = -\gamma \mathbf{v} + \mathbf{f}(t),\tag{3}$$

where m^* is the effective mass of the defect, $d\mathbf{r}/dt = \mathbf{v}$ is the velocity of the defect and $\mathbf{f}(t)$ is the random thermal force, which is assumed to be δ -correlated, namely $\overline{\mathbf{f}(t)\mathbf{f}(t')} = \mathbf{f}^2\delta(t-t')$. If the motion of the defect is affected by an external potential field $U(\mathbf{r})$ then equation 3 acquires the form

$$m^* \frac{d^2 \mathbf{r}}{dt^2} = -\gamma \mathbf{v} - \frac{\partial U}{\partial \mathbf{r}} + \mathbf{f}(t).$$
(4)

In the overdamped limit the Langevin equation becomes

$$\gamma \frac{d\mathbf{r}}{dt} = -\frac{\partial U}{\partial \mathbf{r}} + \mathbf{f}(t).$$
(5)

Applying the Fluctuation-Dissipation Theorem (FDT), see e.g. Ref. (16), we find that $f^2 = 6\gamma k_B T$. Furthermore, evaluating the ensemble averaged mean square displacement of the defect from equation 3, we find that the coefficient D entering the diffusion equation 1, and the parameter γ entering the Langevin equation, are related as $\gamma^{-1} = D/k_B T$. Using these relations, equation 5 can be written as

$$\frac{d\mathbf{r}}{dt} = -\frac{D}{k_B T} \frac{\partial U}{\partial \mathbf{r}} + \sqrt{2D} \boldsymbol{\xi}(t), \tag{6}$$

where the components of the stochastic unit vector $\boldsymbol{\xi}(t) = (\xi_x(t), \xi_y(t), \xi_z(t))$ have correlation properties $\overline{\xi_i(t)\xi_j(t')} = \delta_{ij}\delta(t-t')$. Equation 6 describes the stochastic Brownian motion of a defect, in the same way as equation 1 describes the evolution of the single-particle distribution function for an ensemble of defects.

A solution of the ordinary stochastic differential equation 6, complemented with a suitable initial condition, follows the trajectory of a migrating defect, which can be directly compared with experimental observations. Several examples of such comparison were given in Ref. (2). Figure 4 gives another example, illustrating how a dislocation loop moves near a trapping centre (a vacancy cluster).

However, the main advantage offered by the Langevin dynamics algorithm is *not* that it provides a 'real-space' view of the trajectories of defects. The main strength of the algorithm is in that it offers a way of circumventing the need to solve the multi-dimensional, and hence effectively intractable, partial differential equation 2. The Langevin approach replaces equation 2 with a



Figure 5: (LEFT) Simulated trajectory of motion of a 6nm $1/2\langle 111 \rangle$ dislocation loop escaping from the trapping field of a vacancy cluster. Simulation was performed assuming that the strength of interaction between the loop and the vacancy cluster is described by the interaction potential shown on the right. (RIGHT) Potential energy of interaction between a 6nm $1/2\langle 111 \rangle$ dislocation loop and a vacancy cluster evaluated using isotropic elasticity. The formation volume of the vacancy cluster is -15 Å. Note the relatively long trapping time ~ 700 s.

set of coupled ordinary stochastic differential equations (see Ref. 2 for more detail)

$$\frac{d\mathbf{r}_{1}}{dt} = -\frac{D_{1}}{k_{B}T}\frac{\partial U}{\partial\mathbf{r}_{1}} + \sqrt{2D_{1}}\boldsymbol{\xi}_{1}(t),$$

$$\frac{d\mathbf{r}_{2}}{dt} = -\frac{D_{2}}{k_{B}T}\frac{\partial U}{\partial\mathbf{r}_{2}} + \sqrt{2D_{2}}\boldsymbol{\xi}_{2}(t),$$

$$\frac{d\mathbf{r}_{3}}{dt} = -\frac{D_{3}}{k_{B}T}\frac{\partial U}{\partial\mathbf{r}_{3}} + \sqrt{2D_{3}}\boldsymbol{\xi}_{3}(t),$$

$$\frac{d\mathbf{r}_{N}}{dt} = -\frac{D_{N}}{k_{B}T}\frac{\partial U}{\partial\mathbf{r}_{N}} + \sqrt{2D_{N}}\boldsymbol{\xi}_{N}(t).$$
(7)

Here $U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ is an arbitrary many-body interaction potential describing forces acting between the defects. Since the mathematical structure of equations 7 is fairly similar to the mathematical structure of equations describing the dynamics of atoms in molecular dynamics simulations, there is no difficulty associated with integrating these equations and, if necessary, parallelizing the integration algorithm.

4. Trapping and de-trapping of mobile defects

One of the most puzzling features characterizing the migration of dislocation loops found in *insitu* observations performed using ion-irradiated samples are the long (in some cases hundreds of seconds) defect trapping times. These long trapping times are difficult to explain using a transition state theory argument, which applies to processes occurring at atomic scale. Indeed, assuming an attempt frequency of $\nu^* \sim 10^{13}$ Hz, for T = 675K, from the transition state theory equation, see Ref. (17),

$$\frac{1}{\tau^*} \sim \nu^* \exp(-E_b/k_B T),\tag{8}$$

we find that the binding energy required for trapping a loop at a lattice site for $\tau^* \sim 10$ s must be of the order of $E_b \sim k_B T \ln(\tau^* \nu^*) \approx 2$ eV. This fairly high binding energy, comparable with the formation energy for a vacancy in iron, could in principle be attributed to interaction with complex stable configurations involving carbon or nitrogen impurities. However, even after noting the slightly different levels of purity of the electron- and ion-irradiated samples, this still does not explain why these stable impurity complexes only form under ion irradiation, and do not form under electron irradiation. It is more natural to assume that ion irradiation, producing small vacancy clusters in the core of collision cascades, generates fine vacancy cluster microstructures, interacting with, and trapping, the mobile self-interstitial dislocation loops.

The potential energy of interaction between a mobile loop and a vacancy cluster defect is shown in Figure 5. The energy scale characterizing interaction between the defects for the case shown in this Figure is less than 0.4 eV. It may appear surprising that a binding energy as low as 0.4 eV can actually trap a loop near a vacancy cluster over such a long interval of time. Indeed the Arrhenius exponential factor for T = 675K and $E_b = 0.4$ eV is just $\exp(-E_b/k_BT) \approx 10^{-3}$, and the transition state theory treatment (equation 8) would predict that a loop should become de-trapped on the nano-second timescale. However, in the present case the pre-factor derived from the transition state theory approach does not apply, and instead the rate of escape from a potential well is given by

$$\dot{r} \sim \frac{D}{W^2} \exp(-E_b/k_B T),\tag{9}$$

where D is the diffusion coefficient for the loop, and W is the characteristic width of the potential well, which for the case of elastic interaction between a dislocation loop and a vacancy cluster is of the same order of magnitude as the radius of the dislocation loop. For $D \approx 1.8 \cdot 10^3 \text{ nm}^2 \text{s}^{-1}$ and $W \sim 30 \text{ nm}$, we find that the probability of de-trapping per unit time equals $\dot{r} \sim 2 \cdot 10^{-3} \text{ s}^{-1}$. In other words, the average de-trapping time $\tau^* = 1/\dot{r}$ is 500s, which is in excellent agreement with the results of numerical simulations shown in Figure 5. On the other hand, the transition state theory prediction (see equation 8) for the defect trapping time is of the order of 100 picoseconds, which is different by approximately twelve orders of magnitude from the trapping times observed experimentally, see for example Refs. (10; 12).

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Screw dislocations in bcc transition metals: how to guarantee the correct structure of the dislocation core in a large-scale atomistic simulation

Mark R. Gilbert¹, Sergei L. Dudarev¹, Peter M. Derlet²

¹EURATOM/CCFE Fusion Association, Culham Science Centre, Abingdon, Oxfordshire, OX14 3DB, UK (Mark.Gilbert@ccfe.ac.uk) ²Condensed Matter Theory Group, Paul Scherrer Institut, CH 5323 Villigen PSI, Switzerland

ABSTRACT

Until recently, it was not known if the correct configuration for the core-structure of a $\frac{1}{2}\langle 111 \rangle$ screw dislocation in a bcc transition metal could be produced in a simulation performed using a Finnis-Sinclair interatomic potential. We found that using inter-string interaction laws derived from DFT calculations *and* interatomic potentials, in a multi-string Frenkel-Kontorova model, it is possible to derive a regular and straightforward criterion for the structure of the dislocation core. Our analysis shows that there is a simple rule that decides whether an interatomic potential reproduces the correct (as defined by DFT) core-structure. Results from DFT calculations of inter-string interactions in tungsten are presented, together with a demonstration that the criterion applies in this case.

1. Introduction

The thermally activated motion of screw dislocations is the rate-determining mechanism for plastic deformation and fracture of body-centred-cubic (bcc) metals and alloys, including those developed for structural applications in fusion. From a modelling perspective, it is thus vitally important to realistically represent the equilibrium atomic structure, and the response of the core of screw dislocations to applied stress. The accuracy of a model is largely determined by the particular interatomic potential used for defining the interaction between atoms. Historically, it has never been the case that potentials were fitted with screw dislocations specifically in mind, with the result that the level to which these defects are correctly represented has largely been left to chance.

For example, most recent potentials for bcc Fe, predict the degenerate or, equivalently, the symmetry-broken core structure as the lowest energy configuration¹. However, density functional theory (DFT) calculations² show that the non-degenerate (symmetric) core structure is realized for Fe. Considering that only one widely used interatomic potential for Fe predicts such a core structure, namely that of Mendelev *et al.*³, it is clear that there is a need to develop a simple technique to guarantee the correct core structure when fitting new potentials. In this paper, we briefly introduce the multi-string Frenkel-Kontorova (MSFK) model for this problem, and then demonstrate its application to the case of bcc W.

2. Application of the MSFK model

In the MSFK formalism introduced in Gilbert and Dudarev¹, which follows the work of Takeuchi⁴, [111] strings (or rows) of atoms in the bcc lattice are considered as rigid and non-deformable.

The energy of an interacting system of such strings is defined by the expression¹

$$E(u_1, u_2, \dots, u_N) = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} U_{ij}(z_i + u_i - z_j - u_j),$$
(1)

where *i* ranges over the total number of strings in the system N, z_i and z_j are the vertical [111] positions of strings in the bcc lattice, and summation over *j* includes strings that are the first, second, third, *etc.*, nearest-neighbour strings of string *i*. This equation is a simplified version of *deformable* MSFK considered by Dudarev⁵, and was derived by neglecting the kinetic energy and elastic deformation energy terms. It allows the displacement field of a dislocation to be fully defined by a set of [111] displacements of strings $\{u_i\}$. In¹ it was shown that, at least for the case of bcc Fe, the sum over the *j* neighbours of each string *i* need only include the six first nearest-neighbours to fully describe the core structure of a screw dislocation. Given an inter-string interaction law (U_1) , the equilibrium structure of the dislocation core is obtained by minimising the total energy (1) with respect to u_1, u_2, \ldots, u_N .

In¹, $U_1(d)$, where d is the separation of strings in the [111] direction (equivalent to $[z_i+u_i-z_j-u_j]$ in (1)), was obtained for bcc Fe by Fourier de-convolution of energy versus displacement curves of appropriately chosen (groups of) strings. These curves can be obtained using either DFT calculations or from atomistic simulations using existing interatomic potentials. In the present work, we extend this earlier study to the case of bcc tungsten (W).



Figure 1: The (a) raw, and (b) scaled, energy-change curves derived from the DFT string-pulling calculations for W. These curves show the energy change resulting from pulling a single string, two nearest-neighbour (NN) strings, or two second nearest-neighbour (2NN) strings, rigidly through the lattice.

Performing DFT calculations similar to those described in¹ for Fe, this time for bcc W, we obtain the three energy-change versus string-displacement (*u*) curves shown in Fig. 1a. The curves are all periodic in *u* with a period equal to the $\frac{1}{2}\langle 111 \rangle$ Burgers vector. Using (1), we can express the equations for the three curves in terms of the contributions from the nearest-neighbour interaction laws. To leading order, the expressions are:

$$\Delta E_1(u) = 3[U_1(u - b/3) + U_1(u + b/3)] + \dots,$$

$$\Delta E_{NN}(u) = 5[U_1(u - b/3) + U_1(u + b/3)] + \dots,$$

$$\Delta E_{2NN}(u) = 6[U_1(u - b/3) + U_1(u + b/3)] + \dots.$$
(2)

The dominance of the leading order term, defined by U_1 , is demonstrated by the three scaled curves shown in Fig. 1b. In this graph the three curves from Fig. 1a have been divided by the

leading order factors in equations (2). In Fig. 1b, the fact that the three scaled curves are coincident for a significant proportion of the period demonstrates that the higher-order interaction laws are relatively weak compared to U_1 . However, compared to the results for Fe¹, there is more discrepancy between the scaled curves for W, which may indicate that either the U_1 interaction is less dominant, or that the pair-wise MSFK model is not as applicable for W. On the other hand, we show below that U_1 can still be used to define the correct core structure in W, and in turn to provide a fitting criterion for the construction of an interatomic potential.



Figure 2: The (a) original, and (b) normalised, $U_1(d)$ interaction-laws derived from the DFT calculations. Also shown in (b) is a curve evaluated using an existing interatomic potential for W.

Fig. 2a shows the three $U_1(d)$ curves obtained by performing the Fourier de-convolution described in¹ on the three DFT curves from Fig. 1a. In agreement with recent DFT calculations^{6,7}, we find that all three of the U_1 interaction potentials predict the non-degenerate screw corestructure shown in Fig. 3a, when used to minimize the energy (1) of the isotropic elasticity solution for a screw dislocation in a string-lattice of bcc W. However, it is not the absolute magnitude of the $U_1(d)$ curve that determines the favoured cores structure, but rather its shape¹. Thus, we scale the three curves, as shown in Fig. 2a, to the same maximum (in this case one) and also shift the curves along the energy axis so that the values are strictly non-negative. The resulting three curves are shown in Fig. 2b. Note the interaction laws defined by these three scaled curves favour the same non-degenerate screw core structure (Fig. 3a) as the original unmodified curves of Fig. 2a.



Figure 3: Differential displacement maps⁹ of the alternative core structures for a $\frac{1}{2}\langle 111 \rangle$ screw dislocation in bcc W. (a) the non-degenerate or symmetric core; (b) the degenerate or symmetry-broken configuration.

Also shown in Fig. 2b is a $U_1(d)$ curve obtained from a recent interatomic potential for bcc W. This Finnis-Sinclair potential, which was obtained by Derlet *et al.*⁸, is known to produce

the degenerate screw-dislocation core-structure (Fig. 3b) and this result is reproduced correctly within the MSFK model using the scaled $U_1(d)$ inter-string potential in the figure. Looking at the four curves shown in Fig. 2b, it is immediately clear what particular feature of the curve determines the favoured core structure. The three DFT-derived U_1 curves are all noticeably narrower than the U_1 curve derived from the interatomic potential. While all three of the narrower curves produce the correct core structure, the wider one does not. This agrees with the findings presented in¹, where it was observed that, for bcc Fe, the favoured core structure switches from non-degenerate to degenerate once the profile of the U_1 interaction law reaches a certain width. In¹, this change in behaviour was more precisely defined as being related to the relative distance from the origin of the two inflexion points (extrema of the derivative) of the curve.

3. Conclusion

The $U_1(d)$ function for a particular interatomic potential can be quickly and easily computed. The resulting curve can be compared to the equivalent DFT curves, such as those shown in Fig. 2 for W. If the U_1 from the potential has a noticeably broader peak, then it is likely that the potential will not reproduce the correct core-structure of a $\frac{1}{2}\langle 111 \rangle$ screw dislocation. Even if the expected core configuration is not obvious by visual inspection, it is an easy task to compute the minimum energy configuration and thus perform a direct check of the potential. The criterion outlined here has already been applied to bcc Fe by Chiesa *et al.*¹⁰, and the resulting new potentials produce the correct non-degenerate core structure.

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Theory and Numerical Simulation of Defect and Microstructure Dynamics in Irradiated Oxides**

Anter El-Azab^{1*}, Thomas Hochrainer¹, A.-R. Hassan² and Dieter Wolf³

¹Department of Scientific Computing, Florida State University, Tallahassee, FL, USA

²Materials Science Program, Florida State University, Tallahassee, FL, USA

³Idaho National Laboratory, Idaho Falls, ID, USA

*Corresponding author. Florida State University, 400 Dirac Science Library, Tallahassee, FL 32306-4120. E-mail address: <u>aelazab@fsu.edu</u>

We present a theoretical framework for point defect dynamics and microstructure evolution in irradiated oxide materials. This framework is based on the principles of non-equilibrium thermodynamics and it consists of a set of balance laws of defect concentration, electrical charge density, stress and energy, and all relevant constitutive laws. The defect balance laws are obtained in the form of field equations describing the defect densities evolution in space and time, including vacancies, interstitials, gas atoms and other dissolved elements. The field equations are generalized reaction-diffusion equations that are derived from a rigorous definition of the chemical potentials of the point defect species present in the fuel matrix. Phase changes and microstructure evolution are also incorporated in this framework through the appropriate evolution laws of nucleation and interface dynamics, with non-conserved field variables representing the long-range order in the fuel. Two forms of the final equations will be shown; the first form is suitable for phase-field type simulations of defect and microstructure evolution in fuels and the second form describes the same processes in the corresponding sharp interface limit. Numerical examples will be presented to demonstrate the applicability of the given framework, especially in the area of void and gas bubble nucleation and growth.

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Radiation effects in nanoparticles <u>T. T. Järvi¹</u>, D. Pohl², B. Rellinghaus², L. Schultz², K. Albe³, A. Kuronen⁴, K. Nordlund⁴ and J. Fassbender⁵

 ¹Fraunhofer IWM, Wöhlerstr. 11, 79108 Freiburg, Germany e-mail: tommi.jaervi@iwm.fraunhofer.de
 ²IFW Dresden, Institute for Metallic Materials, POB 270116, 01171 Dresden, Germany
 ³Institut für Materialwissenschaft, Technische Universität Darmstadt, Petersenstr. 23, 64287, Darmstadt, Germany
 ⁴Dept. of Physics, University of Helsinki, POB 43, 00014 Helsinki, Finland
 ⁵Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, POB 510119, 01314 Dresden Germany

Ion irradiation is turning out as a very useful tool for producing nanoparticles in phases that are hard or impossible to obtain otherwise. In addition to promoting chemical ordering in, for instance, FePt particles [1], irradiation has recently been shown to provide a means to remove grain boundaries from alloyed (CuAu, FePt) multiply twinned particles, turning them single-crystalline [2,3]. Irradiation can also be used to densify porous cluster-assembled films without dramatically increasing the grain size [4]. Thus, irradiation provides a versatile tool for controlled engineering of nanoscale systems.

We will give an overview of our recent work on radiation effects in nanoparticles. Specifically, the multiply-twinned to single-crystalline transformation, which has been shown to occur via transient amorphization of the alloyed particles, is discussed [3]. The transformation is surprising, as it occurs in alloys, which are known not to amorphize in bulk.

In addition to phase transitions, we will review defect production by, on one hand, cascade-producing irradiation [5] (e.g., 25 keV Ga on Au) and, on the other, irradiation in the single knock-on regime [6,7] (e.g., 3 keV He on Pt). The defect production mechanisms and the differences between irradiation response of nano-sized and bulk systems are discussed.

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Quantum Dynamics Study of Hydrogen Diffusion in Iron with Lattice Defects

Hajime Kimizuka¹, Hideki Mori² and Shigenobu Ogata³

 ¹Department of Mechanical Science and Bioengineering, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan, e-mail: kimizuka@me.es.osaka-u.ac.jp
 ²Department of Mechanical Science and Bioengineering, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan, e-mail: h-mori@father.me.es.osaka-u.ac.jp
 ³Department of Mechanical Science and Bioengineering, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan, e-mail: h-mori@father.me.es.osaka-u.ac.jp
 ³Department of Mechanical Science and Bioengineering, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan, e-mail: ogata@me.es.osaka-u.ac.jp

We analyze the diffusion behavior of interstitial hydrogen in bcc iron theoretically using path-integral centroid molecular dynamics (CMD) method, which can describe the real-time evolution of particles based on quantum statistical mechanics. In the present approach, the embedded-atom-method (EAM) potential model for the iron-hydrogen interaction is newly developed to reproduce the *ab initio* minimum energy path of hydrogen migration based on the density-functionaltheory (DFT) data in the literature. This potential model allows us to describe the accurate "bare" potential surface, and the effective centroid potential surface can be obtained in quantum regime by incorporating the path-integral average.

Time evolutions of mean-square displacements of hydrogen atoms in the bulk iron are calculated at temperatures of 100-1000 K, and then diffusion coefficients and activation energies of hydrogen migration are evaluated. The obtained results are in excellent agreement with experimental measurements over a wide temperature range. In order to characterize the quantum effects on the hydrogen diffusion process, the CMD results are compared with those obtained from classical molecular dynamics (MD) method. By taking into account of quantum effects, the activation energy is significantly reduced and diffusion process is accelerated even at ambient temperatures. At low temperatures (below 500 K), quantum effects are dramatically enhanced as a temperature decreases, and thus the CMD values of activation energies become quite lower than the classical MD values. This leads to much higher hydrogen diffusivity in the quantum system than the classical system.

These facts indicate that the quantum effects can play a significant role in hydrogen diffusivity over a wide temperature range in bcc iron. In this study, the hydrogen motions in the vicinity of a point defect and a screw-dislocation core are also investigated to evaluate the hydrogen-trapping effects by using our approach. It is noteworthy that no clear anisotropy of hydrogen diffusion is observed along the dislocation lines in bcc iron.

Effect of external deformation on stability and migration properties of point defects in bcc iron

Z.Z. Chen¹, <u>N. Kioussis¹</u>, E. Sanchez¹ and N. Ghoniem²

¹Department of Physics, California State University Northridge, CA, U.S. 91330-8236 E-mail: nick.kioussis@csun.edu ²Department of Mechanical and Aerospace Engineering, University of California Los

Angeles, CA, U.S. 90095

Point defects, self-interstitial atoms (SIA) and vacancies are important carriers mediating damage events in the early stage of cascade in ferritic steels serving in fission and fusion energy facilities. Though intensive attention on the stability and migration properties of point defects in equilibrium conditions has been paid, their properties in the severe conditions of irradiation, where the solid undergoes deformations under applied loads have not been fully explored. Using ab initio calculations, we studied the stability and migration properties of different configurations of single SIA and di-vacancies in bcc-Fe under external deformation. For SIA, we found the <111> SIA rotates to <113> direction under severe uniaxial expansion. External deformation dramatically affects the migration energy landscape of SIA. The results reveal that (i) the volumetric expansion (compression) decreases (increases) the migration energy barrier and renders the diffusion process three- (one-) dimensional; (ii) the uniaxial strain removes (decreases) the migration energy barrier for the <111> to <113> (<113> to <100>) transformation, leading to spontaneous reorientation of the <111> SIA, and (iii) the uniaxial deformation breaks the cubic symmetry of the system and in turn induces anisotropy of the migration rates along different directions. In the case of divacancies, we have studied the effect of volumetric deformation on the binding energy of di-vacancies. <111> di-vacancies dissociates under severe compression. Also, di-vacancies undergo a <100> to <111> transition when the deformation changes from compression to expansion. These calculations demonstrate that changes in the electronic structure induced by elastic deformation lead to additional contributions to the formation and migration energies, which cannot be adequately accounted for neither by elasticity theory nor by interatomic potentials.

Cluster Expansion Modelling of Migration Energy for Vacancy Mediated Difusion in bcc Fe-Cr

Mikhail Yu. Lavrentiev, Duc Nguyen-Manh, Sergei L. Dudarev

EURATOM/CCFE Fusion Association, Abingdon, Oxfordshire OX14 3DB, United Kingdom E-mail: Mikhail.Lavrentiev@ccfe.ac.uk

ABSTRACT

One of the most reliable methods for modelling the evolution of a solid solution on a long time scale is the kinetic Monte Carlo technique. A challenge associated with using this technique is related to the environmental dependence of the migration energy barriers for the atom-defect exchange. Here, we present a Cluster Expansion (CE) approach for calculating the migration energies for vacancy mediated diffusion in Fe-Cr. This approach is based on extending the concept of *local* CE, and applying it to the treatment of activation barriers and vacancy formation energies [1,2]. The method evaluates the migration energy as a function of the environment for the initial positions of an atom and vacancy, and the saddle point. The CE parameters are found by fitting to *ab-initio* Nudged Elastic Band calculations of vacancy migration energies are affected by fluctuations of the direction of magnetic moment, which are particularly significant for the iron component of the solution in the vicinity of the Curie point, is discussed.

1. Introduction

Fe-Cr alloys are the basic material for a large variety of steels used in industrial applications. Furthermore, Fe-Cr based ferritic and ferritic-martensitic steels received attention as candidate materials for nuclear fission and fusion applications [3]. In order to develop and broaden the use of these steels, it is necessary to understand the factors driving the evolution of microstructure, phase decomposition and precipitate growth, and to evaluate the structural stability of steels under neutron irradiation and/or thermal aging.

Investigating the kinetics of precipitation and phase separation in alloys experimentally is not easy because of the long timescale associated with such experiments, and because of the small size and high density of precipitates. It is important to have a reasonably reliable computational tool that can provide a realistic model of evolution for Fe-Cr alloys. The standard model for the time evolution of a solid solution is the atomistic kinetic Monte Carlo, which is often applied to studying phase transformation kinetics during thermal ageing or irradiation [4]. However, to use it and to obtain results that can be compared with the experiment one needs a realistic model for migration energies. Currently, there are several such models which are based on either Kahn-Weinberg decomposition, artificial neural network, or the broken bond approximation [5]. All these models, whilst giving qualitatively similar results that agree with experiment, have various drawbacks. The broken bond approximation, based on the CE model for Fe-Cr without defects [6], seems too crude for a quantitative description of a system with a vacancy. The Kahn-Weinberg decomposition and the artificial neural network approaches, while giving better results, are based on migration energies calculated using the pair potential method and thus are less reliable than DFT. Here, we present a CE approach that uses DFT results for the atom-vacancy migration energies.

2. Cluster Expansion for the Migration Energy Components

In bcc Fe-Cr system, the diffusion and precipitation processes are mostly vacancy-mediated. The schematic drawing illustrating atom-vacancy exchange is shown in Fig. 1 (left panel). Energy profile for the migration pathway is shown in the right panel of Fig. 1 and the migration energy E_m is defined as the difference between the saddle point energy and the initial energy: $E_m = E_s - E_i$. CE of the migration energy is based on its decomposition into



Figure 1. Atom-vacancy exchange. Left panel: vacancy is shown as a square, the atom that is being exchanged as an open circle. Nearest neighbours of the saddle point are shown as grey-filled circles, other atoms as black-filled circles. Right panel: components of the migration energy.

two components, as shown in Fig.1:

$$E_{m} = E_{1} + E_{2} = \left(E_{s} - \frac{E_{i} + E_{f}}{2}\right) + \left(\frac{E_{f} - E_{i}}{2}\right)$$
(1)

The first component here, namely the difference between the saddle point energy and the mean of the initial and final energies $E_1(\sigma) = E_s - (E_i + E_f)/2$ (σ denotes type of the atom that is being exchanged), coincides with the kinetically resolved activation barrier introduced in [1], and depends on the local atomic configuration around the migrating ion at the saddle point. This quantity, as it was shown in [1], can be described using a CE around the migrating atom in the saddle point. In bcc system the mid-point between the initial and final positions of the migration atom has 6 nearest neighbours (shown as grey-filled circles in Fig. 1), 6 second, and 8 third nearest neighbours. They all were used in the CE.

The second component of the migration energy, the difference between the final and the initial energies $E_2 = (E_f - E_i)/2$, can be approximated using the CE similar to the one presented in [2]. There, the effective vacancy formation energy for a multi-component solid

was introduced as the difference between the energy of a crystal with a vacancy and the average of the energies of the crystal with vacancy site occupied by each of the constituents of the solid solution. In our case, we introduce the vacancy formation energy as the difference between the energy of the crystal with a vacancy and the energy of the same crystal with the vacancy site occupied by *the same type of atom* as the one that is being exchanged with the vacancy:

$$\Delta E_{i,f}(\sigma) = E_{i,f} - E(\sigma), \qquad (2)$$

where $E(\sigma)$ denotes the initial or the final configuration of the system but with a vacancy replaced by the atom of the same type σ as the atom that is being exchanged. This definition is particularly useful for the atom-vacancy exchange case, because in the expression for E_2 it involves only the vacancy formation energies for initial and final states, namely:

$$E_2(\sigma) = \left(E_f - E_i\right)/2 = \left(\Delta E_f(\sigma) - \Delta E_i(\sigma)\right)/2$$
(3)

The CE can now be constructed directly for the quantity E_2 , so that one only needs to know the DFT values for the difference $E_f - E_i$. To find the value of E_1 , atoms up to the fourth nearest neighbour of the vacancy were used in the CE.

3. Results and Discussion

For both CE's (for E_1 and E_2), 8 effective cluster interactions were used in fitting the data, corresponding to three or four single-atomic clusters, three two-atomic and one three-atomic cluster. All clusters with more than one atom included only the nearest-neighbour atoms.



Figure 2. Comparison of the DFT and the predicted CE migration energies for Cr-vacancy and Fe-vacancy exchanges.

For E_1 , also the cluster without atoms (0-atomic cluster) was used. Note that this cluster does not contribute to the expansion for E_2 because of cancellation between E_f and E_i . Good overall agreement between DFT calculations and the CE approximation was found for almost all the configurations, except for several jumps occurring in high Cr concentration environment. After they were excluded from the fit (but the jumps in pure Cr remained), about 30 atom-vacancy exchanges were investigated, resulting in about 50 values for the migration energy (in non-symmetrical configurations, two values are obtained for jumps from initial and final configurations). The results of the fit are given in Fig. 2. The mean square error for the Cr-vacancy migration is ~110 meV, for the Fe-vacancy migration it is ~47 meV.

In summary, good agreement between DFT and CE results found for almost all the concentrations, from pure Fe to pure Cr, and configurations studied even in the current relatively simple CE model with a small number of effective cluster interactions allows us to take the present study further, and to include more many-atomic clusters. Another possible direction for further investigation is to include the temperature dependence of migration energies. While in the current model the migration energies do not depend on temperature, it is well known that both self-diffusion and solute diffusion coefficients in bcc Fe vary near the Curie point [7,8], reflecting the change in the migration energy. This change is related to the loss of magnetic order in the system and it has to be taken into account in the CE model in order to describe the high-temperature diffusion in Fe-Cr more realistically.

4. Conclusion

We presented an approach that allows calculating migration energies in a solid solution using the cluster expansion, which is directly based on DFT calculations of migration energies. Application of this approach to bcc Fe-Cr alloys has made it possible to formulate a CE model that describes vacancy-mediated diffusion with the mean error of not more than 0.1 eV for almost all concentrations. This approach can be applied to performing kinetic Monte Carlo study of precipitation and phase separation in Fe-Cr and can be extended to take into account the temperature dependence of migration energies near the Curie point of the system.

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Critical Slowing Down near the Curie Temperature in Ferromagnetic Iron

<u>Pui-Wai Ma^{1,2}</u>, C. H. Woo¹, S. L. Dudarev²

¹Department of Electronic and Information Engineering, The Hong Kong Polytechnic University, Hong Kong, SAR, China; ²EURATOM/CCFE Fusion Association, Culham Centre for Fusion Energy, Abingdon, Oxfordshire OX14 3DB, United Kingdom. Email: leo.ma@ccfe.ac.uk

ABSTRACT

Recent analysis showed that *mechanical* properties of iron-based alloys, and steels, are closely linked to their *magnetic* properties, and that the dynamics of magnetic excitations is inseparable from the lattice dynamics of the atoms [1]. In this study we investigate magnetic excitations, and the relaxation timescales characterizing these excitations, in the vicinity of the ferro-paramagnetic phase transition. We show that the relaxation time for magnetic excitations depends on the magnetic specific heat of the material and on the spatial spin-spin correlation functions. The critical slowing down of magnetic relaxation timescales is found to be explicitly related to the divergence of the specific heat near the Curie temperature.

1. Introduction

The critical slowing down of relaxation processes is a phenomenon occurring near phase transitions [2]. In ferromagnetic iron, the relaxation time for magnetic excitations diverges near the Curie temperature T_c [3]. The critical slowing down can be described phenomenologically using the Landau approach [4]. However, such an approach does not reveal the microscopic origin of the observed effects.

In this study, we relate the thermodynamic description of energy transfer between atomic spins (or magnetic moments) and electrons to the fluctuation and dissipation terms entering the microscopic spin equations of motion. Our analysis shows that the critical slowing down is fundamentally related to the real-space microscopic fluctuations of energy in a system of interacting spins. We find that the energy transfer rate is proportional to the spatial spin-spin correlation functions and that a single time constant is not sufficient for describing the dynamics of spin thermalization.

Spin dynamics (SD) simulations show a pronounced singularity of the specific heat near the Curie temperature T_c , which corroborates the above argument. Hence, using a microscopic SD model, we are can understand the microscopic origin of spin thermalization, and conclude that critical slowing down is a many-body effect, fundamentally related to spatial fluctuations of energy in an interacting spin system.

2. Theory

In quasi-equilibrium, the rate of heat (or energy) transfer between the spin and electron subsystems can be described by the heat transfer equation,

$$C_s \frac{dT_s}{dt} = G_{es} \left(T_e - T_s \right), \tag{1}$$

where C_s is the specific heat for the spin system, G_{es} is the heat transfer coefficient, T_e and T_s are the temperatures of the electron and spin sub-systems. T_e can be assumed to be constant due to the high thermal conductivity of electrons. The solution of Eq. (1) has the form $T_s(t) = T_e + (T_s(0) - T_e)e^{-t/\tau_s}$, where $\tau_s = C_s / G_{es}$ is the relaxation time constant. This solution is valid if τ_s is independent of temperature, or if T_s is very close to T_e . If τ_s is temperature dependent, the characteristic timescale of the relaxation process is given by $\int_{T_e(0)}^{(T_e+T_s(0))/2} (\tau_s(T_s)/(T_e - T_s)) dT_s.$

We now match Eq. (1) to a microscopic model, described by a set of coupled Hamilton equations of motion [1], where spin variables evolve under the action of the exchange field of other spins, and a fluctuating thermal Langevin force,

$$\frac{d\mathbf{S}_{i}}{dt} = \frac{1}{\hbar} \Big[\mathbf{S}_{i} \times \big(\mathbf{H}_{i} + \mathbf{h}_{i} \big) - \gamma_{s} \mathbf{S}_{i} \times \big(\mathbf{S}_{i} \times \mathbf{H}_{i} \big) \Big], \qquad (2)$$

where $\mathbf{H}_i = \sum_k J_{ik} \mathbf{S}_k$ is the effective exchange field acting on spin *i*. γ_s is a dimensionless damping constant, which, together with the random magnetic field \mathbf{h}_i , describes the effect of dissipative random forces acting on the spin system. In this study, we assume that the Langevin forces arise from interaction between electrons and spins. Using the recently derived expression for the temperature of a dynamic spin ensemble [5]

$$T_{s} = \frac{\left\langle \sum_{i} |\mathbf{S}_{i} \times \mathbf{H}_{i}|^{2} \right\rangle}{2k_{B} \left\langle \sum_{i} \mathbf{S}_{i} \cdot \mathbf{H}_{i} \right\rangle},\tag{3}$$

after some algebra we find that

$$G_{es} = \frac{2k_B \gamma_s}{\hbar V} \left\langle \sum_i \mathbf{S}_i \cdot \mathbf{H}_i \right\rangle.$$
(4)

Since the exchange coupling parameters J_{ij} , describing interaction between the 1st and 2nd nearest neighbour spins, always dominate the dynamics of spin excitations, we rewrite Eq. (4) in term of spin-spin spatial correlation functions involving the 1st and 2nd neighbors only,

$$G_{es} = \frac{2k_B\gamma_s}{\hbar\nu} \Big[8J_1 \left\langle \mathbf{S}_i \cdot \mathbf{S}_j \right\rangle_1 + 6J_2 \left\langle \mathbf{S}_i \cdot \mathbf{S}_j \right\rangle_2 \Big], \tag{5}$$

where v is the atomic volume and $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_m$ is the m^{th} neighbour spatial correlation function.

3. Simulations and discussion

We now investigate the dynamics of thermalization of spin subsystem by means of a direct SD simulation. Spins are assumed to be located on sites forming a regular rigid BCC lattice. The simulation cells are first thermalized at various temperatures. Note that correlation functions $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_m$ do not vanish at temperature above T_c , where the average magnetization

vanishes [1]. This shows that, at T_c , the short range magnetic order (SRMO) persists, whereas the long range magnetic order (LRMO) does not. Since the correlation function $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_m$ does not vanish at T_c , it varies smoothly near T_c and has a positive finite value for all m. Hence, G_{es} in Eq. (5) is a regular function of T everywhere in the vicinity of T_c . Hence the divergent behaviour of the relaxation time τ_s at T_c , which gives rise to the critical slowing down, is associated with the non-analytic behaviour of $C_s(T)$ at T_c .

The relationship between the energy of the spin system and the spin temperature is non-linear, and it exhibits an abrupt change near T_c . Due to the SRMO, the energy curve maintains its upward trend even for temperatures higher than T_c . Unlike kinematic motion of atoms that can absorb unlimited amount of energy in the form of kinetic energy, the energy of a spin system has an upper limit corresponding to a fully disordered configuration. Eq. (4) shows that the total energy cannot be positive, since G_{es} is always non-negative. On the other hand, the specific heat C_s , which can be found numerically by differentiating energy of the system with respect to temperature [1], shows very characteristic divergent behaviour near the T_c .

Using the values of C_s and G_{es} found in SD simulations, we plot the relaxation time $\tau_s = C_s / G_{es}$ against temperature, as shown in Fig. 1. The relaxation time τ_s diverges at T_c , which follows from the divergence of C_s at the phase transition temperature. Since G_{es} is a monotonically decreasing function of temperature, thermalization occurs faster at low temperatures, and it is very slow near the T_c .



Figure 1. Plot showing the relaxation time as a function of temperature of the spin system. The relaxation time is very short at low temperatures, and it diverges near the Curie temperature, illustrating the occurrence of the critical slowing down near the ferro-paramagnetic phase transition.

One can write the total energy as $E = \sum_{i} E_{i}$, where $E_{i} = -\frac{1}{2} \sum_{j \neq i} J_{ij} \mathbf{S}_{i} \cdot \mathbf{S}_{j}$ is the energy associated with the *i*th spin, and $C_{s} = N(C_{s}^{0} + n_{1}C_{s}^{1} + n_{2}C_{s}^{2} + \cdots)$, where $C_{s}^{0} = (k_{B}T^{2})^{-1}(\langle E_{i}^{2} \rangle - \langle E_{i} \rangle^{2})$, and $C_{s}^{m} = (k_{B}T^{2})^{-1}(\langle E_{i}E_{k}^{m} \rangle - \langle E_{i} \rangle^{2})$, $k \neq i$, n_{m} is the number of

spins and E_k^m is the energy of k^{th} spin in the m^{th} neighbor shell. Simulations show that the spatial fluctuations of energy at long range characterized by C_s^m with large m, being enhanced significantly near the T_c , are responsible for the divergent behavior of C_s . We note that C_s characterizes spatial fluctuations of energy, rather than the spatial correlation of spin orientations related to the magnetic susceptibility of the spin system.

4. Conclusion

In this study, we relate a phenomenological heat transfer equation for the relaxation of weakly interacting spin and electron systems to a set of microscopic Langevin spin equations of motion. We show that the origin of critical slowing down is fundamentally associated with the spatial fluctuations of energy in an interacting system of spins. Long range fluctuations of energy are enhanced near the Curie temperature T_c , resulting in the divergent behaviour of the specific heat C_s , and in the divergence of magnetic relaxation time τ_s . The heat transfer rate is the highest at low temperatures and the lowest near the Curie temperature. We also find that a single thermalization time constant is not sufficient for describing the full dynamics of the relaxation process.

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Stochastic analysis of thermally activated dislocation processes simulated by Molecular dynamics

Ghiath MONNET

EDF – R&D, MMC, Avenue des Renardières, 77818 Moret sur Loing, France Email : <u>ghiath.monnet@edf.fr</u>

Thermally activated processes affecting dislocation behavior are often studied by Molecular Dynamics (MD) simulations. Results are known to exhibit a strong stochastic feature concerning interaction time and strength. In this paper, we discuss the theoretical basis of the probabilistic treatment of MD results. We first investigate the survival probability density as a function of the simulation conditions and temperature. We show how this probability is connected to the rate function, reflecting the physics of the process. Depending on the loading conditions, it is shown how the probability density profile varies strongly on the mechanical loading condition. Then we discuss the methods of analyses of MD results used in the literature and we clarify their basic assumptions. We propose at last a general analysis method that can be used in all simulation conditions in order to determine the rate function of the process.

Coordinated Climb of the Dislocation Network under Irradiation Dan Mordehai¹, Georges Martin²

¹Department of Materials Engineering, Technion - Israel Institute of Technology, 32000 Haifa, Israel. Email:danmord@tx.technion.ac.il ²CEA-Siège, Cab. H.C., 91191 Gif-sur-Yvette Cedex, France

In crystalline metals, the dislocation network is the main source of internal strain. Irradiation, steadily injects new sources of internal strain in the metal (point defects, defect clusters). As a consequence, the evolution of the dislocation network is driven by irradiation. Examples are irradiation enhanced dislocation annealing, irradiation driven re-crystallization and irradiation induced plasticity at temperatures and stress levels where plastic strain does not show up in the absence of irradiation. While the atomistic mechanisms by which the forcing proceeds have long been suggested: the partitioning of defect elimination between dislocations and other defect sinks, both in stationary or transient regimes, some of these phenomena are left unexplained. In this work we show that dislocation sink strengths for point defects are altered in the presence of neighboring dislocations and their climb motion is coordinated with the dislocation microstructure. We show that polarisability effects, at the root of SIPA creep (Stress Induced Preferential Absorption), provide the mechanism for coordinated climb, which eases dislocation annealing. In particular, we demonstrate that coordinated dislocation climb accelerates dislocation dipole annihilation and decreases the misorientation angle across a dislocation wall.

Damage Rate Dependence of Void Nucleation in W

<u>Kazunori Morishita¹</u>, Junichi Yoshimatsu², Yasunori Yamamoto² and Yoshiyuki Watanabe²

¹Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan ²Graduate School of Energy Science, Kyoto University, Uji, Kyoto 611-0011, Japan <u>k-morishita@iae.kyoto-u.ac.jp</u>

Component materials of a nuclear fusion reactor as an attractive future energy source, such as the first-wall structural materials and divertor materials, are exposed to the bombardment of energetic plasma-particles and neutrons, which may cause various changes in material's microstructure and mechanical property. These are, in many cases, undesirable damage for reactors. Knowledge on material's response to fusion irradiation is required for reactor materials design, but it should be obtained using alternative existing irradiation facilities such as nuclear fission reactors and ion accelerators, because there are no actual fusion devices at present. A precise understanding of radiation damage processes is required to achieve the reliable materials design on a basis of accurate understanding of the difference of irradiation conditions between the alternative environment and the actual environment, which is, for example, a difference in displacement damage rate (dpa/s).

Radiation damage processes occurred in materials during irradiation are, in essence, the multiscale phenomena, and a physical description of the processes involves a wide variety of physics processes, i.e., athermal ballistic binary collisions between the irradiating projectiles and lattice atoms in the initial stage, the collective motion and energy dissipation among lattice atoms in the subsequent thermal spike stage, followed by the stage of thermal activation process including defect cluster formation in materials. To model these complicated processes, multiple evaluation methods are needed to investigate them at the individual time and length scales. Also, bridging the information of different scales thus individually obtained is important to understand the entire processes.

In this paper, the Monte-Carlo simulations and the rate theory equation calculations are compared from the viewpoint of multiscale modeling, and the Monte-Carlo technique is employed to investigate the nucleation and growth process of defect clusters in materials during irradiation, where the behavior of defect cluster embryos is accurately treated by considering the stochastic fluctuation of defect flux in materials. Our results show void nucleation rates in pure tungsten as a function of temperature and damage rate. It may indicate that the observed damage rate dependence of void swelling is attributed, not only by the damage rate dependence of void growth rate, but also by that of nucleation rate. This knowledge will enable us to predict material's behavior in fusion environment precisely from that obtained by the existing irradiation facilities.

Kinetic Monte Carlo simulation of irradiation damage accumulation with the elastic interaction between SIA loops and dislocations

Kenichi Nakashima, Naoki Soneda

Central Research Institute of Electric Power Industry, 2-11-1, Iwado-kita, Komae, Tokyo 201-8511 JAPAN. ken-ichi@criepi.denken.or.jp

Accurate prediction of neutron irradiation embrittlement of highly-irradiated reactor pressure vessel (RPV) materials is very important for the structural integrity assessment of RPVs under long term operation. We have performed a computer simulation study to understand the radiation damage accumulation in bcc Fe using the kinetic Monte-Carlo (KMC) simulation technique.

In the conventional KMC approach, defects and its clusters have the interaction radiuses, and they interact with each other only when they are close within its radiuses. A new KMC model includes the elastic interaction that works between self-interstitial atom (SIA) loops remotely through their strain fields. The effect of elastic interaction is introduced by modifying the migration energy of SIA loops.

The effect of displacement cascade is realized by injecting the cascade data which is obtained from the simulation results of the molecular dynamics. We demonstrated the new KMC simulation to investigate the importance of the interaction between SIA loops, and then we found the clear difference on the special distribution of SIA loops and its size histogram compared with the conventional one.

From point defect jumps to diffusion models of irradiated alloys

Maylise NASTAR¹ and Thomas GARNIER¹

¹CEA /Saclay, Service de Recherches en Métallurgie Physique, 91 191 Gif-sur-Yvette, FRANCE mnastar@cea.fr

Point defects such as vacancies and interstitials are created by irradiation. Their migration towards point defect sinks such as grain boundaries induces atomic fluxes in the same or opposite direction leading to the formation of a segregation profile at proximity of sinks. Starting from the atomic jump frequencies we use the Self Consistent Mean Field (SCMF) diffusion theory to describe flux couplings controlled by the vacancy and interstitial diffusion mechanisms^{1,2,3}. In the specific case of face centered cubic alloys, the resulting Onsager matrix of the phenomenological coefficients accounts for the possible change of sign of the off-diagonal terms as a function of short range order and composition. From the present formulation of fluxes, we derive a unified model of radiation induced segregation for both dilute and concentrated alloys. Segregation profiles are predicted as a function of the microscopic parameters, temperature and nominal composition.

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Hydrogen trapping into a single vacancy in tungsten <u>Kazuhito Ohsawa¹</u>, Masatake Yamaguchi² and Masatoshi Yagi¹

¹Research Institute for Applied Mechanics, Kyushu University, 6-1 Kasuga-koen, Kasuga-shi, Fukuoka 816-8580, Japan (ohsawa@riam.kyushu-u.ac.jp)
²Center for Computational Science and e-Systems, Japan Atomic Energy Agency, Tokaimura, Ibaraki, 319-1195, Japan

Hydrogen (H) retention in metals is an important subject in the field of metallurgical science. By the way, H and its isotope retention in tungsten (W) is a new problem associated with International Thermonuclear Experimental Reactor (ITER), because W is one of the plausible materials of diverter armor tiles used in ITER due to the excellent thermal and sputtering properties. However, the diverter armor tiles are exposed to high energy plasma flux. Then, a lot of vacancies will be formed in W under the irradiation environment. In the present work, we investigated H trapping into a single vacancy in W by first principle simulations. It is well-known that a single H is trapped close to the octahedral interstitial site in a

single vacancy in BCC metals. However, in the case of some H atoms trapped in the single vacancy, it is possible to be a variety of meta-stable H structures. In the present works, H atoms were randomly distributed in a single vacancy in W as the initial positions and the structural relaxations were iterated to find the energetically lowest structure. We found some new stable H structures in the single vacancy. The trapping energy estimated in the present works is shown in the right figure. The H structures found in the present simulations are more stable than those in some previous works.



Dependence of the total (left) and averaged (right) trapping energy for H atoms on the number of H in a single vacancy in W.

Ab initio study of point defect dynamics: defect clusters and threshold displacement energies in bcc Fe

Pär Olsson and Christophe Domain

EDF R&D, Dept. MMC, Les Renardieres, 77250 Moret sur Loing, France par.olsson@edf.fr

During the past decade, *ab initio* predictions have provided new insights about defect properties in iron and iron based alloys, relevant for studies of radiation damage and microstructural evolution. Detailed information about the properties of point defects and point defect clusters has been shown to be well described using *ab initio* methods such as Density Functional Theory (DFT). In particular, for self-interstitial defects the quality of the force prediction has been shown to play a significant role.

Here, a DFT study of point defect cluster properties in bcc iron is presented. The canonical parallel self-interstitial clusters are shown to be less stable than their non-parallel counterparts. The stability with respect to cluster size and Burgers vector has been studied. The implications for the evolution of the microstructure are discussed in the framework of parameterizations of larger scale models, such as kinetic Monte-Carlo.

Moreover, due to the recent progress in computation speed which renders *ab initio* molecular dynamics feasible, a study of the threshold displacement energy surface in iron is here presented. This basic materials property has previously largely been estimated using semi-empirical potentials and to a smaller degree using experiments. The implications of a fully dynamic Born-Oppenheimer *ab initio* treatment is presented and discussed.

ATOMIC-SCALE MODELLING OF DISLOCATION-OBSTACLE INTERACTIONS IN IRRADIATED METALS

Yuri Osetsky¹, Roger Stoller¹ and David Bacon²

¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA ² Department of Engineering, University of Liverpool, Brownlow Hill, LiverpoolL69 3GH, UK,

Abstract:

Abstract Irradiation of metals with high-energy particles produces nano-scale defect clusters, such as voids, dislocation loops, stacking-fault tetrahedra and irradiationinduced precipitates. They are obstacles to dislocation glide during plastic flow and give rise to hardening and, in some conditions, deformation localisation. Approximations based on the elasticity theory of defects offer the simplest treatment of strengthening, but are deficient in many respects. Atomic-scale computer simulation of dislocation dynamics has therefore been developed to provide detail of mechanisms and quantitative information on the influence of stress, strain rate and temperature which cannot be determined at the continuum level. Recent results of modelling dislocations gliding under stress against obstacles in a variety of metals across a range of temperature are considered. The effects observed include obstacle cutting, absorption and drag. Simulations of 0K provide a direct comparison with results from continuum treatment of dislocations, and although some processes can be represented within the continuum approximation, others cannot.

Simulation Studies of Diffusion Behavior in Al/U interfaces

V. P. Ramunni¹, M. I. Pascuet¹ and <u>J. R. Fernández^{1,2}</u>

¹Consejo Nacional de Investigaciones Científicas y Tecnológicas, 1917 Rivadavia Av., 1033, Buenos Aires, Argentina ²Materials Dept., Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica 1499 Gral. Paz Av., 1650, Buenos Aires, Argentina corresponding author: pascuet@cnea.gov.ar

ABSTRACT

Atomic mobility at the Al(fcc)/U(A20) interface by using different computer simulation techniques is studied. Suitable interatomic EAM potentials for the U-Al system are used for this purpose. Vacancy and impurity properties are investigated in α U and Al bulk phases and near the interface. Results suggest a faster Al mobility into α U than vice versa.

1. Introduction

The U alloy with low Mo content dispersed in Al matrix is one of the prototypes for low enrichment high density nuclear fuels. When these metals are brought into contact, diffusion in the Al/U-Mo interface gives rise to interaction phases. Fission gas pores nucleate in these new phases during service producing swelling and deteriorating the alloy properties [1]. An important technological goal is to delay or directly avoid undesirable phase formation by inhibiting interdiffusion of Al and U components.

In a first approach to treat this problem, the atomic mobility by vacancy mechanism at the interface is studied for a model U-Al alloy, using computer simulation techniques. Previously obtained interatomic EAM potentials for the U-Al system [2,3] are used for this purpose. The pure Al potential is extracted from the literature [2], it describes correctly lattices structure and stability and vacancy properties. Similarly, the pure U potential reproduces approximately αU orthorrombic (strukturbericht A20) lattice parameters, its stability against other simple structures, vacancy properties and also exhibits an allotropic transformation from αU to γU (bcc), although at relatively lower temperatures than the real metal [3]. The interspecies interaction describe reasonably well some structural characteristics of the three ordered compounds, Al₂U (Laves C15), Al₃U (cubic L1₂) and Al₄U (orthorrombic D1_b) [4].

2. Defect properties in the bulk

Single and multiple vacancy (V) and impurity (I) formation energies are calculated using static minimization of the energy as a function of atomic coordinates. Thermodynamic analysis in the limit of dilute solutions [5] gives the following expressions for the single and double defect clusters:

$$E_V^f = \varepsilon_V + \mu_H \qquad ; \quad E_I^f = \varepsilon_I - \mu_I + \mu_H E_{2I}^f = \varepsilon_{2I} - 2(\mu_I - \mu_H) \qquad ; \quad E_{I-V}^f = \varepsilon_{I-V} - \mu_I + 2\mu_H$$
(1)

where *H* refers to a host atom, ε_P is the energy difference between the lattice with defect *P* and the perfect lattice, and μ_i is the chemical potential for species *i*. The calculated values for the single defects are 1.36 and 0.71 eV for the vacancy in pure U and Al, respectively, and -0.29 and -0.32 eV for the Al and U impurities. The negative values indicate the system preference to mix atoms of different species. Fig. 1 shows defect pairs I-V and 2I at increasing distances on each phase.



Figure 1: Formation energies for defect pairs I-V and 2I as a function of the neighbor layer. Horizontal dashed lines show the corresponding values at infinite distance.

The clustering behavior of U impurities in Al is worth to mention. Fig. 1 shows that two U impurities have their lowest formation energy when they are separated by a cubic lattice parameter of the Al fcc lattice. When three and four U impurities are arranged in different configurations, it is seen that the lowest energies correspond to the corners of a cubic fcc cell. This behavior is consistent with a coherent nucleation of the cubic $L1_2$ intermetallic phase Al₃U in the Al fcc lattice.

Vacancy migration is also investigated. For pure Al, the vacancy migration energy is 0.65eV [2] while for pure U it ranges from 0.18 (1st neighbors jump) to 0.69eV (3rd neighbors jump) [3]. Fig. 2 shows the change in migration energy when an impurity is present.



Figure 2: Vacancy migration energies (in eV) close to an impurity: a) fcc Al and b) A20 α U lattices. Bold numbers in circles indicate neighbor layer. Full (dashed) circles represent atoms in (over) the *xy* plane. Gray circles stand for impurities.

The results show that a vacancy will not easily exchange with a nearby U impurity in Al while a much faster interchange is expected with an Al impurity in α U, suggesting a relatively faster diffusion in the latter case. This is in agreement with experimental evidence [1].

3. Defect properties at the Al/U interface

Two interface configurations have been considered to study defects properties. The first one, consists of a U/Al bicrystal slab, oriented in such a way as to bring the two close packed planes and the two compact directions of each phase together, i.e., $(111)_{AI}$ // $(001)_{\alpha U}$ and $[\overline{1} \ 10]_{Al}$ // $[100]_{\alpha U}$. The slab is formed by twenty compact planes on each phase. Atomic forces generated in the bicrystal are then relaxed under periodic boundary conditions in the interface plane and free surface conditions in the perpendicular direction. Periodic boundaries impose commensurability between both phases at the interface plane. To satisfy this condition as well as possible, blocks of $31 \times a_{Al}/2[\overline{1} \ 10]$ by $60 \times a_{Al}/2[\overline{1} \ \overline{1} \ 2]$ for Al and $32 \times a_{U}[100]$ by $49 \times b_{\rm U}[010]$ for αU (where $a_{\rm Al}=4.05$ Å [2], $a_{\rm U}=2.7745$ Å and $b_{\rm U}=6.0718$ Å [3]) are chosen as the shortest periodic lengths. After relaxation, the interface shows zones of good and bad atomic fitting, which repeat every about $11a_{AI}/4[\overline{1}\ \overline{1}\ 2]$ along v direction. Fig. 3 shows two different projections of one of such bad fitting zones, where it is observed that atoms pile up in high energy positions. A vacancy created in the first (001) plane of U in this zone produce a large relaxation of atoms in the same plane and shows a delocalized shape, giving a formation energy $E^{f} \sim -1 \text{eV} < 0$. Vacancies generated in the second (001) U plane and first and second (111) Al plane are unstable and decay to the first (001) U plane. In the case of the Al vacancies, a U atom moves into the Al phase. Vacancies created in planes farther away recover their corresponding bulk value.



Figure 3: Bicrystalline U/Al slab: a) *yz* projection, plane numbering acording to distance from the interface (dashed line) and b) *xy* projection, region of bad atomic fitting (ontop positions). Gray (black) atoms stand for U (Al) atoms.

Short molecular dynamics simulations (10^5 steps of 10^{-15} s) for the same configuration at increasing temperatures (from 300K to 700K) show Al atoms reaching up to the third (001) U plane while U atoms stay on the first Al plane. No vacancies are added on such simulations. It is observed that some compact [$\overline{1}$ 10] directions of the first Al plane relax and accommodate one U atom of the first U plane. This behavior, instead of an Al moving into the first U plane, could be understood by taking into account that the formation energy of a U impurity in Al is lower than the reverse. Although the exact mechanism was not observed, the vacancies created in such a process are believed to be responsible for the Al diffusion into α U.

The other configuration considered is a slab formed by two polycrystalline blocks. Each block is formed by 10 nanograins containing around 5000 atoms each, with random orientations. Fig. 4 shows a schematic representation of the box cell used in these simulations. As before, periodic boundary conditions in x and y directions of the interface plane are applied and free

surfaces are considered in the perpendicular direction. Simulations at 600K for relatively short times $(3.5 \times 10^5 \text{ steps of } 10^{-15} \text{s})$ show interdiffusion of species through grain boundaries. At this temperature, the transformation of αU into bcc γU near the intersection of the free surface and grain boundaries starts to be observed.



Figure 4: Polycrystaline U/Al slab. Dashed lines indicate the interface plane.

4. Summary and conclusions

In this work, the U and Al mobility is studied in a model U-Al alloy. Static calculations of impurities in the bulk phases show a strong tendency of species to mix. The change in vacancy migration energies when an impurity is present suggests a faster diffusion of Al in α U than U in Al. In a Al(111)/U(001) interface, the vacancy is only stable on the first (001) U plane and is not localized with any particular lattice site. Molecular dynamics show that, even when no initial vacancy is added, vacancies are created in the first (001) U plane by U atoms jumping into the first (111) Al plane. The final configurations show that Al atoms move deeper into α U. As expected, the presence of grain boundaries on each phase accelerates the interdiffusion of species. Further studies are still in progress.

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Phase Field Modeling of Void Swelling in Irradiated Materials

Srujan Rokkam¹, <u>Anter El-Azab²</u>*, Dieter Wolf³

¹Mechanical Engineering Department, Florida State University, Tallahassee, FL, USA ²Department of Scientific Computing, Florida State University, Tallahassee, FL, USA ³Idaho National Laboratory, Idaho Falls, ID, USA

* Corresponding author. E-mail address: aelazab@fsu.edu

ABSTRACT

A phase field model for microstructure evolution in irradiated material is presented. Point defect fields are described by Cahn-Hilliard type equations, while void nucleation and growth dynamics is described in terms of a structural order parameter that is governed by an Allen-Cahn type equation. Irradiation induced point defects are modeled as stochastic sources in the Cahn-Hilliard equations. We present 2D results for void nucleation and growth in a pure metal, as well as the swelling behavior due to irradiation.

1. Introduction

Particle irradiation results in intense point defect generation via atomic collision cascades. The diffusion and reactions of these defects leads to microstructural changes that are responsible for dimensional instabilities and degradation of the mechanical performance or structural integrity reactor materials [1]. An important problem in this regard is the formation of voids (or cavities) and associated swelling of irradiated materials. Voids are aggregates of vacancies that form in the material subject to irradiation by a clustering and growth process. The traditional approaches for modelling void dynamics treat void nucleation and growth stages separately; the classical nucleation theory and rate theory of void growth are the commonly used theoretical tools. Both theories neglect the interaction between the nucleating or growing voids. It is known, however, that microstructural evolution of irradiated materials is sensitive to the spatial distribution of diffusing defects and the microstructure details. As such, there is a need to develop spatially resolved models of microstructure evolution in irradiated materials. Here, we present a phase field model that treats processes of void nucleation, growth and material swelling simultaneously. By its nature, phase-field type models are spatially resolved and can easily capture the effects of the spatial correlations of the emerging and growing microstructural features. In this model, void formation in the irradiated materials is viewed as a process of condensation of vacancies from a supersaturated solution of vacancies, interstitials and regular lattice atoms. Further, void surface is treated as an interface between vacancy agglomerates (voids) and solid matrix which evolves dynamically due to non-equilibrium conditions that exist during irradiation.

2. Phase Field Model

The phase field model developed herein describes the void microstructure and defect distribution using continuous field variables within a diffuse-interface framework. The void-matrix interface is characterized using an order parameter $\eta(\mathbf{x},t)$, which varies continuously from $\eta = 1$ in the void phase to $\eta = 0$ in the matrix phase over a narrow diffuse interface. The

spatial distribution of point defects is described by fractional concentration fields $c_v(\mathbf{x},t)$ and $c_i(\mathbf{x},t)$ for vacancies and interstitials, respectively. The material system is thus heterogeneous with spatially varying point defect concentrations in the matrix, void, and interface regions. Based on gradient thermodynamics of Cahn-Hilliard [2] and the theory of anti-phase boundary introduced by Allen-Cahn [3], we formulate free energy functional of an irradiated metal comprising vacancies, interstitials, voids and regular matrix regions as follows,

$$F(c_{v}, c_{v}, \eta) = \int_{V} \left[h(\eta) f_{o}^{m}(c_{v}, c_{i}) + j(\eta) f^{vd}(c_{v}, c_{i}) + wg(\eta) + \kappa_{v} \left| \nabla c_{v} \right|^{2} + \kappa_{i} \left| \nabla c_{i} \right|^{2} + \kappa_{\eta} \left| \nabla \eta \right|^{2} + f^{el}(c_{v}, c_{i}, \eta) \right] dV$$

$$(1)$$

where, $f_o^{m}(c_v, c_i)$ is the local bulk energy density of the matrix which accounts for both the enthalpic and entropic contributions due to point-defects; $h(\eta)$ and $j(\eta)$ are shape functions which vary continuously from $h(\eta = 0) = 1$ and $j(\eta = 0) = 0$ in the matrix phase to $h(\eta = 1) = 0$ and $j(\eta = 1) = 1$ in the void phase. The term $f^{vd}(c_v, c_i)$ is the energy of the void phase which is identically zero in the void and $wg(\eta)$ is a Landau double well term. The gradient energy coefficients $\kappa_v, \kappa_i, \kappa_\eta$ correspond to energy penalties due to inhomogeneity in vacancy concentration, interstitial concentration and order parameter field, respectively. In the absence of stress and gradient contributions, the energy terms in Eqn. (1) define two stable wells: one at $\eta = 0, c_v = c_v^o, c_i = c_i^o$ corresponding to matrix phase with defect concentrations equal to thermal equilibrium values (c_v^o, c_i^o) , and another at $c_v = 1, c_i = 0, \eta = 1$ corresponding to the void phase with only vacancies and no interstitials.

The temporal evolution of vacancy and interstitial concentration fields can be prescribed using a Cahn-Hilliard type equation which is modified to account for the point defects created in the system due to collision cascades and defects which are removed from the system through mutual recombination or reactions with extended defects.

$$\frac{\partial c_{v}(\mathbf{x},t)}{\partial t} = \nabla \cdot \mathbf{M}_{v} \nabla \frac{1}{N} \frac{\partial F}{\partial c_{v}} + \mathbf{P}_{v}(\mathbf{x},t) - \mathbf{R}_{vi}(c_{v},c_{i}) - \mathbf{R}_{v}^{\sin ks}(c_{v}) + \xi_{v}(\mathbf{x},t)$$
(2)

$$\frac{\partial c_{i}(\mathbf{x},t)}{\partial t} = \nabla \cdot \mathbf{M}_{i} \nabla \frac{1}{N} \frac{\partial F}{\partial c_{i}} + \mathbf{P}_{i}(\mathbf{x},t) - \mathbf{R}_{vi}(c_{v},c_{i}) - \mathbf{R}_{i}^{sinks}(c_{i}) + \xi_{i}(\mathbf{x},t)$$
(3)

The kinetics of the void formation is captured using a Allen-Cahn type description of void order parameter field $\eta(\mathbf{x},t)$.

$$\frac{\partial \eta(\mathbf{x},t)}{\partial t} = -L\frac{\partial F}{\partial \eta} + \xi_{\eta}(\mathbf{x},t)$$
(4)

In Eqns. (2)-(3) $P_{\alpha}(\mathbf{x},t)$ is a stochastic source term which gives the rate at which α type point defect is being created in the system due to atomic displacement cascades. The sink terms $R_{vi}(c_v,c_i)$ and $R_{\alpha}^{sinks}(c_{\alpha})$ account for the rate at which point defects are removed from the system due to mutual annihilation (between vacancies and interstitial) and due to reaction with sinks or extended defects, respectively. $\xi_{\alpha}(\mathbf{x},t)$ accounts for the fluctuations in the

respective field. M_{ν} and $M_{\rm i}$ are point defect mobilities and L is the mobility of void-matrix interface.

3. Sample Numerical Results

The kinetic equations (2)-(4) are reduced into their non-dimensional form and solved using finite difference schemes for a set of two dimensional test problems. First we look at the scenario of void nucleation for a system subject to radiation damage conditions. Figure 1 shows the time history of different fields corresponding to a scenario where a system initially containing thermal concentration of defects is subjected to irradiation so that vacancies and interstitials are stochastically introduced into the system. Vacancies in the system cluster to form voids, thereby resulting in the creation of void-matrix interface. Subsequent to a transient nucleation stage, voids are found to coarsen.



Figure 1. Time evolution of field variables showing void nucleation under irradiation.

Next we investigate the effect of radiation induced point defects on swelling. Shown in Figure 2 is a material slab with two free surfaces. Point defects produced during irradiation increases their concentrations several times their thermal equilibrium values. The interstitials introduced into the system tend to reach the free surface faster and displace that surface into the free space. In effect the material domain expands due to the accumulation of migrating interstitials on its surface. The resulting bulk regions with low interstitial concentration and high vacancy supersaturation are favourable for void nucleation. As such vacancy clusters in the form of voids are formed within the bulk matrix which in turn provides additional sinks for migrating interstitials and as such stabilize or restrict further swelling of the material.

4. Concluding Remarks

A phase field model for void formation is introduced which accounts for point defects produced under irradiation through stochastic source terms. Our phase field model can capture different aspects of void dynamics and swelling. In particular, we observed nucleation of voids under irradiation, growth/shrinkage of voids based on supersaturated/unsaturated

conditions in the surrounding matrix, swelling of matrix phase due to volume of interstitials migrating to the free surface of the matrix. Contrary to the populist belief, we observe that the swelling of the material can occur prior to the nucleation of voids, by absorption of interstitials at the material surface. In fact void nucleation restricts the amount of swelling in the material. The dependence of swelling on irradiation temperature, dose rate and material properties is under investigation.



Figure 2. Time evolution of field variables $c_v(\mathbf{x},t)$ and $\eta(\mathbf{x},t)$ showing swelling of the irradiated materials and the formation of voids.

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Stress Effects in Defect and Microstructure Evolution under Irradiation**

Anter El-Azab¹*, Shengyu Wang¹, Srujan Rokkam² and Dieter Wolf³

¹Department of Scientific Computing, Florida State University, Tallahassee, FL, USA ²Mechanical Engineering Department, Florida State University, Tallahassee, FL, USA ³Idaho National Laboratory, Idaho Falls, ID, USA

*Corresponding author. Florida State University, 400 Dirac Science Library, Tallahassee, FL 32306-4120. E-mail address: <u>aelazab@fsu.edu</u>

We investigate the effect of stress on the evolution of point defect fields and void nucleation and growth in irradiated materials. The stress is incorporated into a phase field formalism of the problem of defect and microstructure dynamics by the coupling of point defects with the trace of the stress tensor and by the inhomogeneity effect associated with the emerging voids in the irradiated material. This formalism requires the solution of a subsidiary stress equilibrium problem, which is cast in the form of an eigenstrain problem. Analysis of the coupled phase field/elastic problem shows that the model recovers exactly the corresponding sharp interface formalism of point defect diffusion and void growth under applied stress, with zero traction boundary condition over the interior void surfaces. In the case of gas bubbles, a traction boundary condition in terms of the gas pressure is recovered. We present the overall formalism of the problem and discuss a number of results that illustrate the effect of applied stress on the overall defect and microstructure dynamics. In particular, the effect of stress on the anisotropy of diffusion of point defects and on the formation of void patterns will be shown.

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Elastic Representation of Radiation-Induced Defects With Force Multipoles

Dariush Seif and Nasr M. Ghoniem

University of California, Los Angeles Los Angeles, CA. 90095-1597 U.S.A. (dariush@seas.ucla.edu)

ABSTRACT

We present here a computational method for the efficient determination of defect energetics, and for calculations involving defect-defect interactions. A hybrid method has been developed to couple the results of atomistic calculations with classical isotropic elasticity theory to extract a continuum representation of various radiation-induced defects through the use of force multipoles. In this method, atomic size defects are represented by a set of force multipoles that move with each defect as it is transported through the crystal lattice. These calculations provide a means to account for the changes in defect energetics due to local strain environments. In uniform strain environments, the use of the elastic dipole tensor is sufficient to calculate interaction energies. However we find the use of higher-order multipole tensors necessary to represent many defects and their interactions in environments with strain gradients, such as in the vicinity of dislocations and grain boundaries. In addition, isotropic elastic Green's functions are found to provide material response very consistent with atomistic simulations when these higher-order terms are implemented. Results of computations are presented for applications including the interaction between Fe and He point defects and their interaction between Fe and He point defects and their interaction with extended defects in α -iron.

1. Introduction

Internal structural components which operate in nuclear fusion environments are subject to significant damage doses stemming from the onslaught of 14 MeV neutrons produced in the D-T cycle. The internal production of point-defects such as self-interstitial atoms (SIA) and vacancies from elastic interactions, and helium from (n, α) -reactions lead to severe material degradation over time, including swelling and low temperature embrittlement. The prediction of damage evolution and component lifetime is highly dependent upon accurate models of point defect production and interactions within the material. The development of truly predictive long-timescale simulation techniques has been quite scarce in recent history due to the trade-offs between computational efficiency and rigorous physical treatments. While an accurate physical model of damage accumulation and evolution requires a comprehensive understanding of point-defect energetics and interactions, there has been an absence in many studies of the consideration of local strain environment effects on defect migration properties and stability. The goal of this work is to combine atomistic simulation with elasticity theory to implement the method of force multipoles to represent defects, and use continuum elasticity calculations to quantify interactions between these defects and with various strain fields. Emphasis is placed on the importance of including higher-order terms in the multipolar expansion. These interactions can be made available to future KMC simulations to account for strain-biased diffusion, and give a physically-based description of the accumulation and evolution of damage in irradiated metals.

2. Theory

The insertion of a point defect into a perfect crystalline lattice creates a displacement field around the defect on surrounding atoms. This displacement field is typically modeled using one of several approaches to represent the defect. These approaches include the inclusion model of Eshelby [1], the method of Kanzaki-forces [2], and the force-multipole method [3]. For our application, we have found the latter to be most beneficial. In this method, the defect is represented as a multipolar expansion of forces acting at the center of the defect. Consider a defect at the origin surrounded by N atoms (v) with separation vectors \mathbf{l}^{v} . Following the formulations of Siems [4] and Teodosiu [5], the displacement field caused by a defect at the origin can expressed as

$$\mathbf{u}_{\mathrm{m}}(\mathbf{x}) = \sum_{\nu=1}^{\mathrm{N}} \mathbf{G}_{\mathrm{ms}}(\mathbf{x} - \mathbf{l}^{\nu}) \mathbf{P}_{\mathrm{s}}^{\nu}, \qquad (1)$$

where G(x) is the elastic Green's tensor function of the material and P^{ν} are the point forces acting on neighboring lattice atom sites, l^{ν} . We note here that repeated indices imply summation. A Taylor series expansion of $G(x-l^{\nu})$ about x gives allows the displacement field to be expressed as

$$u_{m}(\mathbf{x}) = \sum_{k=0}^{\infty} \frac{(-1)^{k}}{k!} G_{ms,q_{1}...q_{k}}(\mathbf{x}) \mathbf{P}_{q_{1}...q_{k}s}^{(k)} = G_{ms}(\mathbf{x}) \mathbf{P}_{s}^{(0)} - G_{ms,n}(\mathbf{x}) \mathbf{P}_{ns}^{(1)} + G_{ms,nq}(\mathbf{x}) \mathbf{P}_{nqs}^{(2)} - ...,$$
(2)

where

$$\mathbf{P}_{q_1...q_ks}^{(k)} = \sum_{\nu=1}^{N} l_{q_1}^{\nu} ... l_{q_k}^{\nu} \mathbf{P}_s^{\nu}, \quad k = 1, 2,, \infty$$
(3)

are called the multipole moments of k^{th} -order. It is important to note that the k=0 moment represents a sum of the applied force vectors over all atoms, which equals zero for equilibrium conditions to be satisfied. The k = 1, 2, and 3 moments are called the dipole, quadrupole, and octopole moments. Eqtn (2) states that the elastic response of a defected material requires knowledge of the Green's function of the material and the values of the multipole moments of the defect. To lowest order, the defect can be represented by the dipole tensor. The interaction energy of a force multipole defect in a displacement field **u** can be expressed as

$$E_{int} = -\sum_{n=1}^{\infty} \frac{1}{n!} u_{m,q_1...q_n}(\mathbf{x}) \mathbf{P}_{q_1...q_nm}^{(n)} = -\mathbf{P}_{im}^{(1)} u_{m,i}(\mathbf{x}) - \frac{1}{2!} \mathbf{P}_{ijm}^{(2)} u_{m,ij}(\mathbf{x}) - \frac{1}{3!} \mathbf{P}_{ijkm}^{(3)} u_{m,ijk}(\mathbf{x}) - \dots$$
(4)

3. Solution Methodology

We have recently developed a hybrid method to compute the values for the multipolar moments of lattice defects using molecular statics (MS) calculations and continuum elasticity theory. Thus far, our focus has been radiation induced defects in the bcc alpha-iron lattice. Our method first requires an atomistic simulation of the defect in the host lattice to acquire the displacement field around the defect. For our molecular statics calculations we have chosen interatomic potentials well suited for simulation of these types of defects. For Fe-Fe, Fe-He, and He-He interactions we have chosen the well known Ackland [6], Juslin-Nordlund [7], and Lennard-Jones interatomic potentials, respectively. In our atomistic calculations the defect was introduced in the center of the simulation box, and a static relaxation (0 K) was implemented via conjugate gradient minimization to allow relaxation of the atoms. The supercell was a cube with an edge length of 18 lattice parameters (~52 Angstroms) and periodic boundary conditions were applied on all sides. After performing the MS calculations, the next step is to use the atomic displacements to obtain a multipolar

representation of the defect via inversion of Eqtn (2). This task requires a differentiable Green's function expression for the material. We have found the isotropic elastic Green's function to provide adequate response of the material as compared to our MS calculations. This response function is well known and provides a tractable closed-form solution simplifying the necessary calculations. We note the Green's function derivatives fall off as $O(r^{-(k+1)})$ in the multipolar description. While this is a very rapid decay for k > 1, and the dipole moment dominates at longer distances, we have typically found the inclusion of up to the octopole tensor to be necessary to accurately match the immediate lattice displacements.

4. Results and Conclusions

Implementing our hybrid method, we have calculated the multipolar moments up to the octopole tensor ($\mathbf{P}^{(3)}$) for various radiation-induced defects in α -Fe. Calculated values for the dipole tensor of several selected defects are given in Tab 1.

	V ^r	P ₁₁	P ₂₂	P ₃₃	P_{12}/P_{21}	P ₂₃	P ₁₃
Fe [110] SIA	1.48	20.02	20.02	18.22	-9.107	0	0
Fe Vacancy	-0.094	-1.23	-1.23	-1.23	0	0	0
He Tetrahedral	0.435	5.77	5.58	5.77	0	0	0
He Octahedral	0.495	5.37	5.37	8.73	0	0	0
He Substitutional	0.267	3.51	3.51	3.51	0	0	0
He ₁₂ V ₄ Cluster	5.32	63.62	70.62	71.51	0.61/-0.0134	0	0

Table 1. Computed relaxation volumes (in Fe at. vols) and dipole moment values (in eV).

In Fig 1 we have plotted the radial displacements versus distance from the defect center. The circles in these plots are those obtained from MS calculations, while the points represent the calculated displacements using the continuum elasticity (CE) multipolar representation via Eqtn (2).



Figure 1. Radial displacements vs. distance for (a)[110] SIA, and (b)He Substitutional.

In Fig 1(a) we see the complex radial displacement field of the [110] SIA and the very good agreement with the multipolar representation. In addition, we calculate a formation energy of 4.02 eV for this defect which compares well with these and several other interatomic potentials. In Fig 1(b) the He substitutional defect displacement field is plotted in the cases in which only the dipole moment is used (squares), as well as where up to the octopole moment is used (points). The importance of including the higher-order terms is made clearly evident in this plot, and is the case for many other defects that have been studied. The discrete lattice

effects that arise even from centro-symmetric defects are found to require higher-order contributions for adequate modeling. In Fig 2 the iso-interaction energy contours are plotted for a [110] SIA with both a $He_{12}V_4$ helium-vacancy cluster and an $a_0/2[111]{110}$ edge dislocation centered at the origin. The calculations are made utilizing Eqtn (4), where the cluster is modeled with multipoles and the elastic solution for an edge dislocation in infinite medium is used.



Figure 2. Iso-Interaction energy contours of a [110] SIA with a (a)He₁₂V₄ cluster, (b) $a_0/2[111]{110}$ edge dislocation.

In Fig 2(a) we see four distinct regions where the SIA either is attracted to or repelled from the cluster. The repulsive regions correspond to zones where the defect may experience a change in orientation to lower its energy. The interaction with the edge dislocation show significant attraction on the tensile side and repulsion on the compressive side. The interactions are far reaching in this case signifying the importance of local strain field consideration of defect formation, migration, and stability.

Our calculations have provided a means to account for the changes in defect energetics due to local strain environment effects. For the force-multipole representation of defects, we have emphasized the use of higher-order multipole moments to accurately represent the MS-predicted lattice response of many defects. These include interstitial and substitutional defects, which are typically only modeled with dipole moment. In these cases we found specific importance of the octopole moment in enhancing the complexity of the lattice response to match the MS calculations. Our solutions have quantified the spatial extent of interactions as well as directional dependence on migration characteristics. The method we describe and its outcomes will allow for more accurate models of defect diffusion and interaction within the radiation damage environment, where long- and short-range elastic interactions govern the accumulation and evolution of defects in the material.

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Stochastic effects on microstructure nucleation under cascadedamage irradiation

A.A. Semenov

Department of Electronic and Information Engineering, The Hong Kong Polytechnic University, Hong Kong SAR, China, e-mail: <u>enalexei@inet.polyu.edu.hk</u>; Institute for Nuclear Research, Russian Academy of Sciences, 60-th October Anniversary Prospect 7a, Moscow, Russia

The arrival rates of point defects on various sinks are not deterministic, but probabilistic and fluctuate all the time because of the random nature of diffusing jumps and cascade occurrence. The process of new phase nucleation is very sensitive to the material parameters and the environmental conditions, and, consequently, the correct treatment of stochastic fluctuations is particularly important when the issue of nucleation of damage microstructure is under consideration. In the master equation, which is conventionally used for the treatment of stochastic fluctuations due to the randomness of point-defect migratory jumps are taken into account.

The relative importance of the cascade-induced fluctuations increases with increasing total sink strength and the sink absorption radius. Omitting the related effects is not a good approximation under cascade-damage irradiation, because the accumulation of small clusters of point defects, which are continuously produced by cascade-damage irradiation, is able to drive the total sink strength for mobile defects to a very high level. In the presentation the generalized kinetic equation for the microstructure evolution under cascade-damage irradiation, including the full statistical effects, will be discussed.

Using the generalized kinetic equation, expressions for the probabilities of nucleation of the damage microstructure components are derived, containing explicit dependence on material properties and irradiation conditions, thus allowing their applications to a wide class of materials and conditions, from which dislocation loop and void nucleation can be investigated. The applications of the general theory to the physically important cases will be also presented. Particular attention will be paid to the effect of one-dimensional diffusion of self-interstitial atoms on void nucleation.

Structure of Self-Interstitial Atom Clusters in Iron and Copper: A Hybrid Ab-initio Continuum Determination

Akiyuki Takahashi¹ and Nasr M. Ghoniem²

¹Department of Mechanical Engineering, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-shi, Chiba, 278-8510, Japan, takahash@rs.noda.tus.ac.jp
²Department of Mechanical and Aerospace Engineering, University of California, Los Angeles, Los Angeles, CA, 90095, ghoniem@seas.ucla.edu

ABSTRACT

The dislocation core structure of Self-Interstitial Atom (SIA) clusters in bcc iron and fcc copper is determined using the hybrid ab-initio-continuum method, which is a combination of the Parametric Dislocation Dynamics (PDD) method and a descritized computational form of the Peierls-Nabarro model. The dislocation core structure of SIA clusters in iron does not have clear dependence on the size of the cluster, which is almost identical to that of an infinitely long straight edge dislocation. On the other hand, in copper, the dislocation core structure of SIA clusters has a strong dependence on the size of the clusters. Small SIA clusters have a non-dissociated compact dislocation core. As the size of the cluster is increased, the dislocation core structure approaches to that of a straight edge dislocation. Additionally, the local stress is found to have a significant effect on the atomic arrangement of SIA clusters in copper. An applied external shear stress delocalizes the core of an SIA cluster in copper.

1. Introduction

During energetic particle interaction with crystalline solids, self-interstitial atoms (SIA) readily aggregate in the near vicinity of collision cascades initiated by energetic ions or neutrons, and they cluster into tightly bound coherent configurations known as self-interstitial atom clusters. To understand the contribution of SIA clusters to the variety of phenomena associated with radiation interaction with materials, it is essential to address the fundamental physics of these defects. The geometry of atomic arrangements of SIA clusters often controls their interactions with the microstructure, and hence should be accurately determined.

One of the most successful defect models is that due to Peierls and Nabarro, in which the dislocation core structure is atomistically resolved on the basis of the continuum theory of elasticity¹. In the Peierls-Nabarro (PN) model, the core structure is determined by balancing the crystal lattice restoring forces with elastic interactions between infinitesimal incompatibilities (dislocations) within the dislocation core. Recently, Benerjee *et al.* proposed an atomistic-continuum hybrid computational method that extends the original PN model to dislocation problems of arbitrarily complex shape, and that directly utilizes *ab initio* information to reconstruct lattice restoring forces².

The present study has two objectives. The first objective is to advance the development of the hybrid atomistic-continuum method of Banerjee et al. extending it to the determination of the core structure of SIA clusters. We investigate here the dependence of the core structure of SIA clusters on their sizes, and on the local stress environment in Fe (bcc) and Cu (fcc). The second is to elucidate the influence of applied stress on the atomic structure of SIA clusters and to reveal the conditions for drastic deviations from unstressed configurations.



Figure 1: Geometry of self-interstitial dislocation loops in iron.



Figure 2: Core structure of self-interstitial loops containing (a) 91, (b) 397 and 919 SIAs in iron. Each line represents on infinitesimal dislocation loop.

2. Computational Method

Banerjee $et al.^2$ proposed a hybrid *ab initio* continuum method to enable determination of the core structure of dislocations of arbitrary complex geometry. The approach is an extension of the original Peierls-Nabarro model, in which a balance is sought between forces arising from infinitesimal displacements within the dislocation core and lattice restoring forces. This balance can be expressed as

$$p(x) = \frac{\mu}{\pi(1-\nu)} \int_{-\infty}^{\infty} \frac{1}{x'-x} \frac{du}{dx'} dx'$$
(1)

where, p(x) is the lattice restoring force, μ and ν are the elastic shear modulus and Poission's ratio, respectively, x is the position of an infinitesimal element of displacement where the force balance in Eqn. (1) is evaluated, where x' is the position of any other infinitesimal element of displacement, and u is the sought-after atomic displacement within the dislocation core. To numerically solve Eqn. (1), the dislocation core is first discretized into a number (N) of infinitesimal dislocations, and the Burgers vector of each infinitesimal dislocation is set to b/N to keep the total displacement of the dislocations. The elastic interaction term between displacements in the dislocations. The orientation-dependent slip energy, known as the generalized stacking fault energy, is used to determine p by taking the spatial derivative of the energy. We compute this energy surface using density-functional theory.

3. Core Structure of Self-interstitial Clusters in Iron

In the studies of Osetsky *et al.*³, the most stable SIA clusters in iron were found to be sets of parallel $\langle 111 \rangle$ crowding, and that large clusters from perfect dislocation loops with Burgers vector $\mathbf{b} = \frac{1}{2} \langle 111 \rangle$, We consider here the self-interstitial loop geometry shown in Fig. 1. The self-interstitial loop has a hexahedral shape, and all straight segments in the loop can glide on their own slip plane. The Burgers vector of all segments is $a_0/2[111]$, where a_0 is the lattice constant of bcc iron. We consider prismatic dislocation loops containing SIAs of 91, 397 and



Figure 3: Geometry of SIA cluster modeled as a rhombus-shaped edge dislocation loop in copper. (a) Burgers vector of the full prismatic loop; (b) stair-rod dislocations with line sense.



Figure 4: Core structure of an SIA cluster modeled as a rhombus-shaped edge dislocation loop in copper containing (a) 16 and (b) 400 SIAs.

919 to study the dependence on the size and conform with the hexagonal shape of the loop. Fig. 2 shows the results of the present method for the core structure of self-interstitial loops in iron. In the figure, infinitesimal dislocation arrays representing SIA clusters containing 91, 397 and 919 SIAs are approximately self-similar, and form very compact dislocation cores. By checking the displacement distributions in the dislocation core of SIA loops, it can be found that the displacements are concentrated within a width of 6b, and that the core structure is identical in all loops. Moreover, the core structures of an SIA loop in iron is the same as that of a straight edge dislocation.

4. Core Structure of Self-interstitial Clusters in Copper

Osetsky *et al.* performed MD simulations of SIA clusters and found that the most stable configurations are rhombus pure edge loops $\frac{1}{2} \langle 110 \rangle \{110\}$ and hexagonal Frank loops $\frac{1}{3} \langle 111 \rangle \{111\}^3$. Since the possibility of dissociation into Shockley partial dislocations exists for copper, we consider SIA loops of a rhombus shape as shown in Fig. 3. To deal with the extended core in copper, infinitesimal dislocations representing each segment of the rhombus-shaped loop are classified into leading and trailing partials, each with different Burgers vector. At the corners of each infinitesimal rhombus we ensure the net Burgers vector is zero by adding a stair-rod dislocation. Figure 4 shows the results of the present hybrid simulations. It is noted that infinitesimal dislocations cannot clearly be seen in the figure, indicating that partial dislocations in small self-interstitial loops have a flat core structure. On the other hand, as the size of the self-interstitial loop increases, the spatial dislocations of infinitesimal dislocations.


Figure 5: Dependence of the dislocation core width on (1) the size of SIA cluster and (2) the externally applied shear stress.

5. SIA Cluster Core Response to Applied Shear

The effects of the local stress on the core structure is investigated by applying pure shear stress on the slip plane of the rhombus loop edges along the $[\bar{1}\bar{1}2]$ direction with a positive sense as shown in the inset of Fig. 5. The figure also shows the dependence of the stacking fault width on the number of SIAs within the cluster for positive and negative applied shear, and the unstressed case is also included for comparison. If the shear stress is positive, the leading and trailing partials move away from one another, and the stacking fault between the partials is widened. The opposite takes place for a negative value of the shear stress. It is interesting to see that negative shear renders the core more compact, and nearly independent of sizes larger than approximately 400 SIAs. On the other hand, large positive shear delocalizes the core of the SIA cluster, and for a large-enough shear stress and a size larger than 600 SIAs, the cluster core is totally delocalized. The compressive state within the core becomes nonlocal and of a long-range nature. The results highlight that need to consider the influence of the local stress on the atomic structure, and on the elastic interactions between SIA clusters and other defects.

6. Summary

We summarize here the main physical results of the present work on the core structure of SIA atom clusters in iron and copper: (1) the core structure of self-interstitial loops in iron is very compact and has no clear dependence on the dislocation loop size. (2) The core structure of self-interstitial loops in copper is extended into a combination of a stacking fault and Shockley partial dislocations. The core structure is shown to have a strong dependence on the size of the loop. (3) An applied external shear can delocalize the core of an SIA cluster in copper, with positive shear defined to be on the (111) plane along the $[\overline{112}]$ direction.

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Influence of lattice vibrations on the nucleation free energy of copper-vacancy clusters in bcc-Fe

<u>M. Talati¹</u>, M. Posselt², A.T. Al-Motasem¹ and F. Bergner¹ ¹Institute of Safety Research, ²Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, P.O.Box 510119, D-01314 Dresden, Germany m.talati@fzd.de

Copper-rich precipitates (CRP) are considered to be the main cause of hardening and embrittlement of Cu-bearing RPV steels since these defects act as obstacles to dislocation motion within the grains of polycrystalline bcc-Fe. There is clear evidence that these nanoclusters remain small and have the bcc structure of the surrounding matrix. The effect of irradiation on the microstructure of RPV steels and consequently on their mechanical properties is a multiscale phenomenon. The evolution of CRP over realistic time and length scales can be effectively studied by rate theory. However, many parameters used, such as the nucleation free energies of precipitates, are not very well known from experimental investigations. Atomic-level computer simulations can provide these data. The nucleation free energy is determined by the energy and the entropy change due to cluster formation using isolated (diluted) copper atoms and vacancies as the reference. In the conventional approach the energy and entropy changes are calculated at zero temperature [1]. The few previous attempts to include temperature effects did not lead to consistent results [2-3]. Therefore, present investigations are focused on this topic. In all calculations the most recent classical interatomic potential for the system Fe-Cu is used [4]. Molecular dynamics simulations at different temperatures are performed in order to determine the velocity autocorrelation function which can be transformed into the vibrational density of states. The latter quantity is used to calculate the contributions of lattice vibrations to energy and entropy at a given temperature.

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Atomistic simulations of solid solution hardening in Fe-Cr alloys

D. Terentyev¹ and G.Monnet²

¹<u>SCK-CEN, Boeretang 200, Mol, Belgium, dterenty@sckcen.be</u> ²EDF-R&D, Dept. MMC, Site des Renardières, F-77218 Moret-sur-Loing, France

FeCr alloys are the basis for high Cr ferritic/martensitic steels, which are the current candidate structural materials for future fission and fusion reactors, due to their superior mechanical properties and good radiation resistance. The mechanical property changes in binary Fe-Cr alloys and ferritic-martensitic steels under irradiation are known to be gualitatively similar, therefore these alloys were chosen as a model materials for the investigation of high-Cr steels [this sentence not strictly necessary in an abstract any way]. Fe-Cr alloys containing more than 10% Cr are known to exhibit a phase separation conducting to the formation of coherent Cr-rich precipitates (so called alpha-prime phase), while if the Cr content is less than 10 % partial ordering of Cr atoms occurs, revealed by a negative value of the measured short range order (SRO) parameter. Non irradiated Fe-Cr alloys are known to harden more than Fe because of the well-known effect of solid solution hardening. Under irradiation at the elevated temperature, the formation of alpha-prime nuclei or partial ordering of Cr atoms is expected to occur, due to the accelerated diffusion and/or non-equilibrium segregation. This Cr atom redistribution may provide additional source of hardening. To determine and predict the change of the mechanical properties due to phase transformation, atomistic simulations of dislocation motion under applied stress/strain can be used.

In the present work we study the mobility of dislocations using large scale molecular dynamics simulations with DFT-fitted interatomic potential for Fe-Cr, which have been proven to provide a satisfactory description of both point defects in pure Fe and Fe-Cr alloys and the heat of mixing as obtained from the DFT calculations. The main objective of this work is to establish the mobility of dislocations in binary Fe-Cr alloys with different Cr content as a function of temperature, applied deformation and Cr distribution in the alloys. In particular, in the alloys containing less than 10% Cr several cases were considered, with alloying atoms distributed: (i) randomly, (ii) according to the available experimental data (based on the Mössbauer measurements of aged alloys) and according to the distribution obtained after thermal annealing using the kinetic Monte Carlo techniques with the same interatomic potential. In alloys with more than 10% Cr, in addition to the random and experimental Cr distribution, the interaction between dislocations and Cr-rich precipitates of different sizes is also considered here. The information obtained in this study is expected to be used to parameterise dislocation dynamics models for the prediction of the mechanical behaviour of the corresponding alloys.

Interaction of Carbon with vacancy and interstitial clusters in α -Fe: an atomistic study

D. Terentyev¹, V. Jansson^{1,2}, N. Anento³ and A. Serra³

¹ SCK•CEN, Institute of Nuclear Materials Science, Boeretang 200, 2400 Mol, Belgium ²University of Helsinki, P.O.B. 43 (Pehr Kalms gata 2) FI-00014 University of Helsinki, Finland

³ Departamento Matematica Aplicada III, Universidad Politecnica de Catalunya, Jordi Girons 1-3 (C-2), E-08034 Barcelona, Spain

dterenty@sckcen.be

Interaction of a carbon atom with a variety of vacancy and self-interstitial atom (SIA) clusters was studied using atomistic simulations applying three sets of interatomic potentials for Fe-C system. Among them, we used the most recent Fe-C potential, developed by Hepburn and Ackland [1], which accounts for the saturation of covalent bonding and thus solves well known shortcomings of the previously developed potentials in terms of description of C-C-V complex (covalent directional bonding), C-<110> SIA interaction, C-C interaction and Carbon substitutional energy in Fe matrix. Static and dynamic simulations were carried out to estimate binding and dissociation energies for vacancy-C and SIA–C complexes. Another goal of this work was to investigate a possibility for the drag of C by a <111> SIA cluster and to study the interaction of <111> SIA clusters with V-C complexes, which, being immobile, may block movement of fast one-dimensionally glissile SIA clusters.

The obtained results show that the newly derived potential by Hepburn and Ackland in most of the cases considered predict qualitatively different results as compared to data obtained with the N-body potential [2] and pairwise [3] potentials. In particular, the former potential predicts that (i) the presence of Carbon destabilizes vacancy clusters, (ii) Carbon is attracted to the edge dislocation or $\frac{1}{2}$ <111> dislocation loop only in the compressed zone and repelled from the tensile region, (iii) Carbon destabilize non-parallel SIA clusters. Whereas opposite trends are observed with the two other potentials.

Beside that it is shown that C-V and C₂-V complexes offer a significant resistance to the passage of <111> SIA clusters and the interaction energy between a small $\frac{1}{2}$ <111> dislocation loop and these complexes can be as high as 1 eV, which is essentially higher than the interaction energy for an isolated Carbon atom.

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Multiscale Modeling of Materials Response to Irradiation

Michael Tonks¹, Paul Millett¹, Derek Gaston¹, Anter El-Azab² and Dieter Wolf³

¹Fuels Modeling and Simulation, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, Email: michael.tonks@inl.gov

²Department of Scientific Computing, Florida State University, 400 Dirac Science Library, Tallahassee, FL 32306-4120

³Center for Advanced Modeling and Simulation, Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415

Irradiation-induced microstructure evolution in fuel and cladding material has a large impact on the performance and safety of nuclear reactors. To accurately model the effect of irradiation on fuel performance requires the coupling of information over several length-scales. In this presentation, we outline the multiscale modeling effort on irradiated nuclear fuel at Idaho National Laboratory. The focus of our efforts is a mesoscale phase field model that captures defect migration and nucleation in irradiated polycrystalline materials. During the development of the mesoscale model, atomistic simulations are used to identify critical mechanisms and to determine mesoscale material parameters. In turn, the mesoscale simulations are coupled to macroscale finite element simulations of nuclear fuel pellets. We summarize our simulations at the atomic, meso- and macroscale and discuss the coupling between the various scales.

Atomistic simulations of strain localization in irradiated polycrystalline metals

Tomohito Tsuru¹, Yoshiyuki Kaji¹ and Takashi Tsukada¹

¹Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, 2-4 Shirakata-Shirane, Tokai-mura, Ibaraki 319-1195, Japan, <u>tsuru.tomohito@jaea.go.jp</u>
²Department of mechanical engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

The dislocation channeling observed in irradiated metals is generated as the result of strain localization and it has been thought to be one of the key stress factors in irradiation assisted stress corrosion cracking (IASCC), in which the dislocation accumulation occurs and the stress concentration are produced by the interaction between a number of dislocations and grain boundary. In the present study the strain localization mechanism under deformation is investigated by atomistic simulations. Both the bicrystal and polycrystal models with different grain sizes are prepared by Voronoi polyhedron division and embedded atom method potential which reproduce both the fundamental grain boundary and deformation characteristics is employed. The dislocation nucleation mechanism of bicrystal with twin and some coincidence site lattice grain boundaries under local deformation is investigated, and then the deformation mode of a whole system of a sequence of polycrystalline models are examined compared with single crystalline model. As a result the critical resolved shear stresses of bicrystals are significantly reduced by the presence of grain boundary even in the case of coherent twin boundary. It is found that the specific grain boundaries except for stable boundary are preferentially deformed in the stage of elastic deformation and that dislocations are intensively emitted from the heterogeneous triple grain junctions at the initial stage of plastic deformation. Finally the influences of irradiation defects on plastic deformation are discussed.

Radiation Damage Production and Evolution near Grain Boundaries in Cu

Xian-Ming Bai¹, Arthur F. Voter², Richard G. Hoagland¹, Michael Nastasi³, and <u>Blas P. Uberuaga¹</u>

¹Materials Science and Technology Division, MST-8, ²Theoretical Division, T-1, ³Materials Physics and Applications Division, MPA-CINT, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

It is well accepted that grain boundaries serve as effective sinks for radiationinduced defects (interstitials and vacancies). However, insight into the atomicscale origin of this behavior is still lacking. In order to meet the demands of future nuclear applications, the origin of this enhanced radiation tolerance must be understood.

We use molecular dynamics, temperature accelerated dynamics, and molecular statics to study radiation damage phenomena near a symmetric sigma 11 grain boundary in Cu over three different temporal regimes: the short-time damage production phase of a collision cascade, the longer-time scales over which defect annihilation and aggregation occur, and the thermodynamic-limiting behavior of the system. We find that both the production and the subsequent annealing of the radiation-induced defects are modified significantly by the presence of the grain boundary. In particular, we identify a new mechanism by which interstitials efficiently annihilate vacancies, promoting enhanced defect recombination. We compare to previous experimental results and identify three regimes over which different thermally activated processes are active, resulting in different responses, both better and worse than large-grained counterparts, of the material to irradiation. Our results show that nanostructured materials have a very sensitive response to irradiation and offer new insights into the design of radiation tolerant materials.

Multiscale Study of Small Self-Interstitial Clusters in Beryllium

<u>P. V. Vladimirov¹</u>, V. A. Borodin²

¹Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany; ²RRC Kurchatov Institute, Kurchatov Sq. 1, 123182 Moscow, Russia

ABSTRACT

Beryllium is foreseen as neutron multiplier material for fusion reactor blanket. Predictions of radiation induced microstructure development (e.g. swelling or radiation growth) in beryllium require the knowledge of point defect mobility and their mutual interactions. In order to investigate the possible configurations as well as dynamic behavior of single interstitials and small interstitial clusters, we have used a combination of classical molecular dynamics simulations with analytical bond order interatomic potential for beryllium and *ab initio* technique for detailed estimates of defect energies and migration barriers. We demonstrate that only two self-interstitial positions (basal octahedral (BO) and non-basal crowdion (C)) correspond to true energy minima, while other known high-symmetry configurations are either unstable, or correspond to saddle points. For example, octahedral position (O) is a saddle point for BO-O-BO transition along c axis with migration barrier of 1.1 eV, while basal split (BS) configuration is a saddle point for BO-BS-BO jump in basal plane with migration barrier of only 0.12 eV. We show that at least di-interstitials are stable defects that can have several basic shapes with competing energies. A mechanism of self-similar stacking fault expansion by BO interstitial clustering is proposed.

1. Introduction

Beryllium is considered as candidate material for the first wall of future fusion reactor and as neutron multiplier material for fusion blanket, where its resistance against radiation is very important. Mobility of point defects produced under irradiation and their mutual interactions influence formation of radiation induced microstructure and define macroscopic response of irradiated material (e.g., swelling or irradiation growth) which in beryllium is significantly affected by gas production.

The properties of vacancies and their gas-filled clusters have been already investigated in our previous paper [1]. Therefore this work is focused on the study of the stability of self-interstitial atoms (SIAs) and their clusters in hcp beryllium as well as on investigation of SIA diffusion pathways. Some non-trivial interstitial configurations and their diffusion paths were obtained in molecular dynamic runs using recently developed interaction potential for beryllium [2]. A priori known and newly obtained configurations were relaxed using first-principles density functional theory (DFT) code VASP [3], while migration barriers were estimated by means of the nudged elastic band method implemented in VTST package (see e.g. [4]).

2. Results and discussion

1.1 Single interstitials

Previously we have investigated eight high-symmetry interstitial configurations in beryllium [1]. According to their formation energies (see Fig. 1) these configurations can be roughly divided in two groups: those lying mainly (i) in basal (E_f is below 4.5 eV) and (ii) out of basal plane with higher formation energies. The defect energetics and atomic positions were obtained by conjugate gradient relaxation using VASP with ultrasoft and PAW pseudopotentials. Six configurations from eight are apparently stable: i.e. the interstitial atom after relaxation had the same neighbors as before. Other configurations are unstable: basal crowdion (BC) undergo spontaneous transition to basal octahedral (BO) position, while basal tetrahedral (BT) relaxes to tetrahedral one (T).



Figure 1: Formation energies of various SIA configurations in beryllium [1]

Using the same approach we have investigated single SIA diffusion pathways, which are summarized in Fig. 2. The easiest diffusion path is in-basal plane rotation (BO-BS-BO) requiring only 0.12 eV. SIA movement perpendicular to basal plane is much less favorable and needs 1.1 eV (BO-O-BO). Another path which combines in- and out-of-basal plane components (BO-C-BO) has intermediate diffusion barrier of 0.27 eV. It is seen in Fig. 2c that BO position is the lowest energy ground state, while non-basal crowdion (C) is only a shallow local minimum, which requires only 0.06 eV for decay to BO. Fig. 2a and b also show that BS and O positions are saddle points of respective diffusion jumps and were therefore apparently stable during relaxation.



Figure 2: Diffusion paths of self-interstitials: in-basal-plane path BO-BS-BO (a), path along c axes BO-O-BO and the path inclined with respect to basal plane BO-C-BO.

1.2 Di-interstitials

Di-interstitials can be formed in particular from two BO interstitials. During this process they push the regular lattice atom located between them (the central atom in Fig.3a) into another neighboring BO position forming planar triangular cluster of three BOs around one empty lattice site. We checked that two BO interstitials placed at the second nearest neighbor separation spontaneously form triangular cluster during relaxation indicating the lack of diffusion barrier for this transition.

In addition various forms of non-planar clusters were observed in molecular dynamics runs, which will be not described here due to the lack of space.



Figure 3 Formation of SIA cluster containing 3 interstitial atoms and one vacant lattice site (a) formation mechanism by reaction $BO+BO\rightarrow(BO_3Vac_1) \equiv (3,1)$; (b) relaxed configuration in 100 atom supercell

1.3 Mechanism of formation and nature of planar triangular interstitial clusters

Addition of another BO to the BO₃Vac₁ cluster will result in displacement of two additional lattice atoms into BO positions (see Fig.4a): (BO₃Vac₁)+BO \rightarrow (BO₆Vac₃) (see Fig. 4). This process can be continued: (3,1) \rightarrow (6,3) \rightarrow (10,6) \rightarrow (15,10) \rightarrow ... \rightarrow ((n+1)(n+2)/2, n(n+1)/2), where the first number in parenthesis is a number of interstitials and the second is a number of vacancies in the cluster with sequential index n.



Figure 4 Formation of SIA cluster containing 6 interstitial atoms and 3 vacant lattice sites: (a) formation mechanism by reaction $(3,1)+BO\rightarrow(6,3)$; (b) relaxed configuration in 100 atom supercell

This reaction uncovers a new mechanism of basal self-interstitial cluster formation and selfsimilar growth in hcp materials with stable BO interstitial configuration by clustering of two BO or by attachment of BO to planar triangular SIA cluster. As was mentioned above this clustering does not require overcoming additional energy barrier.

These planar clusters might be confused with interstitial loops, however they do not add an additional crystalline plane as real interstitial loops should do, but present another stacking sequence of planes locally. They can be considered as local stacking faults with the stacking sequence of layers along c axis: ABABCBABA, where ABC sequence is that native for fcc lattice, while hexagonal close packing consists of AB layers.

Such clusters were also observed in molecular dynamics simulations of atomic displacement cascades in zirconium together with irregular and prismatic SIA clusters [5]. The later are formed from several basal SIA clusters stacked on each other and were recognized as I2 intrinsic stacking faults with two fcc stacking sequences on the top and bottom of the prism.

One could suppose that planar clusters of that kind can grow infinitely forming a complete stacking fault layer. However, our molecular dynamics calculations indicated that large planar clusters are unstable against formation of non-planar configurations inserted in planar cluster. For example, one of the cluster atoms can be replaced with a split dumbbell along c-axis.

As have been shown previously di- and tri-vacancy clusters are not stable in beryllium [1], therefore we decided to check whether triangular clusters similar to those described above but formed by agglomeration of vacancies (analog to stacking fault tetrahedral (SFT) observed in fcc metals) are stable. However, our preliminary DFT calculations have shown that formation of SFT in beryllium is energetically unfavorable.

3. Conclusions

Combination of ab initio and MD methods proved to be a useful approach for the study of point defect clusters. In particular, several types of SIA clusters were observed in MD and ab initio: (i) triangular configurations in basal plane (stacking fault), (ii) planar C-C clusters, which may present possible seeds for interstitial loop formation and (iii) non planar clusters.

Further investigations are required to clarify their relations to a- and c-type interstitial loops experimentally observed in beryllium under irradiation.

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Formation of Self-Interstitial Atom Clusters in Cubic Silicon Carbide during Irradiation

Yoshiyuki Watanabe^{1,*}, Kazunori Morishita², Yasunori Yamamoto¹

¹Graduate School of Energy Science, Kyoto University, Kyoto 606-8501, Japan ²Institute of Advanced Energy, Kyoto University, Kyoto 611-0011, Japan ^{*}E-mail: y-watanabe@iae.kyoto-u.ac.jp

ABSTRACT

In order to clarify the formation kinetics of self-interstitial atom (SIA) clusters in cubic silicon carbide during irradiation, nucleation and growth process of SIA-clusters have been evaluated by Kinetic Monte-Carlo simulation technique, in which defect energetics investigated by MD and MS combined method is employed. In the simulations, at relatively high temperatures formation of SIA-clusters is dominated by thermal stability of the clusters, while the formation is dominated by influx of interstitials into the cluster at relatively low temperatures. It follows from these arguments that formation kinetics of SIA-clusters in cubic silicon carbide during irradiation can be classified by temperature into the two types.

1. Introduction

Cubic silicon carbide (beta-SiC) is a component of SiC/SiC composites that are candidates for blanket structural materials of nuclear fusion reactors because of high mechanical strength and low activation properties. A variety of experiments have been performed to evaluate irradiation effects in beta-SiC. Some experiments using Transmission Electron Microscopy (TEM) show that self-interstitial atom (SIA) clusters with a diameter of 2.0 to 3.6 nm are observed in irradiated beta-SiC at temperatures above 600 °C [1-3]. Such microstructural changes cause the degradation of the material's properties; therefore, they should be accurately predicted and controlled to suppress the degradation. However, the formation kinetics of SIA-clusters in beta-SiC is not understood well yet. In our previous work [4, 5], energetics of defects in beta-SiC was investigated using molecular dynamics (MD) and molecular statics (MS) calculations, which is important to clarify the formation kinetics of the clusters.

In the present study, the formation kinetics of SIA-clusters in beta-SiC during irradiation was evaluated by a kinetic Monte-Carlo (KMC) simulation technique that employs the defect energies obtained in our previous work [4, 5].

2. KMC model

Growth or shrinkage of a defect cluster is determined by a balance between influx and outflux of point defects into and from the defect cluster, in which the influx and outflux mean absorption and emission of point defects, respectively. The influx of point defects into a disc-shaped SIA-cluster in beta-SiC is described by the following equation in the unit of s^{-1} :

$$\nu_k^{\text{influx}} = \frac{2\pi^2 R}{\Omega \ln(r^m/r_0)} D_k C_k , \qquad (1)$$

where D_k and C_k are the diffusion coefficient and concentration of the type k point defect in the matrix, respectively, in which k denotes silicon vacancies (V^{Si}), carbon vacancies (V^C),

silicon interstitials (I^{Si}) and carbon interstitials (I^{C}). It is noted that in the present study the vacancies (V^{Si} and V^{C}) were omitted, and the only interstitials (I^{Si} and I^{C}) were treated for simplicity of the model. Ω is the mean atomic volume and *R* is the cluster radius. Here, the cluster volume is given by $V=n\Omega=\pi R^{2}b$, where the cluster size $n=n_{1}^{Si}+n_{1}^{C}$ is the number of interstitials contained in the cluster, in which n_{1}^{Si} and n_{1}^{C} are the numbers of silicon- and carbon-interstitials in an SIA-cluster, respectively, *b* is the thickness of the disc in the <111> direction. The migration energy, related to the diffusion coefficient, for point defects is 1.58 eV for silicon interstitials and 0.78 eV for carbon interstitials [4]. The outflux of point defects from a disc-shaped SIA-cluster is written by the following equation in the unit of s⁻¹:

$$v_k^{\text{outflux}} = \frac{2\pi^2 R}{\Omega \ln(r^m/r_0)} D_k \exp\left(-\frac{E_{\text{B}}^{\text{cluster}-k}}{k_{\text{B}}T}\right),\tag{2}$$

where $E_B^{\text{cluster-}k}$ is the binding energy of a point defect to an SIA-cluster. Since k denotes the interstitials (I^{Si} and I^C) in the present study, the binding energy is between an intestinal and an SIA-cluster, and is given by a function of size and chemical composition ratio of SIA-cluster, as described below.

The binding energy is defined as energy required to remove an interstitial (SIA) from an SIA-cluster, in which estimation of the energy value needs formation energy of the defects. However, since silicon carbide is a binary chemical compound, SIA-clusters with a variety of chemical compositions of silicon- and carbon interstitials could be formed during irradiation; therefore, the formation energy will depend on not only cluster size but also the chemical composition. In our previous work [5], the formation energy of SIA-clusters were obtained by MD and MS combined techniques, and was described using a polynomial function of cluster size as $\alpha n^1 + \beta n^{1/2}$, in which the SIA-clusters have the following three chemical composition ratios: (i) $n_1^{\text{Si}}/n_1^{\text{C}} = \infty$ (clusters consisted of only silicon interstitials), (ii) $n_1^{\text{Si}}/n_1^{\text{C}} = 0$ (clusters consisted of only carbon interstitials) and (iii) $n_1^{\text{Si}}/n_1^{\text{C}} = 1$ (clusters consisted of the same number of silicon and carbon interstitials: stoichiometric composition). Fig. 1 shows the constant numbers α for n^1 and β for $n^{1/2}$ in the three equations for (i), (ii) and (iii), as a function of $s=n_{\rm I}^{\rm C}/(n_{\rm I}^{\rm Si}+n_{\rm I}^{\rm C})$ that is the ratio by number of carbon interstitials to total interstitials in an SIA-cluster. Notice that s=0 for (i) $n_1^{\text{Si}}/n_1^{\text{C}}=\infty$ (only silicon interstitials), s=1for (ii) $n_1^{\text{Si}}/n_1^{\text{C}}=0$ (only carbon interstitials) and s=0.5 for (iii) $n_1^{\text{Si}}/n_1^{\text{C}}=1$ (stoichiometric composition). The broken lines are fitting curves written by quadratic function of s. Using the fitting curves for $\alpha(s)$ and $\beta(s)$, formation energy of SIA-clusters characterized by *n* and *s* can be described as $E_F(n,s)=\alpha(s)n^1+\beta(s)n^{1/2}$, in which $\alpha(s)=4.040s^2-3.540s+1.717$ and $\beta(s)=-7.576s^2+6.728s+0.908$, respectively. This indicates that formation energy of SIA-clusters with any size and chemical composition can be determined. From the equation $E_{\rm F}(n,s)$, the binding energy of a interstitial to an SIA-cluster is given by

$$E_{\rm B}^{\rm cluster-k} = \begin{cases} E_{\rm F} \left(n - 1, \frac{n_{\rm I^{\rm C}}}{n - 1} \right) + E_{\rm F}(1, 0) - E_{\rm F}(n, s) & \text{if } k = {\rm I}^{\rm Si} \\ E_{\rm F} \left(n - 1, \frac{n_{\rm I^{\rm C}}}{n - 1} \right) + E_{\rm F}(1, 1) - E_{\rm F}(n, s) & \text{if } k = {\rm I^{\rm C}} \end{cases},$$
(3)

where, $E_F(1,0)$ and $E_F(1,1)$ are the formation energies of isolated silicon- and carbon-interstitial, respectively, and the employed values ($E_F(1,0)=3.17\text{eV}$ and $E_F(1,1)=3.24$ eV) were already obtained in our previous work [4]. Fig. 2 shows the binding energy between an interstitial and an SIA-cluster with n=4, 6, 10 and 100, as a function of $s=n_1^C/(n_1^{Si}+n_1^C)$. With increasing cluster size, carbon interstitials are difficult to be removed from a silicon-interstitial rich cluster, while silicon interstitials are difficult to be removed from a carbon-interstitial rich cluster. And then, both carbon- and silicon-interstitials are relatively difficult to be removed from a cluster with stoichiometric composition; it indicates that such clusters are thermally stable.





Figure 1: Constant numbers α and β in the equation $\alpha n^1 + \beta n^{1/2}$, as a function of *s* (the ratio by number of carbon interstitials to total interstitials in an SIA-cluster). The broken lines are fitting curves.

Figure 2: Binding energy between a interstitial and an SIA-cluster with n=4, 6, 10 and 100, as a function of *s* (the ratio by number of carbon interstitials to total interstitials in an SIA-cluster).

Now, all the preparations have been completed for the KMC simulations. Events considered here are the absorption and emission of interstitials into and from an SIA-cluster with *n* and *s*, in which the occurrence probability of these events was assumed to be proportional to v_k^{influx} and v_k^{outlux} , respectively. A time step at each event required to know the time evolution of nucleation and growth of SIA-clusters was provided by $\Delta t = -\ln(RN) / \sum_{i=1}^{n} v_i$, where *RN* is random number from 0 to 1 [6]. As the first trial for qualitative interpretation of nucleation and growth of SIA-clusters in beta-SiC during irradiation, this KMC simulation was done at 973 K and 673 K, in which the total diffusion flux $(D_1^{\text{Si}}C_1^{\text{Si}}+D_1^{\text{C}}C_1^{\text{C}})$ of silicon- and carbon-interstitials is always fixed to be 1.0×10^{-19} by appropriate controlling of C_1^{Si} and C_1^{C} , and the ratio $(D_1^{\text{Si}}C_1^{\text{Si}}:D_1^{\text{C}}C_1^{\text{C}})$ by diffusion flux of silicon interstitials to carbon interstitials was changed to be 1:1, 1:10, 1:100 and 1:1000.

3. Results and Discussion

In case of 973 K, incubation period for the nucleation of SIA-clusters in beta-SiC strongly depends on the ratio $(D_1^{Si}C_1^{Si}:D_1^{C}C_1^{C})$ as shown in Fig. 3, and is the shortest at the ratio of 1:1. Moreover, the growth rate of SIA-clusters also much depends on the ratio, as represented in Fig. 4. However, independent of the ratio, the nucleation paths of each SIA-cluster are almost identical, in which $n_1^{Si}:n_1^{C}=1:1$, in short, an SIA-cluster prefers to grow while keeping its chemical composition stoichiometric. This is because such clusters are thermally stable.



Figure 3: Time evolution of size of SIA-clusters in beta-SiC, focused on the nucleation process, for the ratios $(D_1^{\text{Si}}C_1^{\text{Si}}:D_1^{\text{C}}C_1^{\text{C}}=1:1, 1:10, 1:100 \text{ and } 1:1000)$ at 973 K in the KMC simulation.



Fig. 4: Time dependence of size and growth paths of SIA-clusters, focused on the growth process, for the ratios $(D_1^{Si}C_1^{Si}:D_1^{C}C_1^{C}=1:1, 1:10, 1:100 \text{ and } 1:1000)$ at 973 K in the KMC simulation.

In case of 673 K, both incubation period and growth rate of SIA-clusters are independent of the ratio $(D_I^{Si}C_I^{Si}:D_I^{C}C_I^{C})$ by diffusion flux. In addition, the composition of SIA-clusters is determined by the ratio. This is because the emission (thermal dissociation) of interstitials from an SIA-cluster does not occur at 673 K that is a relatively low temperature for SiC materials.

4. Summary

In order to clarify the formation kinetics of SIA-clusters in beta-SiC during irradiation based on the energetics obtained by MD and MS combined technique, the nucleation and growth process of SIA-clusters was evaluated by KMC analysis. As to summary of the analysis, at relatively high temperatures the formation of SIA-clusters is dominated by thermal stability of the clusters, while the formation is dominated by influx of interstitials into the cluster at relatively low temperatures. It follows from these arguments that formation kinetics of SIA-clusters in beta-SiC during irradiation can be classified by temperature into the two types.

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Magnetic Effect on Vacancy Diffusion in BCC Iron

Terry Haohua Wen¹, Pui-Wai Ma^{1,2}, <u>C. H. Woo¹</u>

¹Department of Electronic and Information Engineering, The Hong Kong Polytechnic University, Hong Kong, SAR, China; ²EURATOM/CCFE Fusion Association, Culham Centre for Fusion Energy, Abingdon, Oxfordshire OX14 3DB, United Kingdom.; Email: chung.woo@polyu.edu.hk.

ABSTRACT

The change of the self-diffusion activation energy of BCC iron across the paramagnetic (PM) and ferromagnetic (FM) states phase boundary is well known. While this has long been believed to be due to the magnetic effect on the activation process, the detail mechanistic understanding has yet to be developed. In the present paper, we focus on that part of the activation process played by vacancy migration. We perform computer simulations of the migration of a single vacancy in BCC iron across the phase boundary using spin-lattice dynamics (SLD) [1], allowing active participations of the interacting dynamics of the lattice and spins. We also carry out corresponding lattice-only and spin-only calculations and monitor the effects of change of the magnetic environment. The magnetic effect on each individual component is analyzed. The results are discussed and a conclusion drawn.

1. Introduction

Since Borg [2] discovery in 1960 that the activation energy G_A^V of the self-diffusion in BCC iron abruptly changes from 2.9eV (FM) to 2.5eV (PM) near T_c , numerous models have been suggested to explain this magnetic anomaly phenomenon. A comprehensive review has been given by Lubbehusen [3]. To interpret the effect of FM/PM phase transition, most authors followed the empirical approach of Ruch [4] by simply adding an extra term proportional to the square of spontaneous magnetization to the migration enthalpy. However, this approach is based on mean-field theory, and ignores the effects of the short range magnetic order (SRMO), which is predicted to be important by the Ising model calculation [5]. Further attempts to improve our understanding using more sophisticated theoretic techniques such as ab initio calculations or molecular dynamics (MD) simulations are frustrated by insurmountable difficulties. Thus, while one may comfortably consider the FM state at 0K, vacancy migration under the change of the magnetic environment across the FM/PM phase boundary at T_c is hardly within the reach of *ab initio* calculations. MD simulations are not equipped to take into account the interacting lattice and spin dynamics across the FM/PM phase boundary. MD simulations have been done either with frozen spins, or with frozen lattice like in spin dynamics (SD) simulations. The recent development of SLD simulation by Ma, Woo and Dudarev allows MD simulations to be performed simultaneously together with the spin dynamics, and is ideal for the present investigation. This will be considered in the following.

2. Theory

We start from a Hamiltonian that contains both lattice and spin degrees of freedom [1]:

$$H_{SLD} = \sum_{i} \boldsymbol{p}_{i}^{2} / 2m_{i} + H_{DD}(\boldsymbol{R}) + \frac{1}{2} \sum_{i \neq j} J_{ij}(\boldsymbol{R}) (1 - \boldsymbol{e}_{i} \cdot \boldsymbol{e}_{j})$$
(1)

where p_i is the linear momentum for atom *i*, $R = \{R_i\}$ is the coordinates of all atoms,

 $J_{ij}(\mathbf{R})$ is the exchange interaction function (coordinate-dependent) between atoms *i* and *j*, and \mathbf{e}_i is the unit vector of atomic spin. Since the corresponding frequency of spin motion is approximately 20 times faster than the lattice [1], by taking adiabatic approximation, and write $J_{ij}(\mathbf{R}) = J_{ij}(\mathbf{R}_0) + \delta J_{ij}(\mathbf{R})$, where \mathbf{R}_0 is the equilibrium position. The Hamiltonian (Eqn. (1)) can then be rewritten as a sum of three components:

$$H_{SLD} = H_L + H_S + H_{S-L}$$

$$H_L = \sum_i \mathbf{p}_i^2 / 2m + H_{DD}(\mathbf{R})$$

$$H_S = \frac{1}{2} \sum_{i \neq j} J_{ij}(\mathbf{R}_0) (1 - \mathbf{e}_i \cdot \mathbf{e}_j)$$

$$H_{S-L} = \frac{1}{2} \sum_{i \neq j} \delta J_{ij}(\mathbf{R}) (1 - \mathbf{e}_i \cdot \mathbf{e}_j)$$
(2)

With atomic spins frozen in the collinear ground state, H_L accounts only for the contribution from lattice vibrations. With the lattice frozen, on the other hand, H_s describes the contribution due to the magnetic excitations only. H_{S-L} represents the effect of spin lattice coupling. The corresponding free energy is $G_x = -k_BT \ln Z_x$, where x represents *SLD*, or L, or S, or S-L in Eqn. (2). Vacancy migration due to H_{SLD} and H_L can be carried out using SLD simulations straightforwardly. Working out contributions from H_s , which involves vacancy migration with a lattice frozen, is not straightforward. We adopt the approach of Frenkel and Ladd [6] for this purpose in the following. In Frenkel Ladd method [6], the difference in the free energies between two states, H_1 and H_0 , can be expressed in terms of the thermodynamic integration over and ensemble average with respect to the coupled Hamiltonian $H_{\lambda} = \lambda H_1 + (1-\lambda)H_0$, where $0 \le \lambda \le 1$. Thus,

$$G_{1} - G_{2} = \int_{0}^{1} (\partial G / \partial \lambda) d\lambda = -\frac{k_{B}T}{Z_{\lambda}} \int_{0}^{1} (\partial Z_{\lambda} / \partial \lambda) d\lambda$$

=
$$\int_{0}^{1} \langle \partial H_{\lambda} / \partial \lambda \rangle_{\lambda} d\lambda = \int_{0}^{1} \langle H_{1} - H_{0} \rangle_{\lambda} d\lambda$$
 (3)

Following Eqn. (3), the vacancy migration free energy $G_M^V(S) \equiv G_S^{sp} - G_S^{eq}$ due to H_s , can be estimated, if we set $H_1 = H_S^{sp} = H_S(\mathbf{R}^{sp})$ and $H_0 = H_S^{eq} = H_S(\mathbf{R}^{eq})$, where \mathbf{R}^{sp} and \mathbf{R}^{eq} are the lattice configurations at saddle point and equilibrium states, respectively, obtained from conjugated gradient calculations [7].

3. Simulation

A single vacancy is created by removing an atom from the centre of the simulation box containing $20 \times 20 \times 20$ BCC unit cells. The isothermal-isochoric (NVT) ensemble is used. Two cases are considered. The average atomic volume is either (1) equal to the relaxed one at the corresponding temperature under zero-pressure (i.e., with thermal expansion), or (2) equal to the one at zero temperature (i.e., without thermal expansion). It should be noted that, the vacancy migration is treated as random walk in this interpretation, where the vacancy jumps are considered uncorrelated. The total simulation time is 10ns, with a time step of 1fs. The vacancy diffusion coefficient is obtained from the mean successful jump frequency taken in the simulation, using $D = a^2 v/8$, where a is the lattice constant [8].



Figure 1. The Arrhenius plots of SLD simulations. The lines are linear fittings.

We show the Arrhenius plots for both H_L and H_{SLD} in Figure 1. It can be seen that the diffusivity for H_{SLD} is non-Arrhenius, showing a significant difference at T_c , decreasing from 0.80eV in FM and 0.65eV in PM as temperature increase. This result is in good agreement with experimental data [9]. The slope of the Arrhenius plot for H_L gives a value of 0.70eV for H_M^V , which remains changed across the phase boundary despite the change in magnetic environment. This strongly indicates that the non-Arrhenius behaviour of the vacancy migration enthalpy calculated from H_{SLD} is related to the magnetic excitations and not to the phonons. The contribution to G_M^V from H_S is calculated and presented in Figure 2(a) as a function of temperature, both with or without the thermal expansion. The corresponding contribution to H_M^V is obtained by numerically differentiating G_M^V , according to $H_M^V = \partial (G_M^V / T) / \partial (1/T)$, plotted in Figure 2(b).



Figure 2. The vacancy migration (A) free energy G_M^V and (B) enthalpy H_M^V due to spin-spin interactions by freezing lattice with and without thermal expansion, respectively, by using the Frenkel-Ladd method.

In Figure 2(b), H_M^V has a peak at T_C , where the magnetic correlation changes. The non-zero value of H_M^V in the PM state indicates the SRMO is still affecting the vacancy migration even though the average magnetic moment has disappeared. This is in good agreement with Ising model result [5] and theoretical analysis [¹⁰]. In Figure 3, we combine the contributions of lattice dynamics with frozen spin (LD) and spin dynamics with frozen lattice (SD) together $(H_{L+S} = H_L + H_S \text{ in Eqn. (2)})$ in the Arrhenius plot of the effective diffusion coefficient $(\ln (D/D_0) \sim T^{-1})$, and compare to the results obtained from SLD simulations. From Figure 3 the change of H_M^V at FM/PM phase boundary can be estimated at 0.77eV in FM and 0.68 in PM, showing a difference of 0.09eV, which is about 60% of the 0.15eV obtained from SLD

simulation. It can be seen that H_s increases the migration barrier by 0.07eV in FM and reduces the barrier by 0.02eV in PM. In this regard, the balance of 40%, a further increase of 0.03eV in FM, and a further decrease of 0.02eV in PM can be attributed to the effects of the interaction between the lattice vibrations and spin waves.



Figure 3. The Arrhenius plot of the effective diffusion coefficent. "*LD*": lattice dynamics with spin frozen. "*SD*": spin dynamics with lattice frozen.

4. Conclusion

Spin-lattice dynamics simulation results support that the change in magnetic environment during FM/PM phase transition does result in the abrupt change in the vacancy migration energy. It is clear that magnetic excitation plays an important role on vacancy diffusion, because neglecting the spin waves results in the vacancy energy that remain constant during the magnetic phase transition. The magnetic effect acts to increase the vacancy migration energy in the FM state by 0.1eV and reduce that in the PM state by 0.05eV. About 60% of the magnetic effect comes from the change of the spin waves (magnons) during vacancy migration, and about 40% is due to the change of the spin-lattice coupling. Moreover, the short range magnetic order continues to contribute to the vacancy migration barrier even in the PM state, after the average magnetization vanishes.

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Multi-scale Modeling of Nuclear Fuel

Dieter Wolf^{1*} and Anter El-Azab²

¹Idaho National Laboratory, Idaho Falls, ID, USA

²Department of Scientific Computing, Florida State University, Tallahassee, FL, USA

* Corresponding author. Center for Advanced Modeling and Simulation, Idaho National Laboratory, P.O. Box 1625, Idaho Falls; e-mail address: <u>dieter.wolf@inl.gov</u>

The critical ingredient needed for the development of a predictive, materialsphysics based nuclear fuel modeling capability lies in a better understanding of microstructural processes. However, in spite of the well-known existence of microstructural phenomena in nuclear materials, such as void swelling, fission-gas release and crack development, a comprehensive understanding of how microstructural processes control the thermo-mechanical behavior of nuclear materials remains to be developed. This presentation will provide an overview and vision on how a predictive nuclear fuel modeling capability can be developed by an atomistically-informed mesoscale approach that, in turn, is linked to the continuum level. Three critical elements of this hierarchical modeling approach are:

- capturing irradiation effects within a mesoscale modeling framework that is informed by the lower length scales;
- development of a comprehensive theoretical and computational mesoscale approach that considers all the various, simultaneously occurring and highly coupled microstructural processes within a unified framework; and
- linking these microstructural simulations with continuum fuels-performance simulations via a scale-bridging approach.

The critical need for experiments will also be emphasized, not only for providing key input parameters to the simulations but also for the validation of key predictions.

Grain boundary configurations and thermodynamic equilibrium state of low Cr Fe-Cr alloys studied *ab initio* and by Metropolis Monte Carlo simulations

E.E. Zhurkin^{1,4}, J. Kuriplach², T. Ossowski³, A. Kiejna³, M. Hou⁴

 ¹St.Petersburg State Polytechnic University, Faculty of Physics and Mechanics, K-89, Department of Experimental Nuclear Physics, 29 Polytekhnicheskaya str., 195251, St.Petersburg, Russian Federation, E-mail: ezhurkin@phmf.spbstu.ru
 ²Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, CZ-18000 Prague 8, Czech Republic
 ³Institute of Experimental Physics, University of Wrocław, pl. M. Borna 9, PL-50-204 Wrocław, Poland
 ⁴Physique des Solides Irradiés et des Nanostructures CP234, Faculté des Sciences,

Université Libre de Bruxelles, Bd du Triomphe, B-1050 Bruxelles, Belgium.

ABSTRACT

Several stable configurations of the Σ =5 (210) grain boundary in bcc iron are identified with a dedicated algorithm coupled with Molecular Dynamics (MD) simulations at zero temperature. These are then characterized in detail by means of ab initio relaxations using a spin polarized basis set. Grain boundary energies are estimated and compared with classical predictions using the state-of-the-art potentials. Canonical Metropolis Monte Carlo (MMC) simulations are then used to predict Cr segregation effects in FeCr alloys at several defects, with a special emphasis on the Σ =5 (210) grain boundary. An attempt is made to correlate segregation and ordering with local stress properties.

1. Introduction

High-chromium ferritic/martensitic steels with BCC structure are most promising candidate structural materials for advanced fission and fusion reactors [1]. The reason therefore is their high resistance to irradiation induced effects [2-5]. FeCr alloys represent a class of complex materials and many of their properties are not quite well understood. There is thus a need to develop reliable models. The range of compositions of technological interest is around 9 to 12% chromium. In this range, a change of sign of mixing enthalpy versus composition takes place [6], attributed to frustration effects between ferromagnetic iron and antiferromagnetic Cr. This fact appears to have consequences on several properties of FeCr allovs such as segregation, mechanical properties or swelling under radiation [7,8]. For all these properties, microstructural defects are of importance. The present work comes in line with an effort to understand which microstructure gives rise to which local modification of the alloy properties. To this purpose, surface and grain boundary segregation were studied ab initio [9-11] as well as using equilibrium Monte Carlo techniques [12]. This way, Cr depletion at surfaces was predicted ab initio and confirmed by Metropolis Monte Carlo (MMC) in the whole range of technologically relevant compositions (5 to 20 % Cr) and in a temperature range from 0 K to 900 K, where an order-disorder transition may occur. On the contrary, Cr enrichment was found at edge dislocations and dislocation loops while no significant effect was found at screw dislocations, suggesting the role of local stress in this effect. Acknowledging the importance of local atomic configurations in equilibrium segregation, the present contribution focuses on Grain Boundaries (GB). The symmetrical $\Sigma = 5$ (210) [001] boundary is selected as a case study.

2. Methods

The Metropolis Monte-Carlo (MMC) sampling was used within the isobaric-isothermal (*NPT*) statistical ensemble where N is the number of particles, P the pressure and T the temperature, which are kept constant. The method was described in details in [12, 13]. Molecular dynamics (MD) simulations at constant volume were used as well to relax the initial configurations of grain boundaries. First, MD was used to relax model boxes at given temperature, then the MMC sampling was employed. In both MMC and MD computations, the so-called two-band interatomic potential [14, 15] is used. The $\Sigma=5$ (210) [001] tilt grain boundary (GB) was



Figure 1. An example of 'asconstructed' supercell with 320 atoms containing the Σ =5 (210) GB viewed along the tilt axis [001]. The position of GBs in the cell is indicated by horizontal arrows. The projections of CSL unit cell below and above the central GB are also shown (marked by 'CSL'). first constructed geometrically using the coincidence site lattice (CSL) principle [16]. The smallest rectangular CSL unit cell contains 10 atoms so that the smallest rectangular supercell with two grains and two Σ =5 (210) GBs has 20 atoms. The supercell edges – called in the following *a*, *b*, and *c* – are oriented, respectively, along [001], [1-20], and [210] crystallographic directions of the original bcc lattice of iron. The supercell is periodic in all three directions. For practical simulations the CSL unit cell was multiplied in all three directions and 1800 or 8400 atom supercells were used in most simulations. Fig. 1 shows an example of 'as-constructed' supercell containing 320 atoms.

We first look for possible structural modifications of the studied GB. For this purpose, a number of pure iron boxes with the two grains being mutually shifted along a, b, and c directions were prepared. First, we 'scanned' systematically the space of possible shifts considering 30 boxes. Second, we generated 50 boxes with random shifts (confined to the space of possible shifts). All these boxes were then quenched using MD at zero temperature to find equilibrium atomic positions. This procedure resulted in five different GB structures (modifications) which will be discussed. Both potentials [14] and [15] yield the same GB configurations. The stability of these configurations was also checked using an ab initio method. In particular, we employed Vienna ab initio simulation package (VASP) [17] within the projected augmented wave scheme [18]. Starting supercells

containing 40 atoms for VASP calculations were prepared from much larger MD simulation boxes described above by removing appropriately bulk-like regions between adjacent GBs (i.e. along the direction c) as well as by cutting periodically repeated CSL unit cells in a and b directions. The total energy of such supercells was then minimized by relaxing the atomic positions using the generalized gradient approximation [19] and accounting for spin-polarization in the electron exchange-correlation interaction.

3. Results

The grain boundary energies (γ) of five GB configurations labeled as cI, cII, cIII, cIV, and cV generated using this procedure are given in Table 1. Before calculating GB energies within

Table 1. Calculated grain boundary energies (in units of J/m^2) for cI to cV configurations for MD and VASP cases.

	cI	cII	cIII	cIV	cV
γ MD	1.42	1.26	1.54	1.12	1.64
γ VASP	2.01	1.75	2.02	1.66	—

the MD scheme, the cell dimension along the *c* direction was optimized in order to get the lowest energy. We can see that the MD values obtained using the Olsson et al. potential [14] are ordered in the following way: $\gamma(cIV) < \gamma(cII) < \gamma(cI) < \gamma(cIII) <$ $\gamma(cV)$, which suggests that the cIV configuration is the most stable one, at least at zero temperature. Moreover, the

GB energies determined with the VASP technique exhibit the same order except for the cV configurations that is not stable and transformed to cI during the relaxation performed. This indicates that, indeed, cIV is the most stable configuration and also the Olsson et al. and Bonny potentials [14, 15] provide a very good description of interatomic interactions at the studied GB. The GB energies obtained with the VASP technique are somewhat higher than MD ones, which is due to a different computational procedure. These effects will be discussed elsewhere [20] together with a detailed comparison of MD and VASP configurations.



Figure 2. Average concentration of Cr atoms in each layer (layer 40 is the $\Sigma=5$ {210} GB plane in the middle of the model box) in an Fe₉₀Cr₁₀ at different temperatures.

MMC sampling in combination with MD was used to study Cr segregation effect at GB (cIV configuration). Both mentioned potentials give the similar results; hence we present here the simulation data with Bonny's potential [15]. As an example, Fig. 2 provides the distribution of Cr concentration, x_{cr} , measured along the [210] direction. It is computed at thermodynamic equilibrium by MMC in the case of 10% Cr overall concentration at 100K, 300K and 900K. Cr is clearly seen to segregate at the GB at all temperatures (the same effect is observed in case of 5% Cr). Moreover, as already found in the case of free surfaces [12], composition oscillations are observed most pronouncedly at the lowest temperature with both overall compositions and that are longer range at the lowest x_{cr}. The

short range oscillations are the signature of Cr ordering which correlated with local pressure.



This one is mapped in Fig.3 showing the Cr atoms only, in the [001] projection in the case of $x_{cr} = 0.1$ at 300K. A view is also displayed at certain angle providing some 3D perspective. In the vicinity of the GB, Cr is under tensile

Figure.3. Local pressure map of Σ =5(210): 2D (a) and 3D (b) view in Fe₉₀Cr₁₀ at T=300K

stress and under compressive stress in bulk areas, except in precipitates where it is close to zero. The same structure of the pressure map is obtained at the GB in the absence of segregation (not shown in Fig. 3) where the $\Sigma = 5$ ordering induces a periodic array of under pressurized [001] rows separated by rows at close to zero pressure. Since, in our simulations, the pressure map was pre-existing to segregation, it is concluded to be at the origin of segregated Cr ordering. We could see that vacancies tend to segregate at the studied GB and may also influence Cr segregation. Therefore, as a next step we will investigate in more detail the behavior of vacancies and their clusters at the $\Sigma=5$ (210) GB.

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