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Journal of Nuclear Materials 367–370 (2007) 276–281

journal of nuclear materials

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# Molecular dynamics simulations of point defect interactions in Fe–Cr alloys

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## Abstract

Predicting the performance of Fe–Cr ferritic martensitic steels in fusion energy environments requires an understanding of point defect properties, including the influence of solutes, impurities and other defects on their migration behavior. This paper presents molecular dynamics simulations of the effect of Cr on the diffusion of single, di- and tri-interstitials in Fe–10%Cr alloys. Two Finnis–Sinclair-type potentials were used to model the Fe–Cr alloys, which alternately describe Cr as under- or over-sized in body-centered cubic Fe. In general, the diffusivity of the single interstitials and di- and tri-interstitial clusters was reduced in the Fe–10%Cr alloys, irrespective of interatomic potential, although the underlying mechanism was different. When Cr is undersized, interstitial diffusion is retarded through a trapping mechanism associated with bound Cr-interstitial (mixed dumbbell) complexes, whereas oversized Cr atoms retard interstitial diffusion by enhancing the rotation frequency away from one-dimensionally mobile ⟨1 1 1⟩ interstitial dumbbell configurations.

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## 1. Introduction

Fe–Cr alloys are candidate first wall and breeder blanket materials in future fusion reactors. Radiation damage from high-energy fusion neutrons creates a large excess of point defect and point defect cluster concentrations in displacement cascades, which, in conjunction with transmutant helium and hydrogen, are ultimately responsible for microstructure evolution that can produce deleterious changes to performance-limiting properties. Thus, predicting material performance under irradiation requires an understanding of point defect properties, including their migration and clustering behavior and any modification in this behavior as a result of interaction with solutes, impurities and other defects. In this study, molecular dynamics (MD) simulations employing two different Fe–Cr potentials are used to study the effect of 10% Cr on self-interstitial and small interstitial cluster migration.

Studies of the effect of Cr on displacement cascade evolution in Fe–Cr alloys have observed no effect on defect production [1,2]. Although no differences were observed in the absolute number of defects formed, Cr may have an influence on the migration properties of point defect clusters that can influence eventual defect fate and produce a larger effect on microstructural properties. Recent work by Terentyev [3] has demonstrated decreased interstitial diffusivity in Fe–12%Cr based on EAM

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doi:10.1016/j.jnucmat.2007.03.138

Fe–Cr potentials, although the mechanistic cause was not determined.

In this work, we investigate the effect of Cr on point defect properties and microstructural evolution in irradiated Fe–Cr alloys. The initial focus is on single interstitial and small interstitial cluster transport using MD simulations. Two different Fe–Cr interaction potentials [2] were used, which show differing size effects of Cr in the body-centered cubic (BCC) Fe matrix. The next section describes the simulation method and interaction potentials, and Section 3 presents a discussion of the results of MD simulations on the effect of Cr on single, di-, and tri-interstitial diffusion in Fe–10%Cr alloys. Simulations were also performed for Fe–1%Cr alloys, although the effect of Cr at 1% concentration was minimal, and the results are not presented here.

## 2. Research approach

### 2.1. Simulation technique

Molecular dynamics simulations were performed using the MDCASK code [4] to investigate the effect of 10% Cr on the diffusivity of single, di-, and tri-interstitials. The simulation cell consisted of $50 \times 50 \times 50$ bcc unit cells ($250\,000 + N$ atoms) with periodic boundary conditions and either a single, di- or tri-interstitial ($N = 1$, 2, or 3). Pure Fe and randomly distributed ferritic alloys with 10% Cr were simulated. Single interstitials were initially oriented in the $\langle 111 \rangle$ direction; clusters of di- or tri-interstitials were inserted as parallel $\langle 111 \rangle$ dumbbells. The MD simulations were performed at temperatures from 400 to 1000 K, with additional low temperature simulations for single interstitials at 50 to 200 K. Two different cross-potentials for the Fe–Cr interaction were used, which show contrasting size effects of Cr in the Fe matrix. Simulations were conducted for 500 ps with the defect diffusivity sampled every 10 to 200 ps.

### 2.2. Interatomic potentials

Finnis–Sinclair-type potentials were used to describe the interatomic interactions. The Ackland potential [5] was used to describe pure Fe, and the Finnis–Sinclair potential [6] was used for Cr atom interactions. The Ackland potential correctly predicts the stability and formation energy of self-interstitial atoms in bcc Fe, although it may predict too small of an energy difference between the $\langle 110 \rangle$ and $\langle 111 \rangle$ split-dumbbell configurations according to recent ab-initio results [7]. The diffusion and the migration mechanism of single and small self-interstitial atom clusters is well understood with the Ackland potential [8], and the goal of this project is to understand the effect of Cr on the diffusion mechanism(s) as compared to pure Fe.

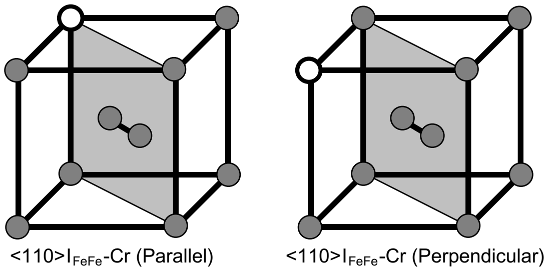
Two different Fe–Cr interaction potentials were obtained from Shim and co-workers [2], which were fit to the heat of mixing and lattice constant data using the method outlined by Konishi et al. [9]. The two cross-potentials show contrasting size effects of Cr in the Fe matrix, although both potentials predict a symmetric, positive mixing enthalpy with increasing Cr content without the negative deviation from ideality at low Cr concentrations predicted by recent ab-initio calculations [10]. The focus of this work is thus the effect of under- and over-sized Cr solute atoms on single, di- and tri-interstitial diffusivity.

The Fe–Cr I potential predicts Cr to be oversized relative to Fe, creating a compressive field around the Cr that is repulsive to neighboring Fe in the matrix. Table 1 presents the binding energies of various dumbbell-Cr configurations. Mixed dumbbells do not form readily in either $\langle 110 \rangle$ or $\langle 111 \rangle$ configuration with binding energies of −0.40 eV and −0.26 eV, respectively. A $\langle 110 \rangle$-oriented Fe dumbbell with a Cr atom oriented perpendicular

Table 1
Binding energies of various dumbbell and Cr configurations

| | Fe–Cr I | Fe–Cr II |
|---|---|---|
| $\langle 110 \rangle$ $I_{FeCr}$ (Mixed) | −0.40 | 0.10 |
| $\langle 111 \rangle$ $I_{FeCr}$ (Mixed) | −0.25 | 0.20 |
| $\langle 110 \rangle$ $I_{FeFe}$–Cr (Parallel) | −0.16 | 0.06 |
| $\langle 110 \rangle$ $I_{FeFe}$–Cr (Perpendicular) | 0.02 | −0.007 |

All energies are given in eV. The schematic illustration below demonstrates the meaning of Cr orientations parallel and perpendicular to the axis of the $\langle 110 \rangle$-oriented self-interstitial atom in Fe (Fe atoms represented by filled circles, while Cr is an open circle).



to the axis of the dumbbell has a very small binding energy of +0.02 eV, while Cr oriented parallel to the dumbbell has a repulsive interaction energy of −0.16 eV. The Fe–Cr II potential predicts undersized Cr in bcc Fe, creating a tensile field around the Cr that is attractive to neighboring Fe in the matrix. Mixed dumbbells are stable in both ⟨1 1 0⟩ and ⟨1 1 1⟩ configurations with binding energies of +0.10 eV and +0.20 eV, respectively. The orientation of a Cr atom parallel to the axis of a ⟨1 1 0⟩ dumbbell has a binding energy of +0.06 eV, while a Cr atom oriented perpendicular to the dumbbell produces a slightly negative interaction energy of −0.01 eV. Recent ab-initio calculations by Domain [11] predict a binding energy of 0.0 and +0.3 eV for ⟨1 1 0⟩ and ⟨1 1 1⟩ mixed dumbbells, respectively, which is in closer agreement with undersized Cr in Fe–Cr II.

## 3. Results and discussion

Fig. 1 shows the percentage of Cr observed in mixed dumbbells in single interstitial and in di- and tri-interstitial clusters for Fe–10%Cr alloys as a function of temperature and interatomic potential. The oversized/repulsive Cr using the Fe–Cr I potential prevents the formation of mixed interstitial dumbbells at all temperatures, and the percentage of Cr in single interstitials is significantly lower (10×) than the matrix Cr concentration. Di- and tri-interstitial clusters do have increased Cr content relative to single interstitials using the Fe–Cr I potential, but do not reach the matrix concentration. Thus, interstitial diffusion in Fe–Cr alloys as predicted by the Fe–Cr I potential, consists of interstitial defects, which are essentially pure Fe dumbbells, diffusing through a matrix containing oversized/repulsive Cr. With the Fe–Cr II potential, single, di-, and tri-interstitials are/significantly enriched in Cr (2×–8× matrix Cr concentration), as expected from the positive binding energy of mixed dumbbells in both ⟨1 1 0⟩ and ⟨1 1 1⟩ orientations. Since mixed dumbbells and even a few Cr–Cr dumbbells readily form, the interstitial defect diffusion behavior predicted by the Fe–Cr II potential is more complex.

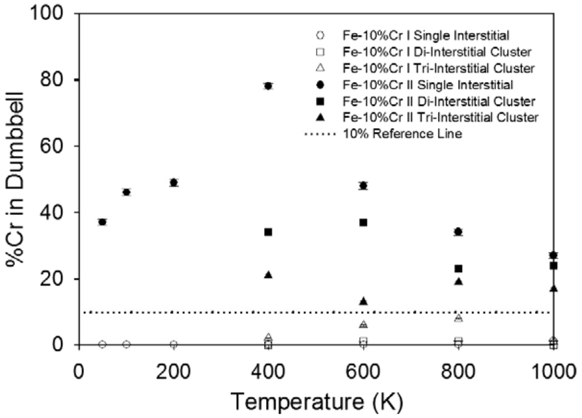


Fig. 1. Percentage of Cr in single interstitial and in di-, tri-interstitial clusters for Fe–10%Cr alloy.

Fig. 2(a) plots the defect diffusivity for the single interstitial in pure Fe and an Fe–10%Cr alloy, using both Fe–Cr potentials. The mean square displacement and diffusivity was calculated by sampling the center of mass of the defect for time intervals between 10 and 200 ps. The simulation data was fit to a standard Arrhenius form, and the resulting diffusion pre-factors and migration (activation) energies are presented in Table 2. For single intersti-

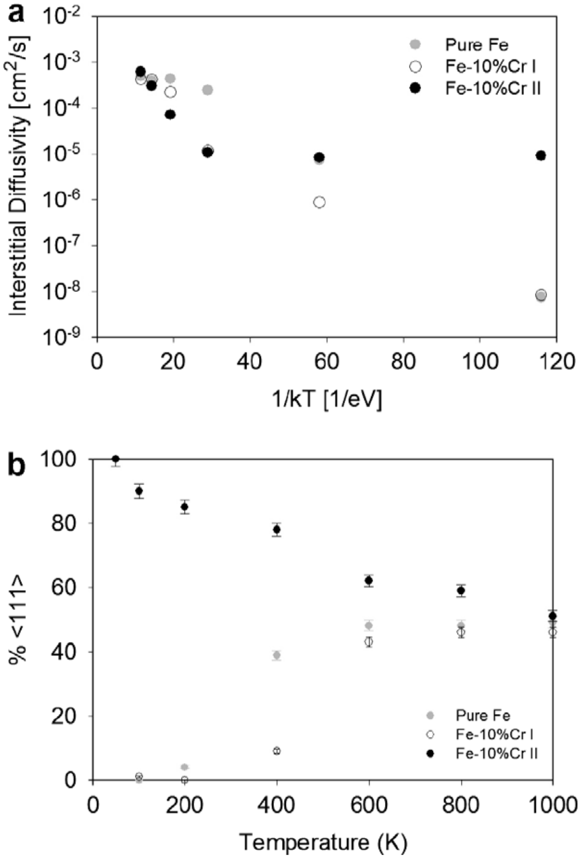


Fig. 2. (a) Diffusivity of single interstitials for pure Fe and Fe–10%Cr alloys. (b) Percentage of time single interstitials are oriented in the ⟨1 1 1⟩ direction for Fe–10%Cr alloy.

Table 2
Calculated pre-factors and migration energies for single, di- and tri- interstitials in pure Fe and 1% and 10% Fe–Cr alloys

| | Potential | Single interstitial | | Di-interstitial | | Tri-interstitial | |
|---|---|---|---|---|---|---|---|
| | | $D_0$ [cm$^2$/s] | $E_m$ [eV] | $D_0$ [cm$^2$/s] | $E_m$ [eV] | $D_0$ [cm$^2$/s] | $E_m$ [eV] |
| Pure Fe | Ackland Fe | $7.7\times10^{-4}$ | 0.04 | $8.0\times10^{-4}$ | 0.03 | $1.3\times10^{-3}$ | 0.06 |
| Fe–1%Cr | Fe–Cr I | $1.1\times10^{-3}$ | 0.06 | $9.6\times10^{-4}$ | 0.06 | $2.5\times10^{-4}$ | 0.05 |
| | Fe–Cr II | $2.4\times10^{-3}$ | 0.11 | $5.7\times10^{-3}$ | 0.16 | $5.6\times10^{-3}$ | 0.03 |
| Fe–10%Cr | Fe–Cr I | $9.4\times10^{-3}$ | 0.22 | $6.5\times10^{-3}$ | 0.11 | $6.3\times10^{-4}$ | 0.12 |
| | Fe–Cr II | $9.6\times10^{-3}$ | 0.24 | $6.0\times10^{-4}$ | 0.10 | $7.3\times10^{-4}$ | 0.10 |

tials (Fig. 2(a)), the effect of 10% Cr on interstitial diffusivity was minimal at the highest simulated temperatures (800 and 1000 K), while the Cr atoms decreased interstitial diffusivity at intermediate temperatures (400 and 600 K), irrespective of the Fe–Cr potential. At lower temperatures (100 and 200 K), significantly more variation in diffusion behavior occurred, although the interstitial was predicted to be most mobile using the Fe–Cr II potential. Little to no interstitial mobility was observed in pure Fe and the Fe–10%Cr alloy using the Fe–Cr I potential at 100 and 200 K, corresponding to the single interstitial oriented predominantly as a ⟨1 1 0⟩ dumbbell. Thus, the Arrhenius fit to the single interstitial diffusion data was limited to the temperature range from 400 to 1000 K. Over this range, both potentials indicate that Cr suppresses interstitial diffusivity except at the highest temperatures, and increases the temperature sensitivity. The fits indicate an increase in the diffusional pre-factor (~12×) and an increase in the activation energy to $0.23 \pm 0.01$ eV for interstitial migration in Fe–10%Cr compared to an essentially athermal value of 0.04 eV in pure Fe. Despite the similar effect of Cr atoms on the single interstitial diffusivity, the underlying mechanism is different with the two different potentials.

The Ackland Fe potential predicts that single self-interstitials migrate by rotating between ⟨1 1 0⟩ and ⟨1 1 1⟩ orientations and undergo subsequent translation along the ⟨1 1 1⟩ directions through a crowdion saddle point [12]. Thus, ⟨1 1 0⟩ orientations represent intermediate stationary orientations during rotations between ⟨1 1 1⟩ translation directions. Hence, the migration mechanism of dumbbells is highly dependent on defect orientation. Fig. 2(b) plots the percentage of time that single interstitials are oriented in the ⟨1 1 1⟩ direction for the 10% Cr concentration, as a function of temperature and the Fe–Cr potential. In general, the interstitial spends more time in ⟨1 1 1⟩ orientations with the Fe–Cr II (undersized Cr atoms) and less with the Fe–Cr I potential (oversized Cr atoms). At temperatures above 600 K, the effect of Cr, regardless of size, on the fraction of ⟨1 1 1⟩ dumbbells is negligible and both the Fe–Cr I and Fe–Cr II simulations results converge towards those of pure Fe, as does the diffusivity (Fig. 2(a)). At intermediate temperatures, the diffusivity is suppressed, regardless of the size of Cr, as shown in Fig. 2(a). The higher concentration of oversized/repulsive Cr atoms using Fe–Cr I decreases the fraction of time spent in ⟨1 1 1⟩ dumbbells compared with pure Fe and produces an increase in the migration energy for Fe–Cr I, presumably associated with more frequent rotations. Dumbbells that encounter a Cr along its axis of migration preferentially rotate to align the Cr atom perpendicular to the dumbbell, leading to decreased Cr content in the interstitial with the Fe–Cr I potential, as shown in Fig. 1. The enhanced rotation into different ⟨1 1 1⟩ orientation retards 1-D migration along any single ⟨1 1 1⟩ direction. The undersized/attractive Cr atoms using the Fe–Cr II potential stabilize the ⟨1 1 1⟩ dumbbell orientation relative to the ⟨1 1 0⟩ especially at intermediate to low temperatures (below 600 K) due to preferential alignment of dumbbells parallel to Cr, including mixed dumbbell formation. The stabilization of the ⟨1 1 1⟩ dumbbell leads to a reduction in rotation into ⟨1 1 0⟩ orientations and is responsible for trapping the interstitial, presumably responsible for the higher migration energy. Visualization of the MD simulations at low temperatures shows that the ⟨1 1 1⟩ dumbbell with the Fe–Cr II potential continues to make lattice jumps due to attraction of neighboring undersized Cr atoms.

Small interstitial clusters consist of parallel ⟨1 1 1⟩-oriented dumbbells, and their migration consists of individual 1-D crowdion jumps along ⟨1 1 1⟩ directions, with rotations into different ⟨1 1 1⟩ orientations providing a 3-D diffusion character [12–14]. Fig. 3 shows the effect of 10% Cr on the diffusivity of di- (Fig. 3(a)) and tri-interstitials (Fig. 3(b)).

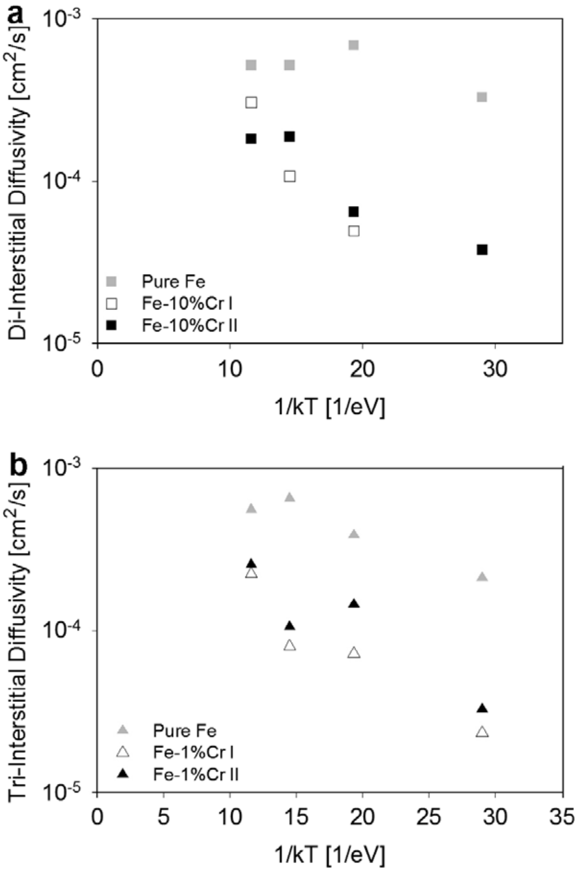


Fig. 3. Diffusivity of (a) di- and (b) tri-interstitials clusters for pure Fe and Fe–10%Cr alloys.

For both di- and tri-interstitials, diffusivity is decreased by Cr, with a somewhat larger decrease predicted by the Fe–Cr I (oversized Cr atom) potential. As with the single interstitial, the temperature dependence of the di- and tri-interstitial diffusivity (as shown in Table 2) is increased by Cr (larger activation energy). However, the effect on the pre-factor is not as pronounced as for the single interstitial.

Fig. 4 shows the center of mass trajectory of di-interstitials during 500 ps at 600 K for pure Fe and Fe–10%Cr alloys using the Fe–Cr I and Fe–Cr II potentials. The di-interstitial in pure Fe has a distinctly 1-D migration behavior with only a single observed rotation between ⟨1 1 1⟩ orientations. The addition of oversized/repulsive Cr atoms using the Fe–Cr I potential prevents prolonged one-dimensional translation segments of interstitial migration along the ⟨1 1 1⟩ directions and assists cluster rotation to align the Cr perpendicularly with the dumbbells. The net effect is to reduce the interstitial cluster diffusivity, although the 3-D character

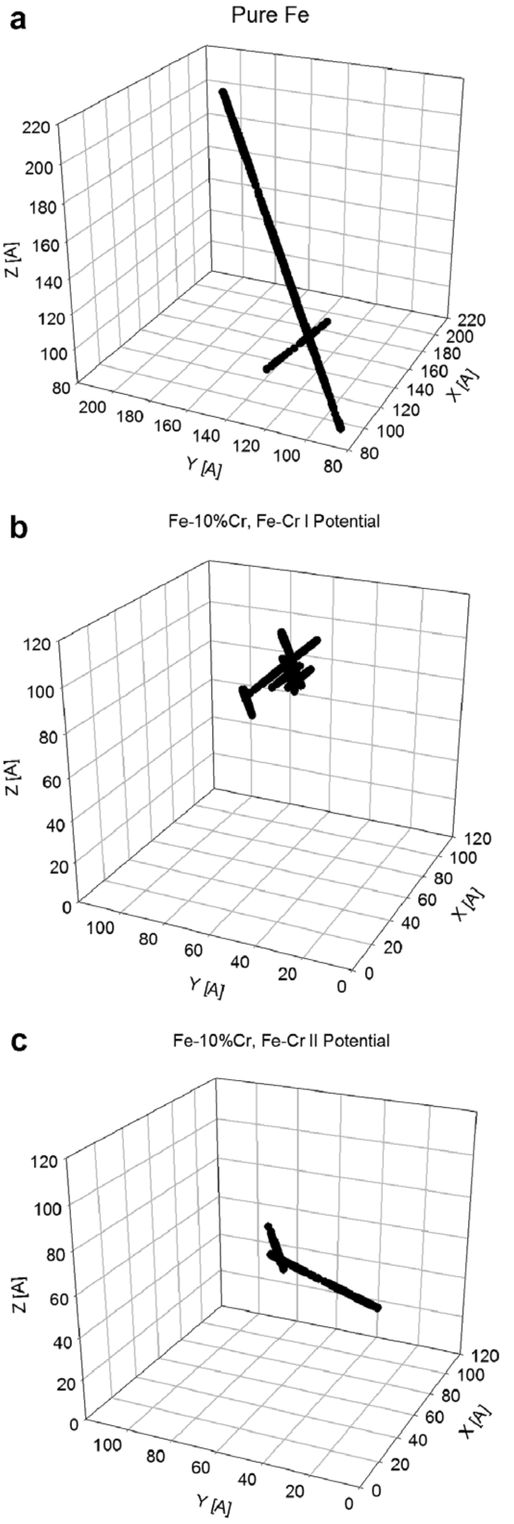


Fig. 4. Center of mass trajectory of di-interstitials at 600 K for pure Fe (a) and Fe–10%Cr alloys using Fe–Cr I (b) and Fe–Cr II (c).

may increase. In contrast, the di-interstitial in a matrix of undersized/attractive Cr using the Fe–Cr II potential shows similar, primarily 1-D translation character as the di-interstitial in pure Fe. However, the undersized/attractive Cr tends to suppress the very long 1-D translations by attracting (trapping) the cluster to jump back and forth between neighboring Cr atoms, thereby limiting the range of 1-D translations and the overall interstitial cluster diffusivity.

## 4. Conclusions

MD simulations, using two different Fe–Cr potentials, have been performed to determine the effect of Cr on the diffusion of single interstitials and small interstitial clusters in Fe–Cr alloys. One potential (Fe–Cr I) predicts that Cr is an over-sized solute atom, while the other (Fe–Cr II) predicts that Cr is undersized. The MD results reveal that Cr decreases the diffusivity of both single interstitials and di- and tri-interstitial clusters, except at the highest temperatures, irrespective of the atomic size of Cr (interatomic potential). Arrhenius fits to the defect diffusivity reveal that Cr increases the activation energy for interstitial/interstitial cluster migration, while also increasing the diffusion pre-factor. While the effect of Cr on interstitial/interstitial cluster diffusivity was similar for the two Fe–Cr potentials, the underlying mechanisms were different. A significant enrichment (2×–8× matrix concentration) of Cr is observed in the interstitial defects using the Fe–Cr II potential (under-sized Cr atom), indicating the formation of mixed dumbbells. The formation of mixed dumbbells, which are energetically preferred, suggests a trapping mechanism that retards interstitial diffusion by decreasing the length of $\langle 111 \rangle$ translational segments for the under-sized Cr solute atom. The Fe–Cr I potential predicts a repulsive interaction between an oversized Cr atom and interstitial defects, which is observed to increase the rotation frequency of single interstitials between $\langle 111 \rangle$ and $\langle 110 \rangle$ orientations and of interstitial clusters between different $\langle 111 \rangle$ orientations. This increased rotation also reduces the diffusional length of one-dimensional $\langle 111 \rangle$ jump segments and correspondingly decreases the interstitial/interstitial cluster diffusivity. Future modeling efforts will quantify the amount of Cr diffusion by interstitials, and develop Monte Carlo models of isochronal annealing recovery to compare with experimental observations.

## Acknowledgement

This work has been supported by the Office of Fusion Energy Sciences, U.S. Department of Energy, under Grant DE-FG02-04ER54750.

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