Nuclear Instruments and Methods in Physics Research B 277 (2012) 136–139

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Irradiation cascades in cementite: 0.1–10 keV Fe recoils

K.O.E. Henriksson *, K. Nordlund

Department of Physics, University of Helsinki, P.O. Box 43, FI-00014 University of Helsinki, Finland

ARTICLE INFO

Article history:
Received 24 October 2011
Available online 3 January 2012

Keywords:
Molecular dynamics simulations
Cementite
Steel
Point defects
Bulk modulus
Elasticity

ABSTRACT

Cementite Fe_3C is a metastable carbide present in many steels. Depending on the treatment, the cementite can give rise to varying microstructures such as bainite and pearlite, to name a few. Cementite – being harder than pure iron – makes the resulting steel harder and tougher, enabling it to be used as a construction steel. This type of steels can be used to build fission reactors and may be used for future fusion reactors, where they will be subjected to neutron irradiation from the core. In this work we use molecular dynamics simulations to study the response of pure cementite when Fe atoms are knocked out of their lattice sites by neutrons. The Fe recoils have an energy varying between 100 and 10 keV. It is also shown that defects in cementite are roughly one order of magnitude more aboundant than those in pure iron, even when using the same irradiation conditions and ion energies of at least 5 and 10 keV.

1. Introduction

Steels used in fission (and future fusion) reactor constructions suffer damage caused by neutrons created in and emitted from the reactor core. Beside transmutation, the neutrons are also responsible for the creation of point defects. Any clusters formed by these will have an impact on the mechanical behavior of the material. They may cause swelling and embrittlement, which reduce the lifetime of the constructions.

Cementite is present in virtually all carbon-bearing steels, as an integral part of the microstructure [1]. Its hardness – measured by the bulk modulus – make it suitable for hindering motion of dislocations, rendering the steel capable of handling larger stresses without fracturing. The hardness is likely to change with time when the steel is subjected to e.g. neutron irradiation in nuclear reactors, since the irradiation creates point defects which have the potential ability to severely disrupt the cementite lattice.

It is the aim of the present study to investigate the defects formed in cementite subjected to (neutron) irradiation. Pure cementite instead of Fe_3C inside a Fe matrix was chosen since the system to be studied then can be made small enough and interface effects can be ignored. A comparison with pure Fe targets is also made. The effect of the neutron irradiation is modelled by giving an iron atom a specific kinetic energy. This primary knock-on atom (PKA) then initiates a cascade in the bulk target. The specifics of the simulations are discussed in Section 2, and the results are reviewed and discussed in Section 3.

2. Methods

2.1. Molecular dynamics simulations

Bulk cementite was used in molecular dynamics simulations (MDS) to study the effect of single Fe recoils. The positions of the atoms in the cementite cell were obtained from the density functional theory calculations in Ref. [2] and further relaxed using the Fe–C interatomic potential in Ref. [3]. The recoiling Fe atom – initiated at the center of the simulation cell – was given a kinetic energy between 100 and 10 keV. In most cases a set of 50 simulations were carried out. The cell sizes are displayed in Table 1. All cells were equilibrated at 300 K for 30 ps using Berendsen temperature and pressure control before any recoil events.

The length of the borders of the equilibrated Cartesian cell was $L_x = N_a a$, $L_y = N_b b$, $L_z = N_c c$, with N_a, N_b, N_c dependent on the PKA energy (see Table 1) the lattice parameters are a = 4.963 Å, b = 6.811 Å, c = 4.486 Å. The zero temperature lattice parameters are a = 5.086 Å, b = 6.521 Å, c = 4.498 Å, (see Ref. [3]), giving a volume expansion at 300 K of ca 2%.

The temperature was controlled linearly towards 300 K at all borders – all having periodic boundary conditions – in a region having a thickness of 6 Å. If an atom entered any of these temperature-control border regions with an energy of at least 10 eV, then the simulation was restarted with the recoil further away from the border, keeping other settings such as recoil direction. No pressure control was used.

At the start of each recoil simulation a Fe atom was given a specific momentum in a random direction. Electronic stopping parametrized by Ziegler et al. [4] was applied to all atoms having an energy of 5 eV or more. The simulations lasted for 30 ps, except

* Corresponding author.
E-mail address: krister.henriksson@helsinki.fi (K.O.E. Henriksson).

0168-583X/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2011.12.055

Table 1
Simulation cell details. N_a, N_b, N_c is the number of cells in directions x, y, z. N is the total number of atoms in the cell. The energy E is given in units of keV.

E	N_a	N_b	N_c	N
0.1	8	8	12	12,288
0.3	10	10	15	24,000
1.0	14	14	21	65,856
3.0	18	18	27	139,968
5.0	26	26	39	421,824
10.0	26	26	39	421,824

Table 2
xth Nearest Neighbor distances xNN at 300 K, as well as the potential cutoff distance r_c, all in units of Ångström, for all different pairs of elements present in cementite. Two significant digits are used.

Pair	1NN	2NN	3NN	4NN	r_c
Fe–Fe	2.2	2.3	2.4	2.5	3.35
Fe–C	1.8	1.9	2.0	2.1	2.70
C–C	2.6	2.8	2.9	3.0	2.00

the 3 keV and 5–10 keV recoils, which lasted for 40 and 50 ps, respectively.

2.2. Defect analysis

A Wigner–Seitz (WS) cell (see e.g. Ref. [5]) analysis was used to find vacancies and interstitials. A WS cell originally occupied by a C atom is considered a C type vacancy if the cell has become empty. It is considered an antisite if the C atom has left and been replaced by a Fe atom. It is considered a Fe interstitial if the C atom is still present and has been accompanied by a Fe atom. The labeling is analogous for a WS cell initially occupied by a Fe atom.

The degree of clustering of the defects was also analyzed. Two vacancies (or interstitials) were considered to form a cluster if they were separated by a distance $r \leqslant R$. A suitable value for R is discussed below. The fraction of vacancies (or interstitials) in clusters of size N or larger – denoted "clustering fraction" – is calculated as

$$f_c(N) = \left(\sum_{i=N}^{M} i \times N_c(i)\right) \Big/ \left(\sum_{i=1}^{M} i \times N_c(i)\right) = 1 - N_{\text{isol}}/N_{\text{def, tot}}, \qquad (1)$$

where M is the number of defects in the largest cluster $N_c(i)$ is the number of clusters containing i defects, $N_{\text{def,tot}}$ is the total number of defects, and N_{isol} is the number of isolated defects, having $N_c \equiv 1$. If nothing else is specified, a value of $N = 2$ was always used. This corresponds to the smallest possible cluster.

To find a suitable value for R it is helpful to look at the typical atomic separations existing in cementite at the relevant temperature of 300 K. These distances are listed in Table 2.

The largest first nearest neighbor (1NN) distance in Table 2 was chosen as the cutoff distance for cluster formation. To account for fluctuations the numerical value 2.70 Å was used.

3. Results and discussion

3.1. Defects

Number of Frenkel pairs and antisites, as well as the number of antisites, are shown in Fig. 1.

The number of Frenkel pairs N_{FP} as a function of the energy E (in keV) can be fitted to a function of the form

$$N_{\text{FP}} = aE^b. \qquad (2)$$

The data in the present study give $a = 13.6 \pm 0.3\ \text{eV}^{-1}$ and $b = 1.17 \pm 0.02$. In comparison, the data from Ref. [6] give

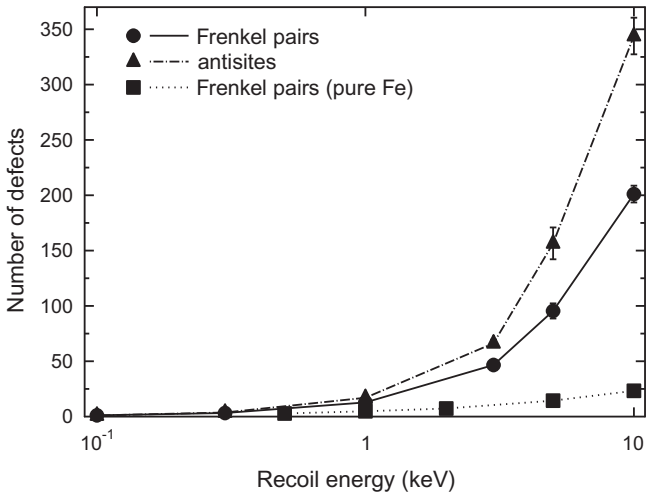

Fig. 1. Number of Frenkel pairs and antisites, as a function of the recoil energy. Results for pure Fe from Ref. [6] are also shown. The error bars indicate the standard error of the mean, as in all other figures in this study.

$a = 4.7 \pm 0.2\ \text{eV}^{-1}$ and $b = 0.70 \pm 0.03$. Since b is slightly larger or smaller than 1 this means that the damage production rises nonlinearly with energy, indicating that the recoils induce non-linear cascades, or "collision spikes".

It should be noted that the number of Frenkel pairs in cementite is roughly nine times larger than the corresponding number for pure Fe, at least in the case of 10 keV recoils. In a compararive molecular dynamics study of metals and semiconductors by Nordlund et al. [7] it was found that the Frenkel pairs in semiconductors are 2–50 times more numerous than in face-centered cubic metals subjected to 10 keV recoils. The present result for cementite (Fe_3C) is in-line with those findings. The reason for this large discrepancy is the covalent nature of the interatomic bonds in semiconductors – these bonds are not as easily reformed as those in metals.

3.2. Defect clusters

The fraction of defects inside clusters containing $\geqslant N$ defects is shown in Fig. 2. The number of clusters containing more than four defects is shown in Fig. 3. As can be seen from Fig. 2(b) the clustering tendency is significantly higher for interstitials than vacancies. Interstitials also have more of the larger clusters (containing more than four defects). The fraction of defects inside clusters show tendencies of saturation when approaching higher energies. This is independent of the defect type, interstitial or vacancy. Qualitatively similar results were obtained when using a larger value for R, namely $R = 3.35$ Å.

3.3. Defects by species

The number of interstitials and vacancies of Fe and C types are displayed in Fig. 4. The number of Fe interstitials and Fe vacancies follow each other quite closely, without being identical. The same holds true for C type defects.

These numbers indicate that Fe defects are roughly three times as numerous as C defects. This can be understood from the cementite composition Fe_3C, which says that there are three times as many Fe atoms as C atoms available. However, the formation of interstitials depends on the threshold displacement energy E_d, i.e. the minimum energy needed to displace an atom from its lattice site. These values are unlikely to be identical for Fe and C in cementite, so a 3:1 ratio of Fe:C interstitials cannot be explained by the composition only.

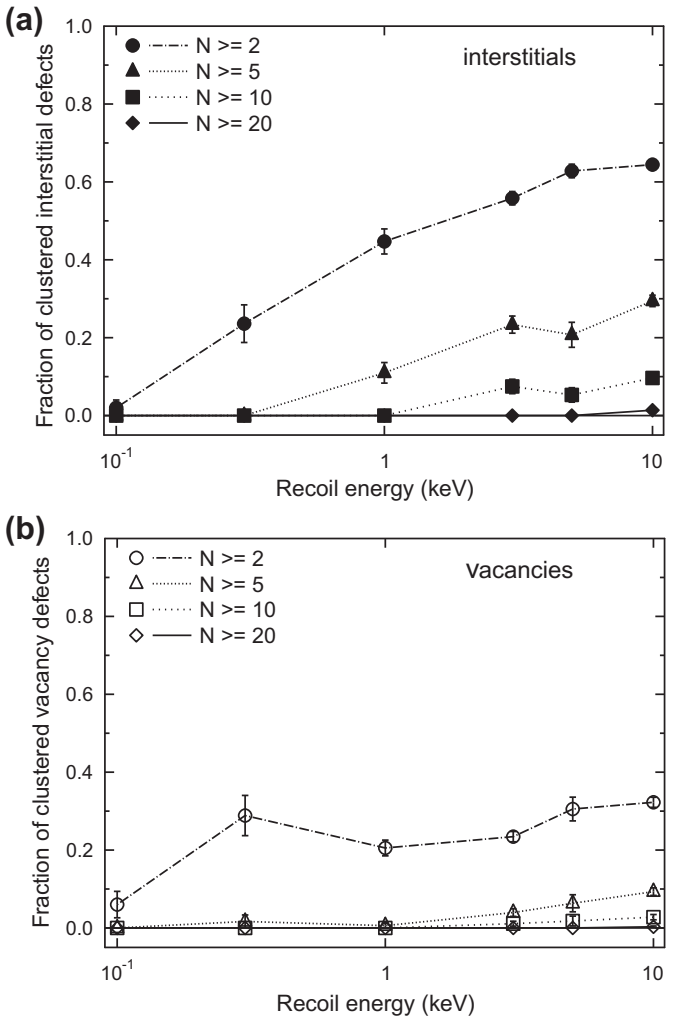

Fig. 2. Fractions of defects inside clusters for (a) interstitials and (b) vacancies, as a function of the recoil energy.

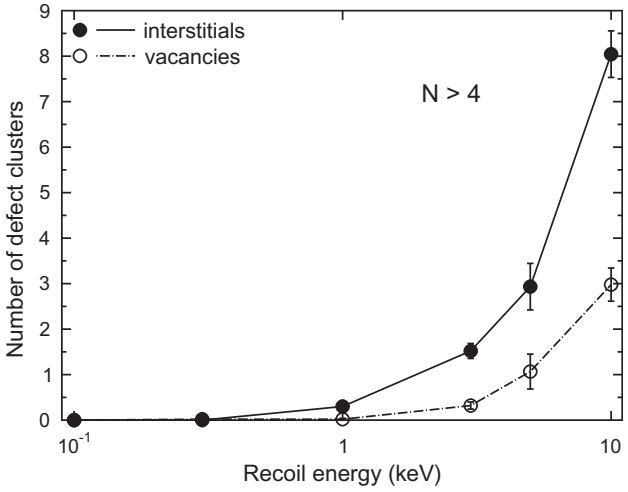

Fig. 3. Number of clusters containing more than four defects, as a function of the recoil energy.

3.4. Coordination

The atoms were also analyzed for their coordination. All Fe atoms were extracted and analyzed. The average number of neighbors

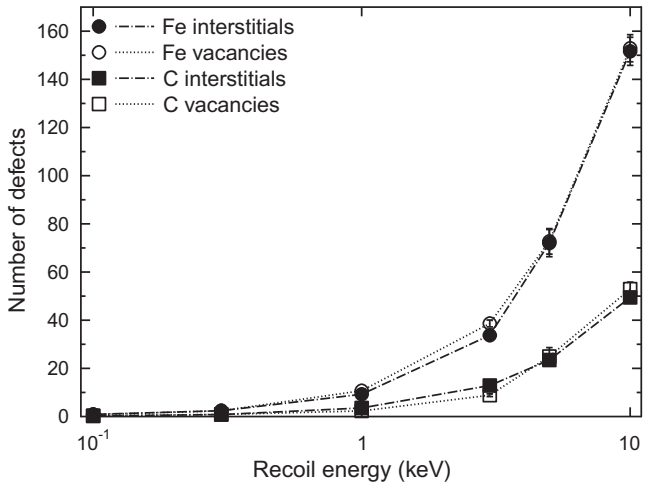

Fig. 4. Number of interstitials and vacancies of Fe and C type, as a function of the recoil energy.

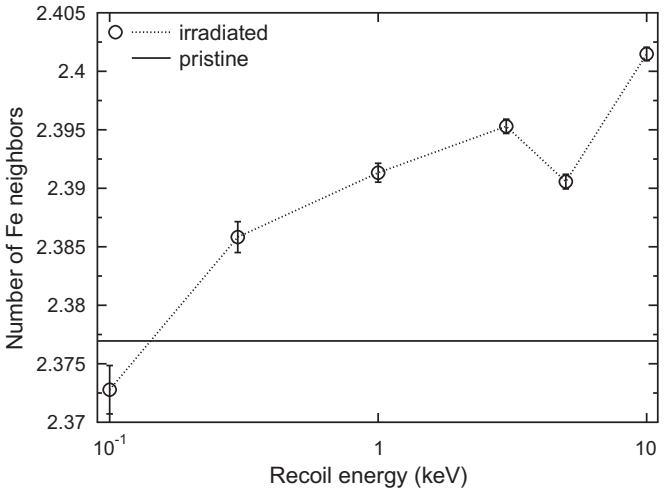

Fig. 5. Average number of Fe neighbors at a distance of 2.70 Å or less.

at a distance of 2.70 Å or less was counted. This distance is the average value of first (1NN) and second nearest neighbors (2NN) in a Fe body-centered cubic (BCC) lattice with lattice parameter a = 2.89 Å. The results are displayed in Fig. 5. For pristine cementite at 300 K the average number of Fe neighbors for Fe atoms is 2.37695.

The results indicate the Fe atoms are collecting more and more Fe neighbors as the recoil energy increases. However, the rise in the neighbor number from lowest energy to highest is only about 1%. A similar investigation of C atoms and their C neighbors, using a distance of 1.98 Å shows that the number of neighbors is 0 for all energies.

4. Conclusion

The molecular dynamics simulations of single recoil events in pure cementite indicates that the number of defects grows super-linearly with the recoil energy. The fraction of interstitials inside clusters is consistently higher than for vacancies, but the exact value depend on the details of the clustering analysis, especially the cutoff radius. The fraction show tendencies of saturation at higher recoil energies. A notable fact is that the number of

Frenkel pairs created in cementite is roughly one order of magnitude larger than the number created in pure iron, at least when using irradiation energies of 5 and 10 keV. This can be attributed to the covalent nature of the interatomic bonds in cementite. Also, the number of Fe type defects is roughly three times the number of C type defects, which could be a result of the Fe_3C composition of cementite, although other factors such as type dependent threshold displacement energies should conceivably play a role. Lastly, the average number of Fe neighbors of Fe atoms increases by about 1% from the lowest recoil energy to the highest, indicating a clustering tendency of Fe atoms. Future investigations will focus on the effect of cumulative recoils inside cementite, especially the development of the elastic response of the cementite bulk.

References

[1] W.D. Callister, Materials Science and Engineering, fifth ed., John Wiley & Sons, New York, USA, 2000.
[2] K.O.E. Henriksson, N. Sandberg, J. Wallenius, Carbides in stainless steels: results from ab initio investigations, Appl. Phys. Lett. 93 (2008) 191912.
[3] K.O.E. Henriksson, K. Nordlund, Simulations of cementite: an analytical potential for the Fe–C system, Phys. Rev. B 79 (2009) 144107.
[4] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Matter, Pergamon, New York, USA, 1985.
[5] N.W. Ashcroft, N.D. Mermin, Solid State Physics, Saunders College, Philadelphia, PA, USA, 1976.
[6] C. Bjorkas, K. Nordlund, L. Malerba, D. Terentyev, P. Olsson, Simulation of displacement cascades in $Fe_{90}Cr_{10}$ using a two band model potential, J. Nucl. Mater. 372 (2–3) (2008) 312–317.
[7] K. Nordlund, M. Ghaly, R.S. Averback, M. Caturla, T. Diaz de la Rubia, J. Tarus, Defect production in collision cascades in elemental semiconductors and fcc metals, Phys. Rev. B 57 (13) (1998) 7556–7570.