

Major elemental asymmetry and recombination effects in irradiated WC

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We study the initial state of irradiation damage in WC, an alloy with a large mass difference between the constituents, using molecular dynamics computer simulations. We find that a vast majority of the resulting isolated defects are carbon. Moreover, an in-cascade defect recombination effect similar to that in metals is observed. Both effects are shown to be related to the high formation energy of W defects.

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The nature of radiation damage induced by atomic recoils in materials is of major importance in a wide range of application areas, ranging from fission and fusion reactors to semiconductor chip manufacturing and manufacturing of thin film coatings. Hence much experimental and simulation effort has been devoted to studying the basic defect production mechanisms in all classes of materials.

Because the initial state of cascade damage is produced on atomic length and picosecond time scales, hardly accessible to experiments, molecular dynamics computer simulations have had a major role in elucidating the damage production mechanisms.¹⁻⁵ Such studies have, however, been mostly carried out on elemental materials. While also some studies of multielement materials such as metal alloys^{6,7} and compound semiconductors^{8,9} have been carried out, these have typically been on materials where the constituent species have a small mass difference or are chemically similar.

We now study radiation damage in hexagonal WC, where the constituent elements W and C have crystallographically equivalent positions, but have more than an order of magnitude difference in atom size and mass, and are dramatically unlike chemically. Thus it can be considered a model material of a hard binary alloy with very unlike constituents. WC is also of practical importance because of its good mechanical and thermal properties^{10,11} and its presence in the wall material of the ITER fusion reactor.¹² Using an interatomic potential capable of describing both the compound and the pure elements well,¹³ we show that the fraction of damage in isolated point defects differs by as much as two orders of magnitude between C and W defects. Moreover, we show that WC exhibits major in-cascade defect recombination, a behavior normally associated with metals. We finally point out that the dramatic elemental difference should have profound consequences on long-term damage development.

To examine collision cascades induced by energetic ions or neutrons in WC, we use a recently developed potential for WC which is well suited for cascade simulations.¹³ This potential gives a realistic description of phenomena such as bond breaking, melting, and point defects. The simulations were performed with the molecular dynamics (MD) code PARCAS.¹⁴ Periodic boundary conditions¹⁵ were used at the simulation cell borders in all three dimensions. The simulation cells were initially thermally equilibrated at 300 K for 10 ps. Berendsen pressure control¹⁶ was used to keep the cell at zero pressure during this initial simulation.

The thermally equilibrated simulation cell was then used for the recoil calculations. In these simulations, Berendsen

temperature control¹⁶ with a time constant of 100 fs was used to scale the temperature at the cell boundary, the thickness of which was taken to be one lattice constant. It has earlier been shown that the temperature scaling at the borders has no statistical effect on the results.¹⁷ A recoil energy ranging from 400 eV to 5 keV was given in a random direction to a W or a C atom near the center of the cell, which during the high-energy simulations consisted of up to 153 600 atoms. At least 14 recoil events for each energy were simulated. One event lasted 20 ps. The Zigler-Biersack-Littmark 1996 (ZBL96) electronic stopping¹⁸ was used. The movement of the atoms was monitored in such a way that, if the energy of any atom in the border region exceeded 10 eV, the simulation was stopped, and then restarted with an initial recoil position placed farther away from the border.

Spheres with a radius of 0.55 Å (one-fourth of the nearest-neighbor distance) and centered on each initial atom site were used to find interstitial atoms and vacancies. An empty sphere corresponded to a vacancy and all atoms outside the spheres were defined as interstitials. All defects were distinguished by atom type (vacancies were categorized by which sublattice they were on). A cluster analysis was also performed, in which a cutoff radius for cluster connectivity of 3.3 Å was used, which includes the nearest-neighbor sites of the opposite atom type and the second-nearest-neighbor sites of the same atom type.

Figure 1 shows the number of Frenkel pairs (FPs) as a function of time in 2 and 5 keV W-recoil cascades. A significant recombination of defects can be seen as the final number of FPs is only about one-tenth of the maximum value in both cases. The data are averages of 20 and 14 events for the 2 and 5 keV simulations, respectively.

The results of the analysis performed on the final stage of the cascades are found in Table I. Data on the amount of interstitial atoms and vacancies of either type are given for single and clustered defects. As expected, W recoils produce a larger number of defects than C recoils due to the large difference in mass. More surprising is the fact that a major domination of C vacancies and interstitial atoms can be seen in each case. This is illustrated in Fig. 2, where the numbers of W and C total and isolated defects after W-recoil cascades are shown. At 5 keV the fraction of isolated W defects is two orders of magnitude lower than the number of C defects.

Next we discuss the possible reasons for these major elemental asymmetries. It is natural to ask whether the dramatic difference between W and C defect production can be understood simply by differences in the high-energy ballistic

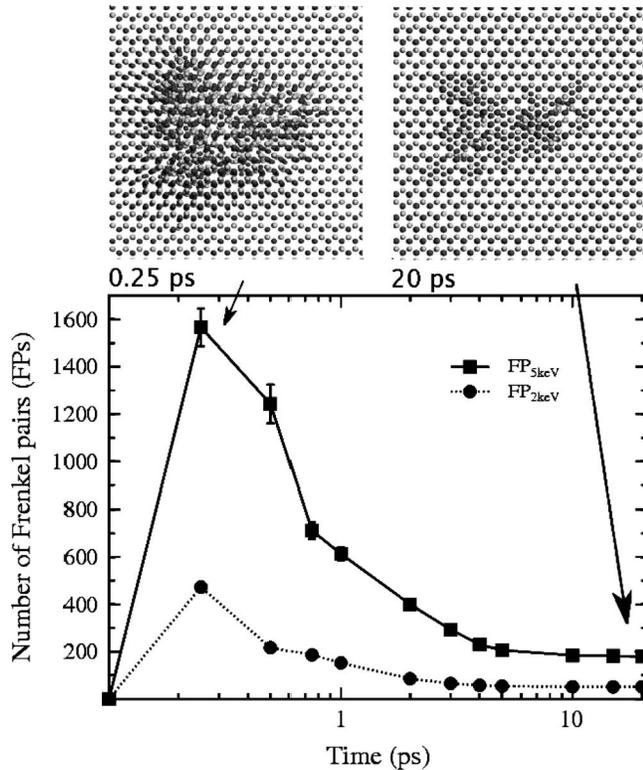


FIG. 1. Defect production in 2 and 5 keV W-recoil cascades in WC. The graph illustrates the number of Frenkel pairs as a function of time and the upper part of the figure shows snapshots, taken at 0.25 (left) and 20 (right), of a 5 keV cascade. The darker spheres represent carbon atoms.

collision behavior associated with the large mass and atom size difference. To determine this, we simulated 5 keV W cascades in WC using the binary collision approximation¹⁹ code SRIM-2003,²⁰ at the same density as that in the MD simulations. We obtained the vacancy coordinates from the simulation, and analyzed the vacancy types from 1000 runs in a similar manner as in the MD simulation cluster analysis. We found that while the SRIM code does predict that only about 10% of the vacancies are isolated, in rough agreement with the MD results, it predicts that about three times more W

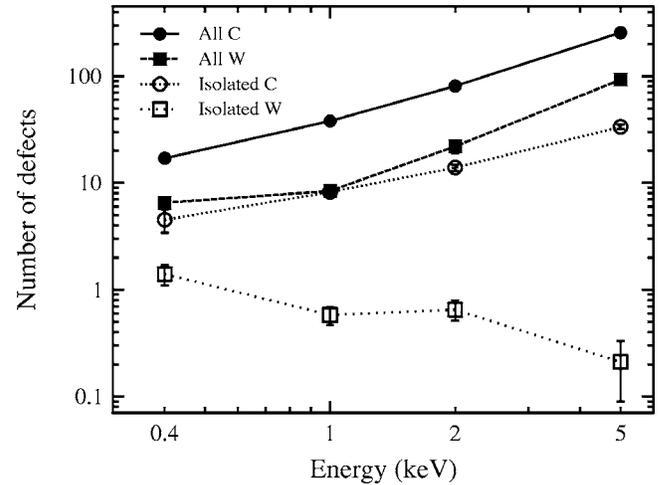


FIG. 2. Total and isolated defects after W-recoil cascades.

than C isolated vacancies are produced, in sharp contrast with the opposite MD result of roughly 10–100 times more isolated C vacancies. Hence we conclude that most of the interesting effects observed in the MD simulations cannot be understood by differences in ballistic behavior only.

To understand whether the difference in defect production could be explained by low-energy ballistic effects, i.e., the threshold displacement energy (which has recently been shown²¹ to be important in GaN), we calculated the average displacement energy $E_{d,ave}^{av}$.²² We used the $r=0.55$ Å sphere defect criterion to detect defects, and simulated W and C recoils separately. We obtained $E_{d,ave}^{av}=24\pm 3$ eV for W and 20 ± 2 eV for C recoils. Since these values are almost equal, the thresholds cannot explain the behavior.

Since these “traditional” effects associated with the ballistic phase of the cascade cannot explain the observed differences, we now consider the development after the ballistic phase is over, i.e., after about 0.25 ps when the massive recombination starts to occur (cf. Fig. 1). We compare the defect numbers at 0.25 and 20 ps for 2 keV W cascades in Table I. The results show that, at an early stage of the cascades, the damage consists of an equal amount of both elements, while at 20 ps most damage has recombined. Such a

TABLE I. The final stage damage distribution. Information on the amount and type of single as well as clustered interstitials (I) and vacancies (V) is given after W- and C-recoil cascades. Results of the analysis performed at 0.25 ps on 2 keV W cascades are also shown.

E (keV)	Recoil	Isolated defects				Defects in clusters			
		V_W	V_C	I_W	I_C	V_W	V_C	I_W	I_C
0.4	W	0.9 ± 0.2	2.0 ± 1.0	0.5 ± 0.2	2.5 ± 0.2	2.4 ± 0.4	6.5 ± 0.6	2.7 ± 0.4	6.0 ± 0.6
	C	0.09 ± 0.04	2.5 ± 0.3	0 ± 0	3.0 ± 0.2	0.17 ± 0.06	3.6 ± 0.4	0.05 ± 0.03	3.3 ± 0.4
1	W	0.50 ± 0.09	3.6 ± 0.3	0.08 ± 0.05	4.6 ± 0.4	3.7 ± 0.6	15.3 ± 1.0	4.1 ± 0.5	14.3 ± 1.1
	C	0.08 ± 0.05	5.6 ± 0.4	0.08 ± 0.05	6.5 ± 0.4	0.60 ± 0.15	8.5 ± 0.7	0.48 ± 0.14	7.7 ± 0.7
2	W	0.55 ± 0.12	6.4 ± 0.5	0.10 ± 0.07	7.5 ± 0.8	10 ± 2	34 ± 3	11 ± 2	33 ± 3
	C	0.31 ± 0.12	10.8 ± 0.9	0.13 ± 0.09	11.3 ± 0.7	1.8 ± 0.5	15 ± 2	1.8 ± 0.6	14 ± 2
5	W	0.14 ± 0.09	15.1 ± 1.1	0.07 ± 0.07	18.4 ± 1.0	47 ± 6	113 ± 7	46 ± 6	110 ± 8
2 keV, 0.25 ps	W	1.6 ± 0.3	0.4 ± 0.2	1.8 ± 0.3	1.1 ± 0.3	238 ± 9	233 ± 8	237 ± 9	233 ± 8

recombination is previously well known from metals, and understood to occur when close by interstitials and vacancies created in the cascade recombine with each other before the molten heat spike zone resolidifies.^{4,23} In the particular case of WC, we note that the formation energies of W defects are very high: about 12 eV for the interstitial and 3 eV for the vacancy, while the ones for C defects are much lower, 0.5 and 2.7 eV for the vacancy and interstitial, respectively.¹³ The formation energies were calculated as described in Ref. 24. Thus recombination of W defects with each other is extremely favorable energetically³², leading to the observed massive recombination. Moreover, when the potential energy related to the high formation energies is released, heat is produced, which prolongs the lifetime of the heat spike and thus enables even more recombination.

The number of isolated C defects is seen to actually increase with time, an effect that can also be ascribed to the difference in formation energy between the two elements. A high formation energy for W defects results in recombination of those defects, whereas a lower energy of C defects makes the C defects relatively stable. During the recrystallization of the heat spike, C defects are therefore left behind, leading to an increase in their number. This explains the large asymmetry between isolated W and C defects.

We finally compare the current results to those of cascades in other materials and discuss the implications for long-term damage development. As mentioned above, a similar major in-cascade recombination effect as seen here, is well known in metals both from experiments and MD simulations.⁴ Although there are previous studies of cascades of materials with a large mass difference, mainly from ionic materials such as MgO and GaN, none of them to our knowledge have reported similar major asymmetries as those observed here. Several studies have examined damage in ionic materials with mass differences of the order of 4–8,^{25–27} but in most of these the interaction models have fixed charges and hence cannot describe the pure elements well, making conclusions on atom-type differences in the damage production and especially clustering uncertain. Irradiation effects in GaN have been studied using a model capable of describing

the pure elements as well, but no dramatic differences were observed.²¹ In GaN the sum of Ga and N defect formation energies is about the same,²⁴ so the absence of asymmetries in GaN is well in line with our explanation of the effect in WC.

It is well known from many other materials that isolated interstitials are mobile after they have been produced in a cascade, and can migrate over long distances on time scales beyond the picosecond one of cascades.^{28–30} The results of this study suggest that, since almost all of the isolated interstitials are C, these carbon atoms can become mobile and migrate, e.g., to a nearby surface. If the surface acts as a perfect sink (a commonly held proposition well established³¹ at least in Si), irradiation could result in C atom segregation at the surface. We note that experiments on thin foils observing C enrichment on the *back* surface beyond the ion range (to avoid confusion with well understood preferential sputtering at the *front* surface¹²) could confirm this proposition.

The mechanisms found in this paper using MD simulations of WC can be present also in many other materials. Any alloy material where the formation energy of defects containing one element is much higher than those of the other element(s), and where the heat spike resolidification is slow enough to allow for recrystallization, can be expected to exhibit similar behaviour as described here for WC.

To summarize, we have shown that irradiation of WC can lead to major elemental asymmetries in the defect production, especially in the fraction of isolated point defects. This effect is explained by the much higher formation energies of W than of C defects, and can thus be expected to occur also in other materials with large elemental differences in defect formation energies.

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