Defect kinetics and resistance to amorphization in zirconium carbide

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A R T I C L E   I N F O

A B S T R A C T

To better understand the radiation response of zirconium carbide (ZrC), and in particular its excellent resistance to amorphization, we have used density functional theory methods to study the kinetics of point defects in ZrC. The migration barriers and recombination barriers of the simple point defects are calculated using the *ab initio* molecular dynamics simulation and the nudged elastic band method. These barriers are used to estimate C and Zr interstitial and vacancy diffusion and Frenkel pair recombination rates. A significant barrier for C Frenkel pair recombination is found but it is shown that a large concentration of C vacancies reduces this barrier dramatically, allowing facile healing of radiation damage. The mechanisms underlying high resistance to amorphization of ZrC were analyzed from the perspectives of structural, thermodynamic, chemical and kinetic properties. This study provides insights into the amorphization resistance of ZrC as well as a foundation for understanding general radiation damage in this material.

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1. Introduction

Zirconium carbide (ZrC) is a promising candidate for structural materials in high temperature gas cooled reactor (HTGCR) as compared to SiC due to its high melting temperature [1], superior resistance to irradiation damage [2,3] and possibly superior resistance to fission product attack and permeation [4]. It has been proposed for use as coating for deep-burn Tristructural-isotropic (TRISO) nuclear fuel particles both as an oxygen getterer and structural cladding [3,5]. By using ZrC in combination with, or in place of, SiC, one may be able to reduce particle rupture, chemical degradation, release of fission product and enable increased gettering of oxygen [2]. The use of ZrC in TRISO fuel or other nuclear applications requires a thorough understanding of its irradiation responses. However, the radiation effects on ZrC are still poorly understood.

ZrC has a rock-salt crystal structure, consisting in two interpenetrating sublattices of Zr and C [6]. As a transition metal carbide, ZrC has an unusual combination of physical properties [7]. In the one hand, it has high melting temperature and hardness [6,7]. On the other hand, it has good electric and thermal conductivities, like metals [6]. There exists a wide range of nonstoichiometric compositions ZrC_x ($0.6 < x < 1.0$) [8] over which the lattice structure remains unchanged. The strong covalent Zr–C bonding confers its mechanical properties [7] and induce its brittleness below the brittle-ductile transition temperature of 1200 °C [9]. Such brittleness of ZrC makes its manufacture difficult and hinders its application. The hardness of ZrC decreases with increasing temperature [6] and it becomes significantly softer at high temperature.

The existing experimental literature data on ZrC irradiation effects is quite limited [10]. Gosset et al. irradiated ZrC with 4 MeV Au ion at room temperature and monitored the microstructural evolution through Grazing Incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM) [11]. They found a moderated swelling and saturated internal strains, which originates from the high density of small faulted dislocation loops. ZrC was irradiated with a 2.6 MeV proton beam at 800 °C by Yang et al. [12]. A high density of Frank loops dominates the irradiated microstructure and a slight lattice expansion was discovered. The hardness and fracture toughness were found to increase with increasing radiation dose. Snead et al. irradiated zone-refined ZrC with fast neutrons at the temperature range of 635–1480 °C [3]. The microstructural defects were dominated by dislocation loops, which underwent a gradual transition from Frank loops to prismatic loops above 1280 °C. Only modest changes were observed under irradiation in the mechanical properties of hardness, elastic

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modulus, and indentation fracture toughness, and the lattice parameter varied slightly (<0.2%). Thus the $ZrC_{0.93}$ was found to be quite stable under irradiation [3]. Up to now, no amorphization has been observed in ZrC [13], which is consistent with the generally stable properties observed under irradiation by Snead et al. [3] This resistance to amorphization (RTA) is not shared by some related carbides, e.g., SiC, and the origin of this amorphization resistance may shed light on both the radiation response of ZrC and amorphization processes in general. This study therefore seeks to understand the basic point defect kinetic properties of ZrC as a starting point to understand its amorphization and more general irradiation response.

Previous computational modeling of defect properties and irradiation effects in ZrC consists of just a few studies. Li et al. calculated the formation energy and migration barrier of C vacancy to develop an interatomic potential model [14]. Classical molecular dynamics (MD) simulation was used by Brutzel et al. to study the primary damage created by collision cascade in a ZrC matrix. No amorphization was observed in their cascades, and the point defects created included C (Zr) interstitials, a few Zr antisites, and clusters of two kinds of interstitials. A comprehensive *ab initio* study of point defect structures and energetics in ZrC was performed by Kim et al. [2] The most stable interstitial structure was determined to be the C interstitial (C–C–C trimer). C vacancies and interstitials were found to be much more stable than Zr vacancies and interstitials. Antisite defects were found to be quite unstable, suggesting chemical disorder will be low in ZrC. Razumovskiy et al. [15] studied the migration of Zr via a vacancy-mediated mechanism in TiC and ZrC. For ZrC they found that the V_{Zr}–$6V_C$ cluster was more stable than the isolated V_{Zr} and that this species migrated with a barrier of 7.46 eV, the same value obtained from experiment [16]. The exact thermodynamic conditions under which this result was calculated (Zr- or C- rich) are not clear to us from the paper but it appears to be a condition where C vacancies are readily available at no energy cost, which is consistent with less C-rich or irradiated conditions. We will discuss further the implications of these results when we consider Zr diffusion below. Jiang et al. [17] directly studied the amorphization process of both ZrC and SiC with *ab initio* molecular dynamics by adding C Frenkel Pairs (C FP) into both systems, annealing briefly, and tracking the long-range structural order. Jiang et al. found that SiC readily amorphized but ZrC did not. This difference was explained in terms of the intrinsic instability of the Si sublattice vs. the intrinsic stability of the Zr sublattice, where the latter protects the ZrC from amorphization under C disorder. Jiang et al. also showed that for ZrC, no matter how many C FPs were added, the point defects did not accumulate to sufficient energy to destabilize the crystalline ZrC as compared to amorphous ZrC. This result suggests that the approximately athermal annealing processes were accessible in ZrC at high point defect concentrations. As will be shown in this work, such a result is surprising given the barriers to point defect recombination for dilute defects, but seems to emerge due to defect interactions at high point defect density. While these previous studies provide a number of valuable insights, they do not provide a complete picture of point defect migration and recombination, so we undertake to provide such a picture in this work.

In this work, we use nudged elastic band (NEB) and *ab initio* molecular dynamics (AIMD) methods to calculate the migration and recombination barriers of point defects in ZrC. The mobility of each point defect is analyzed by calculating the diffusion coefficients of each type. The annealing properties of ZrC were studied by calculating the recombination barriers of isolated Frenkel pairs as well as in the presence of other defects. We then try to understand the fundamental mechanisms underlying the high RTA of ZrC by reviewing previous amorphization models and properties of ZrC.

2. Methods

The *ab initio* calculations were carried out using the Vienna *ab initio* simulation package (VASP) [18–21] based on the density functional theory (DFT) and the projector-augmented-wave (PAW) method. The exchange-correlation was treated in the generalized gradient approximation (GGA), as parameterized by Perdew, Burke, and Ernzerhof (PBE) [22]. The PAW potentials were generated with the following valence electronic configurations: $5s4d5p$ for Zr and $2s2p2$ for C.

Two kinds of ZrC supercells and associated k-point meshes were used. All supercells are multiples of the cubic 8-atom conventional rock-salt cell. A 64-atom $2 \times 2 \times 2$ supercell with a converged $5 * 5 * 5$ k-point mesh was used to study the diffusion of an interstitial or a vacancy, and a 216-atom 3x3x3 supercell with a converged $3 * 3 * 3$ k-point mesh was used to study the recombination of Frenkel pairs. For the Zr FP recombination, $1 * 1 * 1$ k-point mesh was used for the nudged elastic band (NEB) [23] calculation due to convergence problems with the $3 \times 3 \times 3$ k-point mesh. While this lower k-point mesh is not very well converged for the total energy we found it gave acceptable errors for the migration energies. Specifically, for selected situations we checked the barrier calculated for the $1 * 1 * 1$ k-point mesh compared to the barrier from a $3 * 3 * 3$ k-point mesh and found the barrier difference is only about 0.05 eV. Thus the k-point mesh for NEB calculation is $3 * 3 * 3$ for C recombinations, and $1 * 1 * 1$ for Zr recombinations. All calculations used an energy cut-off of 600 eV. In each kind of supercell, the energy error on defect formation and migration energies is less than 1 meV/atom with respect to the k-point convergence and energy cut-off.

The NEB method has been used to calculate the energy barriers for the migration of intrinsic defects and recombination of Frenkel pairs. In both cases, one of the key issues is to find the minimum energy path. To achieve this effectively, we use AIMD simulation as a guide for the path, following the approach used in Ref. [24]. These AIMD runs were performed at a temperature of 2800 K with a time step of 3 fs and lasted for 3–10 ps. The AIMD runs with a smaller time step of 1 fs were also checked, which suggested a similar path as that from the AIMD runs with longer time step of 3 fs.

As described in Ref. [24], the formation energy (E_f) and the migration barrier (E_m) are used as approximations for the free energies of formation (F_f) and migration (F_m), respectively. For the neutral state considered in ZrC (the metallic band structure means that no charged defects will form), the defect formation energy E_f is given by [2]

$$E_f = E_{def} - E_{perfect} + \sum_i \Delta n_i \mu_i \tag{1}$$

where E_{def} is the energy of the defected cell, $E_{perfect}$ is the energy of the perfect cell, Δn_i is the change in the number of species i (i = Zr or C) when the defect forms, and μ_i is the chemical potential of species i. We set $\mu_i = \mu_i^0$ for species i-rich condition. In this work we focus on C-rich conditions, which is consistent with $x \approx 1$ in ZrC_x. Formally one can treat Zr-rich conditions with the transformation μ_{Zr}(Zr-rich) = μ_{ZrC} (C-rich) − ΔE_{ZrC} and μ_C(Zr-rich) = μ_C (C-rich) − ΔE_{ZrC}, where $\Delta_{ZrC} = \mu_{ZrC}^0 - \mu_{Zr}^0 - \mu_C^0 = -1.64$ eV. However, under Zr-rich conditions when the stoichiometry of ZrC_x is far from $x = 1$ the formation energy values might be different from those in the stoichiometric ZrC_x ($x = 1$) [15].

3. Migration barriers and diffusion coefficients

The mobility of intrinsic point defects plays an important role in the resistance to amorphization and general radiation response, since higher mobility generally enables more annealing in materials. Here we focus on the self-diffusion of intrinsic point defects in