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Atomistic simulations of Ni segregation to irradiation induced dislocation loops in Zr-Ni alloys

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ABSTRACT

The role of Ni segregation on the stability of dislocation loops in the Zr-Ni binary system is elucidated by employing molecular dynamics/Monte Carlo simulations. The effect of the concentration of the alloying element on the strain energy around both interstitial and vacancy loops was investigated. Ni atoms are found to accumulate around the dislocation loops. Our results suggest that the driving force of Ni segregation to the loop is a combination effect of the release of the strain energy of the dislocation core and the reduction of energy arising due to annihilation of point defects associated with those Ni atoms previously substitutionally solute far from the loop. The anisotropic stress field of the dislocation loop is presented in cylindrical coordinates, and is used to explain the influence of the alloying element on the stability of the dislocation loop. Furthermore, cascade simulations in the vicinity of dislocation loops were employed in the irradiated Zr-Ni binary system, and a significant enhancement of the stability of the dislocation loops was related to the change of the stress field as well as the core energy of the loop due to the alloying segregation.

1. Introduction

Zirconium alloys are known for their low neutron capture cross section, good mechanical properties and reasonable resistance to corrosion; they are therefore used extensively in nuclear reactors. Zircaloy-2 alloy is one of the best-known alloys used as a fuel cladding in nuclear reactors [1,2]. A low concentration of Ni (<0.1 wt%) is present in the Zircaloy-2 alloy, and has been reported to postpone the precipitation of hydrides and consequent hydrogen embrittlement by assisting H atoms' dissolution in α-Zr [2]. A common issue encountered in zirconium alloys in service is radiation-induced embrittlement due to the formation of dislocation loops. The size of experimentally observed *a*-type and *c*-component/type dislocation loops in zirconium alloys varies from a few nanometers to several hundred nanometers in diameter [3–7]. These dislocation loops form an energetically favourable site for the segregation of alloying elements, and are also barriers to dislocation glide; the alloy consequently undergoes a significant reduction in ductility [8–10].

The question of how irradiation and related phenomena influence material properties has generated a great deal of experimental interest in zirconium alloys [11]. Hood et al. [12,13] measured the self-diffusion coefficient in α-Zr (HCP); however, the relatively low α-Zr (HCP) to β-Zr(BCC) allotropy temperature limits the precision of such measurements. Using transmission electron microscopy (TEM) Griffiths et al. [14] reported a preferential depletion of Fe from $Zr(Cr, Fe)_2$ under neutron irradiation, whereas $Zr_2(Cr, Fe)$ remained crystalline up to higher irradiation doses [15,16]. Yang [17] studied the effect of temperature on the crystalline to amorphous transformation of intermetallic compounds in Zircaloy-2 under irradiation. In a recent work Harte et al. [18] observed a layered chemical segregation of Ni, Cr and Fe in *a*-loop positions in basal traces, and suggested this as associated with the delayed onset of *c*-loop nucleation. Ni segregation towards grain boundaries is not significant, as a chemistry analysis near grain boundaries shows a depletion of Fe and Ni, while Sn can segregate to all boundaries after irradiation [19].

Direct experimental study of irradiation remains a challenge, and certain associated phenomena, such as the micromechanisms of microstructural evolution during radiation, remain unclear. A complimentary approach is computational techniques and simulations, which are capable of scaling to appropriate times and dimensions, offering valuable insight into the non-equilibrium

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evolution that occurs during radiation. However, the only atomic scale study of the Zr-Ni system is the one by Moura et al. [20], who investigated the configurations, formation energies and migration mechanisms of point defects in the ZrNi and Zr_2Ni intermetallic compounds using molecular dynamics (MD) simulations. Therefore, the role and possible contribution of Ni to irradiation growth remains of investigative interest.

The stress field associated with dislocations and its interaction with alloying elements during irradiation has been another topic of interest since the 1950s. Peach and Koehler [21] discussed the effect of atomic constraints on dislocation loop growth. Kroupa [22] formulated the stress field around a circular edge dislocation loop in cylindrical coordinates. Using numerical models, Owen and Mura [23] showed that the magnitude of shear stress is much less than that of the normal stress. Trinkaus et al. [24] suggested that the small loops trapped in a strain field can escape by thermal activation or conservative climb. Khraishi et al. [25] constructed a stress field from Hooke's law, under the assumption of linear elasticity and an infinite isotropic material, and showed that the normal stress converges to that of an infinite edge dislocation as the radius of the loop increases. Prominent studies [26,27] have highlighted the significance of the stress field on the aspect ratio and size of the dislocation loops. Gao and Larson calculated the stress field around a dislocation loop by taking into account the elastic anisotropy of the structure [28]. Using the strain-displacement relation and anisotropic Hooke's law, Wu and his co-workers [29,30] suggested that the influence of a free surface on the strain field of a *c*-type dislocation loops is more significant than that on *a*-type dislocation loops within a thin foil. Luo et al. [31] used MD simulations to study crack nucleation under impact indentation, and they presented the stress evolution of the tensile site under indentation. Using MD cascade simulations of pure zirconium, Dai et al. [32] observed that the habit plane of *a*-type dislocation loops tilt to a new one under irradiation, and that the shape of the dislocation loop changes under radiation, which suggests that the stability of *a*-type loops can be significantly affected by interactions with the PKAs.

Despite all these attempts, to the knowledge of the authors, there have been no atomic scale studies of segregation for mixed type bonding systems in the presence of dislocation loops under radiation. Furthermore, the effect of segregation on the state of stress around dislocation loops has not yet been studied.

The goal of this paper is three-fold. First, we develop a structure identification approach in which a dislocation loop in a multi-component system can be located very precisely. Based on this approach, we quantitatively analyze the segregation of Ni atoms at the dislocation loop. The defect energy of the interstitial and vacancy loops are compared before and after segregation. Second, for the first time, we present the stress fields around interstitial and vacancy loops, in a cylindrical coordinate system; the effect of Ni segregation on the stress field is presented. Finally, irradiation cascade simulations are performed to investigate the effect of Ni segregation on the stability of the dislocation loops.

2. Methodology

The interactions between the components of the Zr-Ni system were approximated by the Finnis-Sinclair embedded-atom method (EAM-FS) empirical potential developed by Wilson and Mendelev [33]. This potential is the modified version of an earlier one developed by Mendelev et al. [34] and is capable of stabilizing ZrNi and Zr_2Ni intermetallic compounds according to the phase diagram.

Variance-constrained semi-grand-canonical (VC-SGC) ensemble [35] was employed to model the segregation. This ensemble is technically a combined version of MD, for structural relaxation, and MC, for composition change and atomic configuration toward equilibrium. The corresponding algorithm has been implemented in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [36]. In the current work, the fraction of swapped atoms was chosen to be 0.2 and the MD runs between the MC swaps comprised 100 integration steps of 1 fs each. The chemical composition is controlled by the chemical potential difference between the two species and the target concentration. When using the VC-SGC ensemble, the initial challenge is determining the chemical potential difference corresponding to the target composition at the equilibrium condition. Several different chemical compositions of Ni are simulated to provide a good statistical result. The size of the simulation box is 32.31 nm × 55.97 nm × 52.11 nm (*X*, *Y* and *Z* directions), and contains ~4 million atoms. The simulation was initially pure Zr at 3 K, and after setting the composition to the target value the system was annealed to the temperature of interest (573 K, which is a common environmental temperature during irradiation) using the VC-SGC technique.

In order to simulate the segregation phenomenon, once equilibrium composition and phase distribution were achieved, the *a*-type dislocation loops were created. In order to create the dislocation loops with burgers vector $\frac{1}{3}11\bar{2}0$, we selected the perfect prism plane $\{01\bar{1}0\}$ as the initial plane for both interstitial and vacancy loops, and thermally equilibrated using the hybrid MD/MC simulations [35] (1 ns in MD combined with 10,000 steps in MC). The initial diameter was chosen to be 10 nm in agreement with experimental observations [3–7]. Vacancy loops were created by removing one layer of atoms in the shape of a cylinder, and interstitial loops were created by replacing one layer of atoms with two layers of atoms with a smaller lattice parameter. Further details on this method of creating dislocation loops are provided in Ref. [32].

Six independent components of the stress tensor for each atom are generated based on the global tensor **S** for a collection of *N* atoms contained in a volume *V* [37]:

$$\mathbf{S}V = \left\langle \sum_{i=1}^{N} m_i v_i \otimes v_i + \mathbf{W}\left(r^N\right) \right\rangle, \tag{1}$$

where m_i and v_i are the mass and instantaneous velocity of the ith atom. The symbol ⊗ indicates the outer, dyadic, or direct tensor product. **W** is the global virial tensor and depends only on the instantaneous atom positions $\mathbf{r}^N = \mathbf{r}_1,\ldots, \mathbf{r}_N$ and the interactions between them. The virial tensor is an extensive quantity and represents the contribution of the interaction potential to the pressure.

The geometry of dislocation loops is such that the stress field analysis would be ideally performed in the cylindrical coordinate system. Therefore, the matrix of stress components for every atom was converted from Cartesian coordinates, obtained from LAMMPS simulations, to cylindrical coordinates.

Of particular interest are 3 normal stress components: S_{rr} (the radial component of stress), $S_{\theta\theta}$ (the tangential component of stress) and S_{zz} (the axial component of stress). Fig. 1 shows the orientation of stresses for a volume element in the cylindrical coordinate system. By definition, positive stress is tensile, whereas negative stress is compressive. Using this method, we present the stress state in cylindrical coordinates on the projection of the loop's plane. A correlation time of 2 ps was used to generate 100 independent snapshots for the statistical analysis of the stress field around the dislocation loop.

When simulating cascades, the initial directions of the PKA are $01\bar{1}0$ (in the direction of the loop axis) or [0001] and$11\bar{2}0$(in the plane of the dislocation loop), and the energy of a primary knock-on atom (PKA) was set to 50 keV. The distance of PKA from the centre