Journal of Nuclear Materials 477 (2016) 215–221

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Ab initio investigation of helium in $Y_2Ti_2O_7$: Mobility and effects on mechanical properties

T. Danielson [a, *], E. Tea [b], C. Hin [a, b]

[a] Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, 635 Prices Fork Road, Blacksburg, VA 24060, USA
[b] Department of Mechanical Engineering, Virginia Polytechnic Institute and State University, 635 Prices Fork Road, Blacksburg, VA 24060, USA

HIGHLIGHTS

- Migration barriers of helium in $Y_2Ti_2O_7$ are calculated using the climbing image nudged elastic band.
- Helium Potential energy surfaces are calculated.
- Mechanical properties of varying helium concentrations are presented.

ARTICLE INFO

Article history:
Received 28 September 2015
Received in revised form
10 May 2016
Accepted 11 May 2016
Available online 13 May 2016

ABSTRACT

Oxide nanoclusters (NCs) in nanostructured ferritic alloys (NFAs) are known to be efficient trapping sites for the transmutation product helium. In this study, the migration barriers and potential energy surfaces of helium in $Y_2Ti_2O_7$ are presented to explain the mobility of helium through oxide NCs and shed light on the accumulation of helium and the trapping mechanisms of the oxides. A complex tunnel-shaped potential energy surface is identified and gives rise to relatively large migration barriers. Subsequently, the effect of helium accumulation on the mechanical properties of $Y_2Ti_2O_7$ oxide nanoclusters is investigated and it is shown that the mechanical properties of the oxide do not significantly degrade as helium accumulates.

1. Introduction

Nanostructured ferritic alloys (NFAs) are a subset of oxide dispersion strengthened steels that have shown significant promise in the development of materials for the next generation of fission and future fusion reactors. NFAs are characterized by a uniformly distributed high number density of complex oxide nanoclusters (NCs). The finest NCs are dispersed primarily throughout the matrix material's grains, but are also found along grain boundaries. The NCs play a critical role in the alloy's ability to withstand the harsh challenges presented in the reactor environment including; high temperatures, high pressures, neutron irradiation and especially, the accumulation of high concentrations of transmutation product helium [1–4].

The accumulation of helium in NFAs has gained widespread interest in recent years both experimentally and computationally in order to understand the decreased susceptibility of the alloys to helium embrittlement. The investigation has collectively shown evidence that the fine-scale oxide NCs dispersed throughout the alloy grains play a key role in trapping helium, preventing the formation of coarser helium bubbles. However, no complete theoretical explanation exists for the trapping of helium at the oxide NCs, or for how the presence of helium affects the structure and mechanical properties of the oxide NCs. Both of these explanations are key components in the development of more thorough and intricate models, such as kinetic Monte Carlo simulations [5–13], to explain the time evolution of the alloys in reactor environments, as reactor experiments can take decades for relevant reactor-lifetime doses.

Previous first-principles calculations have shown the migration barrier for helium in BCC iron to be extremely low (~0.06–0.08 eV) [14,15]. Likewise, the binding energy of individual helium interstitials in BCC iron has been found to be attractive and clusters are further stabilized by the addition of vacancies [14]. Thus, as

Abbreviations: NCs, nanoclusters; NFAs, nanostructured ferritic alloys; DFT, density functional theory; GGA, generalized gradient approximation; PBE, Perdew, Berke and Ernzerhoff.

* Corresponding author.
E-mail address: thomasd1@vt.edu (T. Danielson).

http://dx.doi.org/10.1016/j.jnucmat.2016.05.024
0022-3115/

helium accumulates in the Fe matrix, the low migration barrier in iron and attractive binding energy between He atoms make cluster formation favorable and eventually lead to the coalescence of larger bubbles. Large helium bubbles can become highly pressurized at elevated temperatures and cause swelling and catastrophic cracking. Helium implanter transmission electron microscopy experiments show direct evidence of oxide NCs located within the matrix grains acting as trapping sites for helium bubbles preventing a significant portion of the bubbles' eventual delivery to Fe grain boundaries where nucleation would otherwise be preferential in BCC Fe [1,16–18]. Oxide NCs located along grain boundaries are also noted to be efficient traps, impeding the diffusion of helium atoms and preventing the coarsening of large helium bubbles along the grain boundary networks [16]. While He cluster formation is favorable in the BCC iron matrix, first-principles calculations have shown that this is not the case in the oxide NCs. In the oxides, single helium interstitials occupying separate interstitial sites is the more energetically favorable configuration [19]. The mobility of helium in various oxides has been reported by Erhart [19] to be significantly lower than that in BCC Fe, but no specific path or energy barriers have been given thus far for the $Y_2Ti_2O_7$ system.

The high number density of complex oxide NCs play a crucial role in providing the high creep strength and high yield strength characteristic of NFAs, as well as maintaining the mechanical properties of the bulk alloy under irradiation. The NCs serve to stabilize the grain size and their presence along grain boundaries aids to prevent grain boundary sliding under tensile stresses at the elevated temperatures and pressures of a reactor environment, resulting in increased creep strength [20–23]. Consequently, dislocation glide has been found to be the dominant deformation mechanism in NFAs [20]. The NCs serve to pin dislocations through Orowan looping processes, preventing glide, which ultimately leads to the increased strength of the alloys. Likewise, maintaining a high dislocation density is crucial for maintaining high creep strength as dislocations serve as annihilation sites for point defect damage from incident radiation.

To this point, no theoretical studies exist describing the effects of helium interstitials on the mechanical properties of the oxide NCs, however, it is critical that the NCs maintain their mechanical properties as helium accumulates. If the mechanical properties of the NCs degrade significantly, pinned dislocations may be more likely to shear the precipitates due to the elastic field interaction of the precipitate and dislocation. Each time the precipitate is sheared, its resistance to dislocation motion is again reduced, which can ultimately result in regions of plastic flow [24]. Thus, degradation of oxide mechanical properties may potentially lead to changes in the bulk mechanical properties.

By investigating the mobility of helium in $Y_2Ti_2O_7$, as well as the mechanical properties of the oxide containing helium, we can gain insight into the trapping mechanisms of helium at the oxide-Fe interface in NFAs, as well as the likelihood and degree to which the mechanical properties may degrade as helium accumulates in a reactor environment. This provides valuable insight, not only theoretically for prevention of helium embrittlement in reactor materials, but also for building complex reactor lifetime scale models. In the next section, the computational methods and interstitial locations are described. In Section 3, results on the mechanical properties, mobility of helium and the potential energy landscape from the perspective of a helium atom in $Y_2Ti_2O_7$ are presented. Finally, a discussion of the results and their implications for NFAs is presented.

2. Computational methods

The ground state energy of $Y_2Ti_2O_7$ has been evaluated using density functional theory (DFT) in order to determine the migration barriers, potential energy landscape and bulk moduli of the $Y_2Ti_2O_7$ + He system. DFT calculations have been performed as implemented in the VASP code [25–28] using the projector-augmented wave method [29,30]. The 4s and 4p, 3p and 2s electrons are considered as valence electrons for Y, Ti and O respectively. The generalized gradient approximation (GGA) from Perdew, Berke and Ernzerhoff (PBE) [31,32] has been shown to most accurately describe the behavior of helium [33] and thus, has been used to describe the exchange-correlation functional of the valence electrons. For each calculation, one fully periodic $Y_2Ti_2O_7$ unit cell has been used where the Brillouin zone is sampled using a $4 \times 4 \times 4$ k-point mesh and a plane-wave energy cutoff of 600 eV. During structural relaxation, the total energy is converged to 10^{-6} eV.

The helium interstitial positions and their relative stabilities have been previously investigated using first-principles for the $Y_2Ti_2O_7$ pyrochlore structure and are shown in Fig. 1 [33]. These interstitial positions will be used for the initial and final locations when determining the helium migration barriers and pathways. The climbing image nudged elastic band method [34–36] has been used to calculate the migration barriers. It connects a sequence of supercell images with a spring of constant, k, in a geometrically interpolated path between the initial and final state. From this, a force projection scheme is used where potential forces act perpendicular to the band and spring forces act parallel to the band to relax each image to its ground state. The spring forces keep the images evenly separated on the reaction coordinate axis, while all images undergo successive constrained atomic relaxations. The image with the highest energy climbs up the potential energy surface and locates the saddle point, giving the barrier. As a result, a reversible migration energy and path can be extracted for helium through the host matrix.

To obtain a detailed picture of helium migration in $Y_2Ti_2O_7$, the associated potential energy landscape has also been calculated. It is given by calculating the total energy of a $Y_2Ti_2O_7$ matrix containing a helium atom as a function of its position. For each helium atom position, the nearest neighbor atoms of the $Y_2Ti_2O_7$ matrix are relaxed while the helium position is fixed, so that the helium atom is not allowed to drift to a nearby stable interstitial position. The different helium atom positions map a $8 \times 8 \times 8$ regular mesh of the $Y_2Ti_2O_7$ matrix in order to reveal regions of the crystal with high and low potential energies where helium migration would come at a high or low energetic cost, respectively. The NEB method gives accurate migration barrier energies. The energy landscape does not give barrier energies as accurate as NEB, but provides an additional global picture of the migration paths, completing the helium atom migration study.

The elastic constants quantitatively describe how a crystal will respond to an externally applied strain. Using Hooke's law, which gives the dependence of stress on an applied strain using the elastic stiffness tensor, three independent elastic constants can be obtained for systems with cubic symmetry: C_{11}, C_{12}, and C_{44}. The stress-strain relationships from Hooke's law are expressed in the following way:

$$\sigma_{xx} = C_{11}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{12}\varepsilon_{zz} \quad (1)$$

$$\sigma_{yy} = C_{12}\varepsilon_{xx} + C_{11}\varepsilon_{yy} + C_{12}\varepsilon_{zz} \quad (2)$$

$$\sigma_{zz} = C_{12}\varepsilon_{xx} + C_{12}\varepsilon_{yy} + C_{11}\varepsilon_{zz} \quad (3)$$

$$\sigma_{xy} = C_{44}\varepsilon_{xy} \quad (4)$$