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Atomistic simulations and experimental measurements of helium nano-bubbles in nickel

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ABSTRACT

Deterioration of nickel-based alloy components in fission reactors is associated with the generation of helium from neutron-induced nuclear reactions. In tests at the macroscopic scale, deleterious effects of helium on the mechanical properties of nickel alloys are observed upon the formation and growth of helium bubbles. In order to enhance the understanding of helium effects in nickel, the properties of helium bubbles can be investigated by atomistic scale simulations. In the present work, we have studied helium bubbles in pure nickel, with diameters from 1.0 to 5.0 nm, using molecular dynamics (MD) simulations. The properties of nano-sized helium bubbles as a function of the helium-to-vacancy ratio are calculated at 600 K. The conditions for helium bubbles in mechanical equilibrium with the nickel matrix are determined. The results from simulations are found to be in good agreement with experimental data.

1. Introduction

Helium is chemically inert and essentially insoluble in nickel. Its production, through neutron capture and transmutation, and retention in nickel has been observed to cause degradation in material performance. In fission reactors, a significant amount of helium is created from nickel in a two-step reaction $^{58}\mathrm{Ni}(\mathrm{n},\gamma)$ and $^{59}\mathrm{Ni}(\mathrm{n},\alpha)$. The production and trapping of helium generated in irradiated structural alloys is also expected to affect components in advanced fission reactors, such as the Canadian SCWR [1], and molten salt reactors [2].

Because of its low solubility in nickel-based alloys, the aggregation of helium into bubbles eventually leads to material damage, as manifested in the deterioration of the mechanical properties of the alloys. An extensive review of helium effects in alloys can be found in Ref. [3] and references therein. The importance of helium effects in metals was recognized early on, e.g., the review by Ullmaier [4], but the observed embrittlement of irradiated metals caused by the formation of helium bubbles continues to be an active area of research [3,5]. An understanding of the fundamental mechanisms of helium-embrittlement and the conditions in which material degradation occurs is important in the development of innovative solutions to the helium degradation effects in nickel alloys. Considerable experimental effort has been devoted to understand the behavior of helium in austenitic steels and nickel alloys [3,6]. In experiments, nanoscopic helium bubbles can be directly observed and recorded using electron energy loss spectroscopy (EELS) and scanning transmission electron microscopy (STEM) [3,6,7]. Subsequently, associated properties of helium bubbles can be characterized from the measured bubble diameters and EELS maps of helium.

In atomistic simulation studies, to investigate more complex helium effects, an accurate description of the properties of helium atom impurities and small clusters in the metal lattice is required. Basic properties, such as the solubility, the barrier for migration, trapping sites, and the structure of clusters, are determined by the behavior of helium atoms at different sites in perfect and imperfect lattices. While properties and formation of helium clusters in nickel have been investigated using atomistic simulations [8–10], there are no satisfactory atomistic scale studies of helium bubbles in nickel reported so far. The majority of previous atomistic models of

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helium in nickel have relied on early electronic structure calculations [11], used with a few developed helium-nickel interatomic potentials [12–14]. However, the interatomic potentials used in these studies were later shown to be inaccurate, based on comparisons with recent density functional theory (DFT) studies [10,15,16]. In more recent theoretical investigations, significant efforts have been devoted to develop a reliable He-Ni interatomic potential [10,17]. Despite the fact that recently reported interatomic potentials better represent some of the energetics of helium impurities in nickel, there are still discrepancies with fundamental details of helium-nickel interactions obtained from DFT electronic structure calculations. The description of the bubble-metal interface in atomistic simulations mainly depends on the helium and nickel interactions. In addition, the properties at the interior of helium bubbles are in part determined by the structure at the bubble interface. Consequently, inaccuracies in the currently available He-Ni potentials make them unsuitable for the modeling of helium bubbles in nickel.

In this work, a molecular dynamics study of nano-size helium bubbles in nickel is presented. An improved He-Ni interatomic potential based on a recently proposed potential function [10] is derived. The revised He-Ni potential accurately reproduces the formation energies of single helium defects in nickel as determined from DFT calculations. The improved interatomic potential is used in MD simulations of helium nano-bubbles in nickel. A systematic characterization of size-dependent properties of bubbles with diameters from 1.0 to 5.0 nm is performed. Helium bubbles in mechanical equilibrium conditions are determined from the analysis of the helium-to-vacancy ratio. The properties of bubbles under equilibrium conditions calculated from MD simulations are compared to experimentally determined data. The reported experimental and simulation results are found to be in good agreement.

2. Computational methods

First principles total energy calculations were performed using DFT, within the generalized-gradient approximation (GGA), as implemented in the PWscf electronic-structure code distributed with the Quantum ESPRESSO integrated suite [18]. The exchange and correlation energy contributions were described by the Perdew-Burke-Ernzerhof (PBE) functional [19]. The electronic wavefunction was expanded in a plane-wave basis set determined by the kinetic-energy cut-off of 950 eV. The Brillouin zone integration was performed on an 8×8×8 Monkhorst-Pack *k*-point mesh [20]. A first-order Methfessel-Paxton electron smearing scheme with parameter $\sigma = 0.2$ eV was found suitable for structure optimizations. Spin polarization was considered for pure nickel and with helium impurities. Total energy results were converged up to an error threshold of 0.01 meV per atom. Parameters used in DFT calculations were determined from the convergence of defect formation energies within 1.0 meV of accuracy. Zero-point energy contributions were not included in calculations of the defect formation energies. However, a contribution of ~ 0.01 eV has been estimated [16].

Density functional theory calculations of defect free bulk nickel, and including solute helium atoms, were performed using a 3×3×3 periodic supercell of the conventional fcc unit cell of nickel. The defect free nickel supercell contains a total of 108 atoms. Nickel atoms were described with a scalar relativistic ultrasoft pseudopotential, including a non-linear core correction, while helium atoms were described by a non-relativistic ultrasoft pseudopotential [21]. The initial configurations of the magnetic moments on nickel atoms were provided to start the calculations in the ferromagnetic (fm) ordered state. However, the magnetic moments were left free to relax in total energy and structure optimizations. A calculation of the reference state energy for a helium atom in the gas phase was performed in a cubic supercell of 20 Å in each Cartesian direction. This supercell size was found sufficient to eliminate self-interactions, therefore ensuring substantial accuracy. The calculation only included the Γ-point, while spin-polarization was not considered.

Molecular dynamics simulations were carried out with the large-scale atomic/molecular massively parallel simulator (LAMMPS) code [22] including the GPU accelerator package [23]. Simulations were performed with periodic boundary conditions imposed on all Cartesian directions. The Ni-Ni interactions were described using the potential of Bonny *et al.* [24]. This potential was chosen because it accurately reproduces point defects in nickel. The He-He interactions were modeled using the Beck potential [25]. This potential reproduces the second virial coefficient for helium, and is therefore adequate for the study of helium bubbles in this work. The He-Ni interactions are described using the interatomic potential developed here.

The interstitial and substitutional sites in fcc nickel are indicated in Fig. 1. The formation energies for a single He atom as an interstitial (E_{int}), at the octahedral (oct), tetrahedral (tet) or crowdion (crd) interstitial sites, is given by

$$E_{int} = E(\mathrm{Ni} + \mathrm{He}_{int}) - E(\mathrm{Ni}) - E(\mathrm{He}), \tag{1}$$

where $E(\mathrm{Ni} + \mathrm{He}_{int})$ is the total energy of bulk nickel with an interstitial helium atom impurity, $E(\mathrm{Ni})$ is the energy of perfect bulk nickel with a total of N atoms and $E(\mathrm{He})$ is the energy of an isolated helium atom.

The formation energy of a helium atom as a substitutional (E_{sub}) impurity or a helium cluster (E_f) in a single nickel vacancy is approximated as

$$E_{sub/f} = E(\mathrm{Ni} + \mathrm{He}_n V) - [(N-1)/N]E(\mathrm{Ni}) - nE(\mathrm{He}), \tag{2}$$

where $E(\mathrm{Ni} + \mathrm{He}_n V)$ is the total energy of the nickel supercell with n helium atoms in a nickel vacancy (V). For the particular case of a substitutional helium atom $n = 1$.

The parameters of the He-Ni interatomic potential were determined based on a two-step MD optimization and validation procedure, performed using supercells with dimensions of 3×3×3 and 6×6×6 lattice units, respectively. The validation was performed using DFT results as the reference data. The formation energies of interstitial and substitutional helium defects were determined using the Polak-Ribière formulation of the conjugate gradient method, as implemented in the cfg module in LAMMPS. A force tolerance of 1.0×10^{-6} eV/Å was used in all energy optimizations.

Molecular dynamics simulation of helium bubbles were performed in a cubic nickel supercell of 40×40×40 lattice units,

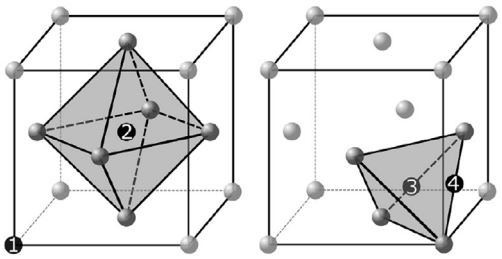

Fig. 1. Substitutional (1) and interstitial octahedral (2), tetrahedral (3), and crowdion (4) helium impurity sites are indicated with solid black circles. Nickel atoms in the conventional fcc unit cell are represent by gray spheres. Gray colored walls indicate the octahedral (left panel) and tetrahedral (right panel) volumes.