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Density functional theory-based derivation of an interatomic pair potential for helium impurities in nickel

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ABSTRACT

Helium is formed in nickel as a by-product of neutron irradiation. Although helium is chemically inert and essentially insoluble in metals, under specific conditions it is known to cause metal embrittlement. Early experimental and theoretical studies on helium diffusion mechanisms have been a source of controversy. Recent density functional theory (DFT) studies of helium impurities in nickel contradict earlier theoretical studies. In this paper, a new functional form and parameters for a helium-nickel interatomic potential are proposed. The new potential used in molecular dynamics (MD) simulations correctly reproduces the relative stability of helium defects and the interstitial migration of helium in nickel. Furthermore, the computed activation energy for diffusion of helium in nickel corroborates experimental findings. The transferability of the potential is verified through a comparison with DFT predictions of the formation energies of the most stable He clusters in a Ni monovacancy.

1. Introduction

Helium is a by-product of neutron irradiation of metals in both nuclear fission and fusion reactors. In thermal spectrum fission reactors nickel is the primary source of helium, via the thermal neutron induced two step reaction ^{58}Ni(n,γ) and ^{59}Ni(n,α). In fast spectrum fission reactors and in fusion reactors helium is produced by fast neutron irradiation through (n, α) transmutation reactions with nickel, chromium, titanium, iron and other metals. The production of helium and its aggregation into bubbles causes metal embrittlement, which has been the subject of extensive study (see Refs. [1], and references therein). Helium embrittlement of nickel alloys is of interest because some Ni-alloy components in thermal spectrum fission reactors are subjected to high neutron exposures during their long residence time within the core [2]. In addition, austenitic stainless steels and nickel-based alloys have been identified as candidates for in-core structural materials in the Generation-IV supercritical water-cooled reactor (SCWR), where they can be subject to high thermal neutron fluxes, resulting in helium production from nickel [3].

While considerable experimental effort has been devoted to understand the behavior of helium in nickel alloys and austenitic steels, there have been relatively few theoretical studies in comparison to more common studies of helium in alpha-iron [1]. Early quantum mechanical electronic structure investigations were performed by Melius et al. [4] to study defects and activation energies for diffusion of helium in nickel. These studies were based on the lattice-defect method, using the Hartree-Fock approximation. The initial studies of Melius et al. formed the basis for a number of later molecular dynamics (MD) studies of helium diffusion [5] and helium bubble formation [6,7].

More recent density functional theory (DFT) [8,9] studies have been performed to determine formation energies of helium defects in nickel [10–12], and dilute austenitic Fe-Cr-Ni alloys [11]. The results of these *ab initio* calculations are consistent with each other, but contradict the earlier results of Melius et al. [4]. It has been found that the minimum energy interstitial location for helium is the tetrahedral position, rather than the octahedral, as previously believed, and that the barrier to interstitial helium diffusion is much lower than previously determined. It was also found that He migration between neighbor tetrahedral sites passes through an octahedral site, with a migration energy barrier of 0.129 eV [11]. The initial nucleation of helium clusters plays an important role in the formation of He bubbles. However, due the relative large size of supercell needed to appropriately model helium clusters in nickel, Empirical potential simulations are needed. As such, it is important to ensure the accuracy of the interatomic potential used for helium-

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nickel interactions in MD simulations.

Despite the shortcomings of earlier simulations studies of helium in nickel, only very recently (in fact nearly coinciding with the work presented here), has there been some progress to derive a potential for helium-nickel appropriate for use in MD studies [13]. The potential of Zhang et al. is a piece-wise function derived following a method analogous to Juslin et al. [14], and was fitted in combination with the embedded-atom method (EAM) potential for nickel developed by Sheng et al. [15]. As such, while suitable for simulations of helium in pure nickel, Zhang et al. potential may be difficult to generalize to ternary mixtures of nickel, iron and chromium, which better represent high nickel alloys and austenitic stainless steels.

In the present paper, we derive an accurate analytic potential for He-Ni, based on combined DFT and MD simulations. First, we investigate the relative stability and the interstitial migration barrier of helium solute impurities in pure nickel, using DFT calculations. In order to accurately model the interatomic interactions between helium and nickel atoms, we systematically analyzed the effects of spin polarization, structure relaxation, and system size on the formation energies of a helium defect in nickel. Then we report a new interatomic function, derived based on the understanding of the interactions between helium and nickel atoms, to describe He interactions in bulk nickel. The parameters of the new interatomic potential were determined by a supervised stochastic optimization algorithm using DFT results as reference data. Molecular dynamics simulations using the new He-Ni potential are shown to closely reproduce DFT formation energies of single helium defects in nickel, the energy barrier to nickel interstitial migration, and helium clusters in a single vacancy. Molecular dynamics simulations are also used with the new He-Ni potential to determine the activation energy for helium interstitial diffusion, which is found to agree with experimentally determined values.

2. Computational methods

Electronic structure calculations were performed using DFT, as implemented in the PWscf code component of the Quantum ESPRESSO integrated suite [16]. The exchange-correlation energy was described with the generalized-gradient approximation (GGA) by the Perdew-Burke-Ernzerhof (PBE) functional [17]. The valence electron wavefunction was expanded in a plane-wave basis set utilizing an upper kinetic-energy cutoff of 950 eV, which was necessary for prediction of defect formation energies within 1.0 meV of accuracy. The Brillouin zone integration was performed on an $8 \times 8 \times 8$ Monkhorst-Pack k-point grid [18]. A first-order Methfessel-Paxton electron smearing scheme with parameter σ=0.2 eV was found appropriate for structure optimizations. Spin polarization was considered for pure nickel and with a helium solute impurity hosted. The local magnetic moments associated to different atoms were approximated by integrating the spin density within spheres centered on each atom. Total energy results were converged up to an error threshold of 0.01 meV per atom. The zero-point energy contributions to the defect formation energies were not calculated. However, a variation of 0.01 eV has been estimated based on prior work [11].

Bulk nickel was modeled by three-dimensional periodic supercells, consisting of $2 \times 2 \times 2$ and $3 \times 3 \times 3$ cubic arrays of the conventional fcc unit cell (see Fig. 1), with a total of $N = 32$ and 108 atoms, respectively. The interactions between the core of nickel atoms and valence electrons were described with a scalar relativistic ultrasoft pseudopotential, including non-linear core correction. The magnetic moments on nickel atoms were initialized to impose a ferromagnetic (fm) ordered state, but left free to relax during geometry and wave function optimizations. Interactions between helium atoms and electrons were described by a non-relativistic ultrasoft pseudopotential. We used the pseudopotentials Ni.pbe-n-rrkjus_psl.0.1.UPF and He.pbe-mt_fhi.UPF from http://www.quantum-espresso.org. In order to obtain the reference energy of a helium atom in the gas phase, a non spin-polarized calculation was performed for a helium atom including only the Γ-point. It was determined that a cubic supercell with a side of 6 Å, or larger, was sufficient to virtually eliminate self-interactions. In our calculations, we used a cubic supercell with a side of 26 Å to ensure sufficient accuracy.

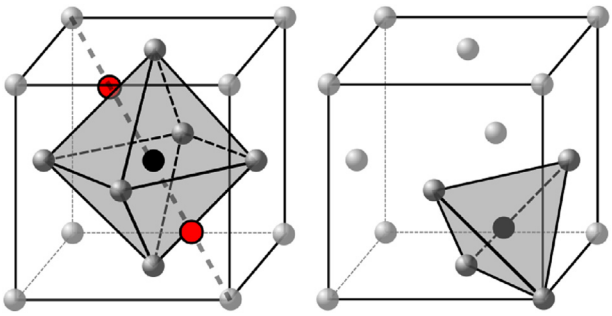

Fig. 1. The volumes of the octahedrally (left panel) and tetrahedrally (right panel) coordinated nickel atoms, inside the conventional fcc unit cell, are illustrated in gray color. Interstitial sites are indicated with a solid black circle. Gray spheres represent the atoms of the nickel lattice. The pathway connecting two tetrahedral sites (red circles) is indicated by a dotted gray line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The formation energies for a single He solute impurity, at the octahedral (oct) and tetrahedral (tet) interstitial sites, (E_{ins}), and substitutional (E_{sub}) site (see Fig. 1), were defined as

$$E_{ins} = E_{\mathrm{Ni+He}} - E_{bulk} - E_{\mathrm{He}} \quad (1)$$

and

$$E_{sub} = E_{\mathrm{Ni+He}} - [(N-1)/N]E_{\mathrm{Ni}} - E_{\mathrm{He}}, \quad (2)$$

respectively. Here, $E_{\mathrm{Ni+He}}$ is the combined total energy of bulk nickel with a helium impurity atom, E_{Ni} the energy of perfect bulk nickel, E_{He} the energy of an isolated helium atom, and N the total number of nickel atoms in the simulation box.

The migration energy barrier (E_b) of a helium atom moving along the pathway connecting two neighbor tetrahedral (T) sites in the [111] direction, was determined using the nudged elastic band (NEB) method. The midpoint in the [001] direction is a crowdion position, which has slightly higher formation energy than the octahedral site [11]. The middle path image was located at the octahedral (O) site; therefore the climbing image scheme was not used. The NEB calculations at the DFT level of theory were performed with the PWneb code distributed with Quantum ESPRESSO. Nudged elastic band calculations were performed in a $2 \times 2 \times 2$ nickel supercell, with the force tolerance set to 0.1 eV/Å to control convergence.

For MD simulations the Ni-Ni interactions were described using the potential of Bonny et al. [19]. This potential was chosen because it accurately reproduces defects in nickel, includes a short-range portion of the pair potential for use in cascade studies, and has cross terms enabling its use to represent nickel, iron, chromium ternary mixtures (e.g. nickel alloys and austenitic stainless steels). The He-He interactions were modeled using the Beck potential [20], which was deemed adequate for the study presented here, since it reproduces the second virial coefficient for helium, and the helium atoms in our models are either in isolation from each other