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Molecular dynamics modeling of helium bubbles in austenitic steels

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ABSTRACT

The austenitic steel devices from pressurized water reactors are continuously subjected to neutron irradiation that produces crystalline point defects and helium atoms in the steel matrix. These species evolve into large defects such as dislocation loops and helium filled bubbles. This paper analyzes, through molecular dynamics simulations with recently developed interatomic potentials, the impact of the helium/steel interface on the helium behavior in nanosize bubbles trapped in an austenitic steel matrix. It is shown that the repulsive helium-steel interactions induce higher pressures in the bubble compared to bulk helium at the same temperature and average density. A new equation of state for helium is proposed in order to take into account these interface effects.

1. Introduction

Austenitic steels are used in the Pressurized Water Reactors (PWR) as materials for the internal components. They are preferred due to their good mechanical properties and their high resistance to corrosion. Some of the most common types of austenitic steels, AISI-304 and AISI-316, are alloys of iron (Fe), chromium (Cr) and nickel (Ni) with small amounts of other elements, such as manganese (Mn), molybdenum (Mo), silicon (Si) and carbon (C) [1]. During their lifetime in the nuclear reactor, the austenitic steel devices are subjected to neutron irradiation at elevated temperature. The collisions between high energy neutrons and steel atoms produce point defects (vacancies and self-interstitial atoms) that can evolve into large clusters of defects such as voids (clusters of vacancies) or dislocation loops (clusters of self-interstitial atoms or vacancies). Transmutation reactions of (n,α) type take place between neutrons and alloy atoms (especially Ni atoms) [2]. The main products of these reactions are helium (He) and hydrogen (H). Small quantities of these two elements can have a strong impact on steel properties, especially the mechanical ones [2].

The helium atoms act as a vacancy trap forming helium-vacancy complexes (helium bubbles) [3,4]. Experimental studies on helium implanted samples of austenitic steels [5–13] revealed the existence of small, mainly spherical, bubbles with diameters ranging from less than a nanometer [7] to more than a hundred of nanometers [6]. The helium bubbles number density in the steel matrix varies from $10^{20}\,m^{-3}$ to $10^{24}\,m^{-3}$. The bubbles average size and number density are strongly depending on the steel temperature and the fluence of implantation [12].

Several theoretical studies have been devoted to understanding the formation of helium bubbles in body-centered cubic (bcc) iron or iron-chromium and the behaviour of helium in these bubbles [14–23]. As the relationship between the average helium density and the pressure in the bubble was found to be strongly altered with respect to bulk helium, new equations of state that take into account the helium/iron interface effects have been proposed for helium in nanobubbles [22,23].

The recent development of a ternary FeNiCr potential [24] opened the door to extending the atomistic studies to helium bubbles in metal alloys similar in structure and composition to some austenitic steels that are frequently used in the nuclear industry. The present work is a molecular dynamics study on the helium behaviour in nanosize bubbles in a face centred cubic (fcc) FeNiCr alloy at compositions similar to AISI-316 austenitic steels. We propose a simple equation of state (EOS) for helium in nanobubbles that takes into account the helium/steel interface effects. This equation is conceived to reasonably describe the helium in nanobubbles for helium densities in agreement with experimental observations and temperature–pressure conditions similar to those in the PWRs.

The paper is structured as follows: Section 2 details the models and methods employed in this study, Section 3 presents the steps taken to build the equation of state for helium in nanobubbles and the results of this study are summarized in Section 4.

2. Models and methods

2.1. Models for helium bubbles in steel

All the calculations presented here were carried out using 3D periodic boundary conditions. The pattern for the periodical model was

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built starting from a supercell of 15 × 15 × 15 fcc elementary cells. The fcc sites of this supercell were randomly filled with Fe, Ni and Cr atoms in order to satisfy two conditions:

- The alloy should exhibit an homogeneous distribution of its components (Fe, Ni, Cr) [25];
- The alloy composition (in weight %) should be: 12% Ni, 17.5% Cr and 70.5% Fe. This composition is similar to AISI-316, but also to some AISI-304 alloys [1].

The resulting system was a perfect fcc supercell, with the cell parameter $a = 5.325$ nm, containing 1530 Ni atoms, 2520 Cr atoms and 9450 Fe atoms. Therefore, the composition of the model system in Ni, Cr and Fe is 11.3 atomic %, 18.7 atomic % and 70 atomic %, respectively.

Cavities with different R_C radii ($R_C = 0.5$ nm to 1.5 nm) were carved by eliminating metal atoms in the middle of this supercell. The cavities were then filled with different numbers of helium atoms in order to cover a range of helium densities, from 20 nm^{-3} to 100 nm^{-3}. This helium density range is in agreement with the experimental findings. Indeed, an Electron Energy-Loss Spectroscopy (EELS) study of helium bubbles in a FeCr martensitic steel [26] found He densities ranging from 20 nm^{-3} (5 nm radius bubbles) to 70 nm^{-3} (2 nm radius bubbles). Another EELS study on a FeCr ferritic alloy [27] found a He density of 61.3 nm^{-3} in bubbles with radii of about 1.4 nm. Finally, a Positron Annihilation Spectroscopy (PAS) study [13], carried out on an austenitic steel of type 316, found a helium density of 56 nm^{-3} in bubbles with radii of about 4 nm.

Previous theoretical and experimental works showed that the gas density in bubbles trapped in a solid matrix cannot surpass a certain value. Beyond this density limit, the bubble volume increases by surface breaking, in the sense that some solid atoms on the bubble surface are pushed into the interstitial sites of the matrix [28,29]. This phenomenon leads to distortions at the solid surface. The surface breaking is followed by a phenomenon of emission of an interstitial dislocation loop (known under the name of loop punch-out mechanism) [29,30] that partially restores the perfect solid surface [17]. In the particular case of helium bubbles in perfect bcc Fe and FeCr alloys, the density limit value for which surface breaking occurs was estimated at 2 He/Vac (~170 nm^{-3}) [15,17]. However, the alloys under irradiation conditions contain a variable amount of vacancies that absorb at the bubble surface in order to establish the equality of their chemical potential at the bubble surface and in the bulk [21]. The vacancy absorption lowers the density limit at which the surface relaxation takes place. This could explain the fact that the experimental helium densities [26,27] are considerably lower than the theoretical limit estimated for these very systems [15,17].

2.2. Simulation methods

The systems created as previously described were relaxed through NPT (constant Number of particles, Pressure and Temperature) molecular dynamics (MD) methods [31] as implemented in the LAMMPS code [32].

The MD simulations were carried out at 500 K and 700 K for an external pressure of 0 GPa. This *T-P* range is very similar with the PWR conditions: temperature from 559 K to 603 K and a relatively low pressure of 0.0155 GPa.

A timestep of 0.2 fs was proved to be appropriate for this type of simulations [22]. The systems were relaxed during 1 ns (5×10^6 MD steps), then the results were accumulated over the next 5×10^6 MD steps at every 100 steps. Thus, for every case, one obtained a set of 50,000 instantaneous values. The properties of interest (pressure in the bubble, density and bubble radius) were then calculated as averages of these instantaneous values.

The pressure in the bubble was computed from the atomic stress tensor diagonal components (provided by LAMMPS in pressure * volume units [32]) of the helium atoms contained in the bubble and the bubble volume. The bubble volume was that of a sphere with the radius (R_B) being calculated as the arithmetic mean between a "cavity minimum radius" and a "cluster maximum radius". The "cavity minimum radius" was defined as the distance between the bubble mass center and the closest matrix atom (Fe, Ni or Cr) and the "cluster maximum radius" as the distance between the bubble mass center and the furthest (helium) atom in the helium cluster. Following this definition [33], the bubble/steel geometrical interface would be situated at the crossing point of the matter densities of the two phases.

2.3. Interatomic potentials

All the simulations were performed using semi empirical interatomic potentials to describe the three types of interactions that are present in the systems: the Fe-Ni-Cr interactions, the M-He (M = Fe, Ni, Cr) interactions and the He-He interactions.

For the Fe-Ni-Cr interactions one used a ternary embedded atom method (EAM) type potential [24]. This potential is able to well reproduce, with respect to Density Functional Theory (DFT) and experimental results, the stability of the fcc phase, the elastic constants and the stacking fault energies for model alloys with compositions similar to AISI-316L austenitic steels. Moreover, the potential provides the stability of the fcc phase for Fe-10Ni-20Cr under large shear strains (5%) in the temperature range from 0 K to 900 K.

The potentials proposed in reference [34] were used to describe the Fe-He and Cr-He interactions. Based on the pair potential formalism, these potentials were fitted in order to correctly reproduce, with respect to DFT results, the migration energies of helium in Fe and Cr and the formation energy of the substitutional and interstitial helium in tetrahedral and octahedral sites in Fe and Cr.

The potential describing the Ni-He interaction was fitted to a set of Ni-He interaction energies obtained by Melius [35] using the Hartree-Fock approximation. The form of this potential is given below:

$$V(r) = \begin{cases} \left(A + \frac{B}{r} + \frac{C}{r^2}\right)e^{-Dr} & r < r_i \\ P_3 r^3 + P_2 r^2 + P_1 r + P_0 & r_i \leqslant r \leqslant r_c \\ 0 & r > r_c \end{cases} \quad (1)$$

The potential parameters, together with the cutoff radii, are given in Table 1.

To our knowledge, two other Ni-He potentials have been recently proposed: one by Zhang et al. [36] and the other one by Torres et al. [37]. These two potentials are both able to well reproduce, with respect to DFT results, the incorporation energies of helium in substitution and interstitial tetrahedral and octahedral sites in Ni and the helium migration barrier between two tetrahedral sites. The Zhang potential coincides with our potential for $r > 0.1$ nm but tends to be less repulsive for $r < 0.1$ nm, while the Torres potential is much less repulsive. In a series of test calculations, the Ni-He potential used in the present work (referred to as Melius potential) was compared with the most different of the two previously mentioned potentials, the Torres potential. These test calculations showed practically no difference (see Table 2) between the bubble radii (R_B), average densities (ρ) and pressures in the bubble (P_B) calculated with the two Ni-He potentials.

A comparison [38] between two He-He potentials, the Ross-Young

Table 1
Parameters for the Ni-He potential used in the present work. The unit for energy is the electronvolt (eV) and the unit for distance is the angstrom (Å).

A (eV)	B (eV·Å)	C (eV·Å^2)	D (Å^{-1})	r_i (Å)
349.732	−917.546	727.518	2.54144	4.0
P_0 (eV)	P_1 (eV·Å^{-1})	P_2 (eV·Å^{-2})	P_3 (eV·Å^{-3})	r_c (Å)
3.71640E−1	−2.01704E−1	3.60846E−2	−2.12190E−3	5.0