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The diffusion of point defects in uranium mononitride: Combination of DFT and atomistic simulation with novel potential

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ABSTRACT

The properties of point defects in uranium mononitride (UN) are studied by *ab initio* calculations and molecular dynamics simulations with a new interatomic potential. Density functional theory (DFT) calculations are used for fitting of the parameters of the angular-dependent interatomic potential, as well as for evaluation of the defects formation and migration energies. Molecular dynamics (MD) simulations are applied to analyse what migration mechanisms are activated at finite temperatures and to calculate diffusion coefficients of point defects. It is shown that the U antisite defects play an important role in the U-rich UN_{1-x}. During migration the interstitial uranium is able to knock-out nitrogen atom, and this act leads to formation of U in antisite and N interstitial. This effect results in dependence of the diffusivity of U-interstitials on the concentration of defects in the N sublattice. Another peculiarity of UN is the large athermal concentration of U-vacancies in the N-rich UN_{1+x}. This is due to close formation energies of nitrogen Frenkel pairs and Schottky defects. In addition, the applicability of the new potential for description of various phase transitions in UN is discussed.

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1. Introduction

Uranium mononitride (UN) is proposed as one of the candidates for application as a fuel for Generation IV fast neutron reactors. This material combines advantages of different nuclear fuels, such as uranium alloys and UO_2. For example, UN has high melting temperature (about 3000 K) [1,2], together with high values of uranium density and thermal conductivity [3–5].

Changes of properties of the nitride fuel under the reactor irradiation [5–7] are relatively poor studied in comparison to uranium dioxide. The knowledge of defects diffusion mechanisms and stability of cubic mononitride phase UN_{1+x} should be useful for analysis of the fabrication conditions of fuel pellets and behaviour of the fuel in reactor. Moreover, diffusion coefficients of point defects and fission products are involved in mechanistic models for prediction of the fission products release and fuel swelling [8].

Phase diagram of the uranium-nitrogen system has been widely studied experimentally, many results are summarized in Refs. [1,9]. However, development of the thermodynamic model for non-stoichiometric UN [10,11] is severely limited due to a narrow area of homogeneity on *T-x* diagram and subsequent restrictions to measurements of the exact composition. In various works [12–15] the phase transitions taking place in UN at high pressure have been discussed, but the question about description of UN phase diagram remains open.

A small deviation of composition from exact stoichiometry U/N = 1 results in a large change of concentrations and/or type of the dominant point defects. Hence, significant alteration of U or N self-diffusion coefficient should be expected. However, experimental data for mixed uranium-plutonium nitride do not show strong dependence of the diffusivity on nitrogen partial pressure [16]. There is no defined model for components self-diffusion in such materials as nitrides, also the types of dominant defects are not quite clear.

Molecular dynamics simulation is a powerfull tool for study of physical properties of matter at the atomistic level [17–19]. However, the correct interatomic potential is needed to apply this method [20,21]. In 2000 Kurosaki et al. [22] have reported the pair interatomic potential (with using of Coulomb interaction) created for investigation of UN in atomistic simulations. This potential has been aimed on description of the thermophysical properties of UN but it has not taken into account the energies of defects which are

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important for consideration of the radiation damage. Furthermore, an interatomic potentials for the nuclear materials should describe behaviour of the matter in a wide range of pressures, temperatures and compounds [23–27]. In this work we develop a new interatomic potential for UN which reproduces thermodynamic and mechanical properties of this material, and at the same time describes basic energies of the point defects.

Energies of the point defects in UN crystal lattice have been studied previously in several works [28–31] by means of density functional theory. Various defects typical for ionic crystals have been considered. While UN may be classified as ceramic material, this matter is a metal with interesting electronic structure [32–34,13,35] and magnetic properties [36]. At the same time, several structures of point defects commonly appearing in metals and alloys have not been analysed for UN so far: split interstitials (dumbbell configuration) and substitutional defects. The data about formation energies of various point defects are significant and can be used in thermodynamic calculations of phase stability [10,11].

It should be noted that the present research is performed by means of DFT calculation together with molecular dynamics (i.e. atomistic simulation). In this combination of computational approaches one method discovers important features which must be taken into account when the other one is applied. Stochastic nature of MD (detailed discussion can be found in Ref. [37]) provides convenient way for analysis of the diffusion processes activated at finite temperatures. The developed interatomic potential becomes a bridge between DFT and MD approaches. In this manner, this study describes two basic levels (quantum and atomistic modelling) in the multiscale approach [38–41].

2. Development of a new interatomic potential

In this work we develop the interatomic potential for UN in the form of Angular-Dependent Potential (ADP) [42]. For ADP the total potential energy U is given by the following formula:

$$U = \sum_{i>j} \varphi_{\alpha\beta}(r_{ij}) + \sum_i F_\alpha(\overline{\rho}_i) + \frac{1}{2}\sum_{i,k}\left(\mu_i^k\right)^2 + \frac{1}{2}\sum_{i,k,l}\left(\lambda_i^{kl}\right)^2 - \frac{1}{6}\sum_i \nu_i^2, \tag{1}$$

where

$$\begin{aligned} \overline{\rho_i} &= \sum_{j\neq i} \rho_\beta(r_{ij}), \\ \mu_i^k &= \sum_{j\neq i} u_{\alpha\beta}(r_{ij}) r_{ij}^k, \\ \lambda_i^{kl} &= \sum_{j\neq i} w_{\alpha\beta}(r_{ij}) r_{ij}^k r_{ij}^l, \\ \nu_i &= \sum_k \lambda_i^{kk}. \end{aligned} \tag{2}$$

Here indices i and j enumerate atoms and superscripts $k, l = 1, 2, 3$ refer to the Cartesian components of vectors and tensors. Indices α and β are the element types of atoms. The first term in (1) represents interactions between atoms with a pair potential φ. The summation is over all j-th neighbours of i-th atom within the cutoff distance r_{cut}=6.2 Å. F is the embedding energy which is a function of the total electron density $\overline{\rho}$. The first and the second terms in (1) give principal contribution to the system energy. The μ and λ terms introduce non-central interactions through the dipole vectors and quadrupole tensors. They are aimed to penalize deviations of local environment from the cubic symmetry. All potential functions are represented as cubic splines. It should be noted that the potential used does not have long-range interactions.

The *force-matching* method [43] is used for the development of the potential, as implemented in the Potfit code [44]. This method provides a way to construct physically justified interatomic potentials from the fitting database which does not contain experimental data. The idea is to adjust the interatomic potential functions to optimally reproduce per-atom forces (together with total energies and stresses) computed at the *ab initio* level for a fine-tuned set of reference structures.

The reference data are calculated using the DFT code VASP 5.2 [45]. The reference structures contain approximately 200 atoms in a simulation box with periodic boundary conditions. The exact number of atoms depends on the phase structure, its density, and the number of defects included. The Brillouin zone is sampled with the 2×2×2 Monkhorst-Pack **k**-point mesh. The cut-off energy of a plane-wave basis set is 520 eV. We use projector augmented wave pseudopotentials included in the VASP package and the exchange-correlation functional within generalized-gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof. Fourteen electrons $6s^2 6p^6 5f^3 6d^1 7s^2$ for uranium and five electrons $2s^2 2p^3$ for nitrogen are taken into account as valence electrons.

For construction of the ADP we use 72 configurations containing 13845 atoms altogether. These configurations represent 6 structures of pure U (liquid and solid phases at different densities), 5 structures of pure N (gaseous and dense fluid phases) and 61 binary UN structures (including 35 configurations with concentrations deviating from the exact stoichiometry U/N = 1). All these atomic configurations have been taken from classical atomistic simulations at different temperatures and densities (for this purpose the potential from work [22] was applied at the initial step).

The fitting procedure consists of the following steps: (1) fitting the parameters of a new potential to the reference *ab initio* database; (2) testing the calculated potential with respect to certain properties (for example, lattice parameters, defect energies, melting temperatures); (3) recalculating the initial set of configurations with the fitted potential. This procedure is performed in an iterative manner in order to improve the description of the desired properties. The target function for minimization is given by the following sum:

$$Z = Z_f + Z_C, \tag{3}$$

$$Z_f = \sum_{i=1}^{N_f} \sum_{\alpha=x,y,z} W_i \frac{\left(f_{i\alpha}^{\mathrm{ADP}} - f_{i\alpha}^{\mathrm{DFT}}\right)^2}{\left(f_{i\alpha}^{\mathrm{DFT}}\right)^2 + \varepsilon_i}, \tag{4}$$

$$Z_C = \sum_{j=1}^{N_C} W_j \frac{\left(A_j^{\mathrm{ADP}} - A_j^{\mathrm{DFT}}\right)^2}{\left(A_j^{\mathrm{DFT}}\right)^2 + \varepsilon_j}. \tag{5}$$

The reference data are represented by per-atom forces f and integral characteristics A (one value of the energy and six components of the stress tensor for each configuration). Z_f and Z_C are two parts of the target function for forces and integral characteristics, respectively. N_f is the total number of atoms for which the forces are taken into account during the minimization. N_C is the total number of configurations. The values of ε_i and ε_j, both are small and positive, are necessary to avoid extremely small denominators (and consecutive large meaningless contributions) when the reference DFT value is too small. W_i and W_j are the weights attributed to different terms taking part in the potential optimization procedure. Index “DFT” denotes the reference values; “ADP” denotes the values computed with the fitted potential.

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