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Nuclear Instruments and Methods in Physics Research B 266 (2008) 2671–2675

NIM B
Beam Interactions with Materials & Atoms

www.elsevier.com/locate/nimb

First-principles modelling of radiation defects in advanced nuclear fuels

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Abstract

We present and discuss the results of the first-principles calculations of Frenkel defects and O impurities in uranium mononitride (UN) perspective for fast reactor nuclear fuels. Special attention is paid to the calculation of defect migration energies. We demonstrate that the *interstitialcy* mechanism (with the formation of a N–N dumbbell along the [1 1 1] axis) is energetically more favorable than the direct [1 0 0] hops. As a result, for the interstitial N ions we predict a diffusion mechanism similar to that known in isostructural fcc materials with a different chemical nature (KCl, MgO). The calculated effective N charge considerably depends on the ion position and environment (a host lattice site, interstitial or saddle point) which strongly limits the applicability of classical defect modelling based on formal invariant charges. Lastly, the calculated migration energy for the interstitial impurity O ions is quite low (2.84 eV), which indicates their high mobility and ability for reactions with other defects.

PACS: 61.66.Fn; 61.72.Bb; 61.72.Ji; 61.80.Az; 66.30.Lw

Keywords: Uranium mononitride (UN); Frenkel defects; O impurity; Defect migration; First-principles calculations; Supercell model

1. Introduction

Nuclear fuel safety, partitioning and transmutation, as well as the characterisation of spent fuel need better knowledge of the underlying basic mechanisms governing the behavior of the materials under irradiation conditions, as well as during storage after irradiation. The detailed understanding of the atomic and electronic structures and defect mobility under various conditions requires a *multi-time-scale modelling* approach. There is a great need to complement the available experimental/phenomenological methods by means of atomistic (nano-scale) techniques such as molecular dynamics (MD) or kinetic Monte Carlo (KMC), in combination with first-principles and semi-empirical static calculations. Since the availability and accuracy of the inter-atomic potentials, including those for multi-component compounds, represents a major issue for the application of atomistic techniques such as MD or KMC, it is essential to compare the results among various techniques and experiments for self-consistency and validation. The first-principles calculations are a key element here, to be used for potential fitting and testing of Shell Model (SM) and more refined Force Field (FF) and MD calculations. This, in turn, is essential for providing the updated correlations for materials properties that are used in the fuel performance codes (e.g. TRANSURANUS), and for which experimental data are rare or non-existing.

Defect modelling studies have been mostly performed for oxide fuels (mostly UO_2) over several decades, first using classical SM [1–3] and recently using first-principles quantum mechanical methods [4–6]. Metal nitride fast reactor fuels offer an enhanced performance as compared to the conventional oxide fuels, due to their higher intrinsic thermal conductivity, good sodium compatibility, and, in the case of fuel reprocessing, high solubility in nitric acid

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0168-583X/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2008.03.226

[7]. Consequently, in the frame of international projects such as the Generation-IV initiative, these types of fuels are receiving renewed attention. With EURATOM joining the forum, the Institute for Transuranium Elements (ITU) has restarted its activities in this field after a similar research was stopped in the mid 1980s. In particular, design and interpretation of experiments along with a detailed characterisation of both fresh and irradiated nitride fuels was resumed. These experimental activities need complementary theoretical modelling and analysis.

Pioneering first-principles non-spin-polarized calculations were performed for UN bulk by Brooks using LMTO approach [8]. Sedmidubsky et al. calculated the formation enthalpies of actinide nitrides on the basis of total energies found in WIEN2k code in the framework of 'APW+lo' method [9]. Recently, Evarestov et al. [10] performed the detailed spin-polarized LCAO calculations using Gaussian code with periodic boundary conditions. Recently we also performed several atomic scale first-principles calculations of UN-type fuels [11,12] using the density functional theory (DFT) combined with the plane wave basis set as implemented into the VASP and CASTEP computer codes. Both codes were able to successfully reproduce the basic properties of the pure UN, UN_2 and U_2N_3 (lattice constant, bulk modulus and cohesive energy). The calculated effective (Bader) charges [13] calculated for UN bulk using VASP are $\pm 1.6e$ which is indicative of the complex chemical bonding, with covalency contributions due to U and N orbital hybridization, also observed in the projected density of states (DOS). The calculated in the VASP code value of spin moment on U ions in the antiferromagnetic unit cell ($\sim 0.9\ \mu_B$) is close to the experimental value [14].

As the next step, we calculated in these papers [11,12] N and U vacancies (V_N and V_U) in a cubic UN at different concentrations. We found that N vacancies very slightly affect the UN lattice constant, even at concentrations as high as 25%. For this defect, the lattice response is confined to small inward displacements of the nearest-neighbour uranium ions and a very local defect-induced electronic density redistribution. The relevant decrease in a defective supercell volume (the *defect volume*) is quite small, around 3.5 $Å^3$. This value does not practically depend on the defect concentration.

Conversely, U vacancies induce somewhat larger (but still small) defect volumes (4.75 $Å^3$), which increase in magnitude as a function of defect concentration (up to 10.58 $Å^3$ at 25%). In this case, the nearest-neighbour nitrogen atoms are displaced outwards and the positive charge is distributed over the first- and (to lesser extent) second-neighbour atoms. The results of our simulations clearly indicate that nitride fuels are able to accumulate high defect concentrations under self-irradiation.

We also found that the formation energy of 4.6 eV for a pair of nitrogen Frenkel defects (vacancy-interstitials) is associated with a considerable lattice relaxation characterised by the energy gain of 2.3 eV. Unlike U and N vacancies, the interstitial N ions induce lattice *expansion* (the defect volume of 5.13 $Å^3$).

The Frenkel pair formation energy is larger, but close to the Schottky pair formation energy (3.8 eV), which means that both intrinsic vacancies and interstitial defects could make comparable contributions to the transport properties.

In this paper, we study in detail the migration mechanism and activation energy for the interstitial N ions. Since UN fuel always contains a considerable amount of O impurities resulting from its fast oxidation, we also modelled such O impurities at different positions (substitution for a host N ion or interstitial) and their migration.

2. Method

The DFT computer code VASP 4.6 [15] employing the formalism of projector augmented-wave (PAW) method including the plane-wave basis set, the Perdew–Wang-91 GGA non-local exchange-correlation functional [16] and the scalar relativistic PAW potentials representing the core electrons of U (with $6s^26p^65f^26d^27s^2$ valence shell), N ($2s^22p^3$) and O ($2s^22p^4$) atoms (containing 14, 5 and 6 valence electrons, respectively) were used. The plane-wave cut-off energy was set to be 400 eV sufficient for the pseudopotentials chosen. We used the Monkhorst–Pack integration scheme [17] for $8 \times 8 \times 8$ k-point mesh in the Brillouin zone.

For the UN rock-salt fcc structure, we considered supercells of different size, built by expanding the translation vectors of the primitive cell by $2 \times 2 \times 2$ (16 atoms), $3 \times 3 \times 3$ (54 atoms) and $4 \times 4 \times 4$ (128 atoms). After the analysis of the perfect UN properties, we placed defects in these supercells which differ by the inter-defect distances and thus interactions. In our spin-polarized calculations, both the local atomic structure (geometry) around a defect and the lattice parameter were optimized. The effective atomic charges were calculated using the topological Bader method [18].

3. Results

3.1. Interstitial N ions

One of the main parameters determining fuel performance is the concentration and mobility of defects. When Frenkel defects are formed, both vacancy and interstitial are mobile and could independently migrate in the lattice until these meet each other or meet other defects. Usually, interstitial anions in fcc crystals are more mobile than the vacancies. As known from the radiation physics of metal oxides and alkali halides [19], there are two possible migration paths for interstitial anions (Fig. 1): direct jumps from a cube center along the [0 0 1] direction with the face centre as the saddle point (Fig. 1(b)), or along the [1 1 1] direction with the dumbbell as the saddle point configuration (the so-called *collinear interstitialcy mechanism*). Such a N–N dumbbell is centered at a regular N site and could be in principle oriented along either [1 1 0] or [1 1 1] directions (Fig. 1(c), (d)).