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Ab-initio study of C and O impurities in uranium nitride

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ABSTRACT

Uranium nitride (UN) has been considered a potential fuel for Generation IV (GEN-IV) nuclear reactors as well as a possible new fuel for Light Water Reactors (LWR), which would permit an extension of the fuel residence time in the reactor. Carbon and oxygen impurities play a key role in the UN microstructure, influencing important parameters such as creep, swelling, gas release under irradiation, compatibility with structural steel and coolants, and thermal stability.

In this work, a systematic study of the electronic structure of UN containing C and O impurities using first-principles calculations by the Density Functional Theory (DFT) method is presented. In order to describe accurately the localized U 5*f* electrons, the DFT + *U* formalism was adopted. Moreover, to avoid convergence toward metastable states, the Occupation Matrix Control (OMC) methodology was applied.

The incorporation of C and O in the N-vacancy is found to be energetically favorable. In addition, only for O, the incorporation in the interstitial position is energetically possible, showing some degree of solubility for this element in this site. The binding energies show that the pairs ($C-N_{vac}$) and ($O-N_{vac}$) interact much further than the other defects, which indicate the possible occurrence of vacancy drag phenomena and clustering of these impurities in grain boundaries, dislocations and free surfaces. The migration energy of an impurity by single N-vacancy show that C and O employ different paths during diffusion. Oxygen migration requires significantly lower energy than carbon. This fact is due to flexibility in the U–O chemical bonds, which bend during the diffusion forming a *pseudo* UO_2 coordination. On the other hand, C and N have a directional and inflexible chemical bond with uranium; always requiring the *octahedral* coordination. These findings provide detailed insight into how these impurities behave in the UN matrix, and can be of great interest for assisting the development of this new nuclear fuel for next-generation reactors.

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1. Introduction

UN is considered as a potential fuel for Generation IV nuclear reactors (GEN-IV) [1,2]. It is an attractive fuel option due to the combination of high fissile nuclide density, high thermal conductivity, and its high melting point [3]. Additionally, it has been considered as a new fuel option for commercial Light Water Reactors, allowing a prolongation of the fuel residence time in the reactor, which enhances the economy of electricity production by the existing fleet [4]. However, UN powder is highly pyrophoric, which makes the fabrication process expensive due to the requirement of an inert atmosphere.

Nevertheless, due to the historical focus on UO_2 fuel, there is a significant lack of data about systems involving UN fuel. To pave the way for qualifying a UN fuel, a number of important issues must be addressed and better understood, e.g. creep, swelling, gas release under irradiation, compatibility with structural steel and coolants, and thermal stability. Previous experimental investigations of UN show that the level of C and O impurities can influence these parameters [5]. It was noted that in the concentration range of 0.1–0.15 wt% the presence of these impurity elements strongly increased the swelling. In higher concentrations (0.3–0.45%), carbonization of the inner surface of the cladding during the irradiation has been reported [6,7]. The mutual presence of C and O is hypothesized to be a catalyst for cladding carbonization [4], but an exhaustive explanation for this phenomenon is still missing. As a consequence, the C and O mass specification for the fuel was established to not exceed 0.15% for reliable operation of fuel elements [8], which significantly increases the difficulty in the development and establishment of a fabrication process.

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Moreover, there are also uncertainties regarding the influence of C and O on the fundamental properties of UN, such as the lattice parameter. Various experimental studies have reported that C impurities linearly increase the UN lattice parameter [9–11]. On the other hand, Muromura et al. [11] conclude that O does not influence this parameter (at least in the same range of concentrations as C, around 0.0–0.095 wt%). This can suggest that the UN structure can effectively accommodate O without building up significant (local) strain, but until now, there is no theoretical model to prove or disprove this hypothesis.

In order to understand such phenomena, an analysis at the atomic-scale perspective can provide critical answers. Presently, Density Functional Theory (DFT), including the Hubbard U formalism (DFT + *U*) [12–14] can be applied to correctly model the highly-localized and correlated electrons in UN. A review of existing literature reveals the existence of only a few theoretical investigations for the UN system [15–21], though none of them address, properly, the influence of C and O impurities. There have been previous studies for the effect of O, however, the calculations were not performed as correlated material [22–25] but, rather, with the standard general gradient approximation GGA. An extension using the DFT + *U* is thus highly motivated.

In this paper, a detailed investigation of the electronic behavior of C and O in the UN structure using the DFT + *U* formalism is presented. Incorporation energies are discussed on the basis of the thermodynamic preferences of the system. Calculations of binding energies are presented as an attempt to identify possible clustering trends. Furthermore, impurity transport is addressed in order to identify the possible diffusion mechanisms and evaluate the different behaviors of these elements in a dynamic system. The aim of this work is to contribute to the understanding of C and O behavior in UN, in a general effort of explaining some of the experimental observations described in the literature. The results presented here are also important for the development of the fabrication technology and fuel performance analysis of UN fuels.

2. Methodology

The DFT calculations were performed using the scalar relativistic projector augmented wave (PAW) and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [26,27], as implemented in the Vienna Ab Initio Simulation Package (VASP) [28–30]. In order to describe accurately the strong, on-site Coulomb repulsion among the localized U *5f*-electrons, the generalized gradient approximation + *U* formalism for the exchange-correlation term was adopted. Furthermore, the occupation matrix control (OMC) scheme, developed by Dorado et al. [31–33], was used to avoid convergence toward metastable states (for detailed information see ref. [34]). The *U* and *J* parameters were specified as 2 eV and 0.1 eV, respectively, since these values give rise to lattice parameter and magnetic properties in good agreement with experiments [15,35]. Here these parameters were adopted for all cases. In this way the application of the *U* and *J* values is an approximation, since the appropriate values may change slightly as a function of local non-stoichiometry. In light of the slight changes a small variation of *U* and *J* would induce, this approximation is considered reasonable.

The valence electrons explicitly treated in the calculations were $6s^2 6p^6 6d^2 5f^2 7s^2$ for U; $2s^2 2p^2$ for C; $2s^2 2p^3$ for N; and $2s^2 2p^4$ for O. The plane-wave cutoff was set to 600 eV. The simulations were performed using 64-atom and 216-atom supercells, for which 4 × 4 × 4 and 2 × 2 × 2 Monkhorst-Pack meshes [36] were used, respectively. The localized spins on the uranium ions were assumed to be ordered in an antiferromagnetic (AFM) single layering since this is the experimental configuration for UN below 53 K [37,38]. Spin-orbit coupling and non-collinear magnetic ordering effects were ignored in order to simplify the calculations.

The structural optimization was carried first allow the volume change which result in a slightly orthorhombic structure with lattice parameters: a = 4.9005 Å, b = 4.9722 Å and c = 5.0352 Å. The higher distortion is observed in the z-direction, aligned with the spins moments, in agreement with the experimental observation (tetragonal structure with c/a = 0.99935 at 4 K in experiments) [39]. The defects were then introduced, allowing for atomic relaxation with all symmetries removed but restraining the cell shape and the volume. The internal structural parameters were relaxed until the total energy was converged to at most 10^{-5} eV. The nudged elastic band (NEB) method [40,41] was employed for the evaluation of the migration barriers using three intermediate images. The cases simulated were vacancy and interstitial diffusion. In this way, the minimum energy path between two stable configurations could be determined.

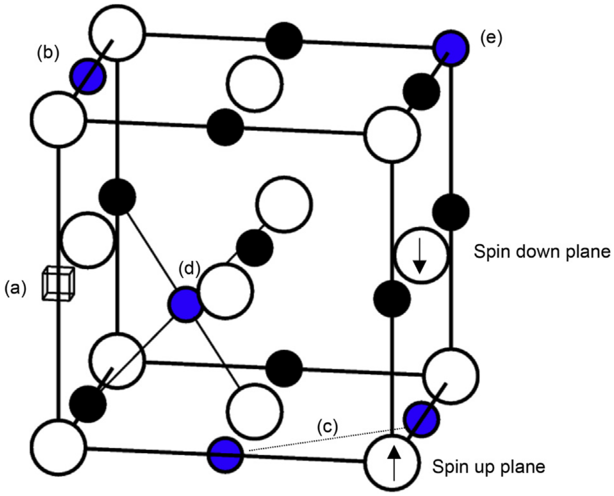

Fig. 1. UN unit cell illustrating the simulated defects; (a) N vacancy, (b) impurity in N position, (c) impurities in two nearest neighbor N sites, (d) impurity in interstitial position, and (e) impurity in U position.

Table 1
Incorporation energies (eV) of carbon and oxygen impurities in UN computed with the GGA + *U* formalism and OMC scheme. The references states used are the chemical potential of graphite, N_2 (g), and O_2 (g). Negative values indicate the energetically favorable incorporation.

Defect	Formation energy (eV)	Incorporation energy (eV)
N_{vac}	2.27	–
C_N		−3.22
O_N		−5.90
C_N–O_N 1 nn		
Same spin		−8.90
Opposed spin		−8.89
C_N–C_N 1 nn		
Same spin		−6.25
Opposed spin		−6.49
O_N–O_N 1 nn		
Same spin		−11.68
Opposed spin		−11.78
N_{int}		1.69
C_{int}		1.45
O_{int}		−2.71
N_U		Not stable[a]
C_U		Not stable[a]
O_U		Not stable[a]

[a] Relaxed to another position.

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