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Investigation of the influence of off-stoichiometry on the radiation damage evolution in uranium dioxide

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ABSTRACT

The work presented herein brings in valuable contribution to the study of radiation damage in uranium dioxide. In particular, the effect of off-stoichiometric compositions on the damage evolution during a displacement cascade has been investigated, which appears to be a novel study, to the best of literature review achieved. The study has been performed by means of molecular dynamics simulations and, using a powerful tool developed for the purpose, the damage has been analysed thoroughly as cascade-induced point defects and point defect clusters. The results have revealed first of all that the composition does not affect the damage development in the time frame corresponding to the thermal spike. Second of all, as the displacement cascade relaxes and persistent damage shows up in the structures, the results have indicated that off-stoichiometric compositions induced mitigation or even recovery of the damage created by the cascade, due to different mechanisms that depend on the nature and the amount of initial point defects distributed in the material due to off-stoichiometry. Third and last of all, it has been observed that the clustering behaviour in off-stoichiometric structures is also affected accordingly, and overall, the results have evidenced the formation in hyper-stoichiometric structures of interstitial clusters referred to as "split-interstitial clusters", as alluded to in other very recent studies.

1. Introduction

Uranium dioxide (UO_2) is used as fuel material in most of the commercial nuclear power plants currently in operation worldwide. During its lifetime in the reactor, it has to perform safely for years under severe conditions of radiation damage. The damage results mostly from either the energy losses of the recoiled fission fragments by nuclear (not electronic) interactions with the atoms constituting the UO_2 host lattice or their occasional collisions with fast neutrons from fission events. The main consequences are the accumulation of fission products in the fuel matrix and the creation of highly defective structures that affect strongly the properties of the fuel, e.g. grain size, porosity, stoichiometry, thermal properties, or fission product capture (Whapham and Sheldon, 1963; Matzke et al., 2000). In addition to these in-service issues, radiation damage also arises from the radioactive decay of fission products, mainly α-decay and to a lesser extent β- and γ-decay. The importance of such decay processes lies mainly in the prediction of the long-term behaviour of spent fuel when it is disposed as waste (Staicu et al., 2010; Kato et al., 2009). Thus, for optimal and safe operation and storage, it appears capital to have a thorough knowledge of the degradation behaviour of UO_2 under irradiation. Although experimental studies over the last decades have largely addressed this issue, mainly from an engineering point of view, they could unfortunately not provide a fundamental understanding of radiation damage processes and mechanisms. These are important due to safety and economic issues, especially the research on the microstructural evolution of fuel at high burnups or the development of new fuel types. This limitation is due to the lack of techniques that can probe the typical time (picoseconds) and length scales (nanometres) of the elementary processes driving the damage evolution. Molecular dynamics (MD) simulations have already proved to be a versatile tool for accessing these scales. In this way, they provide detailed information about the elementary steps of the individual processes involved (Stoller, 2012).

Yet, to the best of our knowledge, all the related MD studies on radiation damage in uranium dioxide (van Brutzel et al., 2003; van Brutzel et al., 2006; van Brutzel and Rarivomanantsoa, 2006; van Brutzel and Vincent-Aublant, 2008; van Brutzel et al., 2009; Devanathan et al., 2009; Martin et al., 2009, 2011, 2010) have only been considering so far stoichiometric $UO_{2.00}$. It is known, however, from thermodynamic data (Guéneau et al., 2012), that UO_2 is mostly found in off-stoichiometric compositions. The hyper-stoichiometric UO_{2+x}, with an off-stoichiometry in the range

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$0 \leq x \leq 0.25$ is the predominant oxide under normal operating conditions, but the formation of oxide phases of higher off-stoichiometry like U_4O_9, U_3O_8, or UO_3 is also possible according to the phase diagram. The hypo-stoichiometric oxides UO_{2-x} can also form, especially at very high temperatures. Their off-stoichiometry lies generally in the range $0 \leq x \leq 0.05$, but even oxides like $UO_{1.67}$ form at ~2800 K.

In this work, MD simulations using the CP2K program package (CP2K Developers Group, 2000–2013) have been performed in order to fully characterize the radiation damage induced in the bulk off-stoichiometric $UO_{2\pm x}$ structures. More precisely, for each defective structure, the formation and evolution of all point defects (vacancies and interstitials) and their corresponding clusters have been described in detail during all stages of the displacement cascade. This has allowed, by contrasting the results obtained among them or with those obtained in stoichiometric structures, to gain more insight into the behaviour of uranium dioxide lattice under irradiation.

2. Computational methodology

The study presented herein has been conducted using the rigid-ion potential of Morelon et al. (2003), which has been primarily designed for the specific purpose of cascade simulations. The analytical form of the potential consists of a Buckingham-type term for the non-bonded interactions attached to the Coulomb potential, as detailed in Devynck et al. (2012) and Krack, (2012). In addition, the repulsive potential proposed by Ziegler et al. (1985) has been smoothly joined to avoid unphysical attractions between very close atoms as this may easily happen during a displacement cascade simulation.

The radiation damage investigated corresponds to the distribution of point defects (PD) and their corresponding clusters after a displacement cascade. The latter has been initiated in simulation boxes that have been thermalized for 20 ps at 1000 K and 0 GPa. Thereafter 10 keV of kinetic energy has been transferred to a uranium primary knock-on atom (PKA) solely in the <111> direction as earlier studies have not found any anisotropy effects in uranium dioxide (van Brutzel and Rarivomanantsoa, 2006). Moreover, the chosen PKA energy is enough to model the important features arising from a displacement cascade, since high energy PKAs induce branching into sub-cascades of smaller energies (Stoller, 2012). Termination of the cascades has been considered as soon as the average temperature of the sample has reached the target temperature of 1000 K, i.e. the PKA energy has been dissipated to a thermal region of ~0.55 nm thickness at the box walls. Within this region the temperature has been kept at 1000 K using velocity rescaling in order to absorb the excess kinetic energy arising from the cascade.

Because the simulation boxes considered embed periodic boundary conditions (PBC) to mimic the material bulk, it is capital to ensure that the displacement cascade develops within these boundaries to avoid unphysical self-interaction of the cascade. In this respect cubic simulation boxes with an edge length of ~23 nm have been used. The off-stoichiometric structures have been constructed based on the stoichiometric $UO_{2.00}$ structure either by randomly adding interstitial oxygen atoms in octahedral lattice sites (hyper-stoichiometric) or by randomly creating oxygen vacancies (hypo-stoichiometric). A delicate issue in MD simulations of off-stoichiometric structures is the treatment of the high negative or positive charge of the sample yielded by adding or removing oxygen ions, respectively. In order to counterbalance this charge for maintaining the overall charge neutrality of the simulation cell, the charge compensation model creating a uniform neutralizing background charge being smeared out over the whole simulation cell has been used, as it is provided in the framework of the Ewald method.

The damage production and evolution during the cascade has been analysed based on the identification of all the PD created in the box. For this purpose, an efficient tool has been developed that is capable of detecting unambiguously for each time step all individual PD formed and further performing cluster analysis. For the detection of PD, the tool is based on a Wigner-Seitz cell approach and allows to identify defects of type interstitial (isolated in an octahedral site or paired with a normal lattice atom in a dumbbell), vacancy, or antisite, as depicted in Fig 1.

The search for defect clusters is based on first nearest neighbour (1nn) criterion for the analysis and allows the identification of three groups of clusters shown in Fig 2:

- Interstitial clusters form when isolated interstitials and/or dumbbells of uranium and/or oxygen are connected in a network in which each species is at least 1nn to one of the others. Fig 2 highlights for example an interstitial cluster formed between two dumbbells and one isolated interstitial.
- For vacancy clusters, the same rule applies but between uranium and/or oxygen vacancies. Fig 2 shows an example of such cluster, formed in this case between three uranium and two oxygen atoms.
- New features, referred herein to as split-interstitial clusters (SIC). They have been revealed by recent *first-principle* studies (Geng et al., 2008; Andersson et al., 2009, 2012). The split di-interstitial as depicted in Fig 2 has been obtained as the stable cluster stemming from the relaxation of the structure known as Willis 2:2:2 cluster, which appears to be metastable. It can be described as a triangular oxygen cluster located in the (111) plane and centred in the vicinity of an oxygen vacancy with which it forms a tetrahedron. In this work, the possibility of SIC formation consisting of four neighbouring oxygen interstitials has also been considered, in which case the oxygen vacancy would be located at the centre of the pyramid formed by the four interstitials. Finally, it is also considered that such SIC can further cluster and form larger aggregates.

3. Results and discussion

The objective of this study is to investigate the main effect of defective structures on the formation and evolution of PD and their corresponding clusters during a displacement cascade event. In this respect, for identical conditions of simulation, the results obtained in stoichiometric $UO_{2.00}$ have been compared with those obtained in two hypo-stoichiometric structures, $UO_{1.95}$ and $UO_{1.99}$, and four hyper-stoichiometric structures, $UO_{2.01}$, $UO_{2.05}$, $UO_{2.10}$, and $UO_{2.15}$. In order to reduce statistical errors, several simulations have been conducted for each stoichiometric composition in the scheme presented in Table 1, except for $UO_{2.10}$, and $UO_{2.15}$. The most important issue as regards off-stoichiometric structures has been to estimate at best the fraction of PD and clusters presumably generated by displacement cascades only. Indeed, as a substantial number of PD (and also clusters in some cases) are present in the simulation boxes of these structures prior to the cascade and dynamically evolve during the cascade, unambiguous identification of the effects strictly ascribed to the cascade is therefore very difficult to achieve. In this work, the assumption has been made that the impact due to the initial distribution of defects in simulation boxes to account for off-stoichiometry is, on average, the sum of this initial number of defects and eventually the mean number of additional defects formed at the end of the relaxation phase. Concerning defect clusters, the impact has been assumed equal on average to the mean number of clusters found in simulation boxes