Journal of Nuclear Materials 467 (2015) 1–8

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Lattice location and annealing behaviour of helium atoms implanted in uranium dioxide single crystals

T. Belhabib [a, *], P. Desgardin [a], T. Sauvage [a], H. Erramli [b], M.F. Barthe [a], F. Garrido [c], G. Carlot [d], L. Nowicki [e], P. Garcia [d]

[a] CNRS, UPR3079 CEMHTI, Université d'Orléans, 3A rue de la Férollerie, 45071 Orléans Cedex2, France
[b] Université Cadi Ayyad, Faculté des Sciences Semlalia - Avenue du Prince My Abdellah, BP 2390 Marrakech, Morocco
[c] CSNSM, CNRS-IN2P3-Université Paris-Sud, Bâtiments 104-108, F-91405 Orsay Campus, France
[d] Commissariat à l'Energie Atomique (CEA), Centre de Cadarache, CEA/Cad/DEC, 13108 St-Paul-lez-Durance, France
[e] National Center for Nuclear Research, A. Soltana T, 05-400 Otwock, Poland

ARTICLE INFO

Article history:
Received 30 March 2015
Received in revised form
30 August 2015
Accepted 1 September 2015
Available online 4 September 2015

Keywords:
Uranium dioxide
Helium
Lattice location
Nuclear reaction analysis
Rutherford backscattering spectrometry
Interstitial octahedral site
Monte-Carlo simulation

ABSTRACT

Helium behaviour in irradiated uranium dioxide may play an important role in the mechanical stability of nuclear fuels during and after its use in nuclear power plants. Helium migration mechanisms in bulk UO_2 have already been the subject of theoretical studies but there is a lack of experimental data relating to the most stable location in the crystal. To this end, we have studied uranium dioxide samples implanted with helium ions at low fluence before and after thermal annealing in the range 600 and 800 °C. UO_2 single crystals were implanted with 50 keV ^{3}He ions at the fluence of 1×10^{15} at cm^{-2} and the location in the lattice of helium atoms was investigated using NRA (Nuclear Reaction Analysis) based on the reaction of ^{3}He with deuterons (^{3}He (d,p) ^{4}He) in a channelling mode, recording angular scans across axes and planes. Furthermore, the uranium sub-lattice was analysed by the classical RBS method. After implantation, the experimental angular scans recorded across the main crystallographic axes and along major planes show that the helium atoms in their large majority occupy octahedral interstitial sites. No modification of the occupied crystallographic site was found after annealing at 600 °C. Conversely, no crystallographic relationship between matrix and helium signals was revealed following annealing at 800 °C. The latter feature is likely related to the clustering of implanted helium atoms into gas-filled bubbles. These experimental results have been quantified and interpreted using Monte Carlo simulations with the McChasy code.

1. Introduction

During disposal and/or ultimate storage, uranium dioxide fuels may contain significant amounts of helium, generated through radioactive decay of actinides produced during the irradiation process [1–3]. Minor actinides incineration and utilization of plutonium as a fissile material in the future generation of reactors (Generation IV) will produce even more helium. In addition, after 10000 years of storage, helium concentrations in nuclear fuel are expected to reach up to 0.7 at % in UO_2 and about 4% in MOX (Mixed Oxide Fuel) [4,5]. Because of its very low expected solubility, helium may precipitate and form more stable gas-filled bubbles which in turn may cause the material to swell triggering concerns about ageing of the fuel and its mechanical integrity [1]. Experimental study performed by Wiss et al. [6] showed that the accumulation of helium will produce bubbles that result in much larger gaseous-induced swelling that substantially increases the stresses in the constrained spent fuel. Insight into diffusion mechanisms of helium in the matrix can be gained from determining the position of helium atoms in the crystal and characterizing the presence and behaviour of other defects such as vacancies [7]. Although much work has been carried out in recent years [4,8,9], data available in the literature on helium behaviour in UO_2 are still scarce if one wishes to model in-reactor ageing of the material or extrapolate its behaviour to long-term storage situations. In this regard, the determination of the location of helium atoms in the crystal structure is a key parameter for evaluating the possible migration processes in the solid.

* Corresponding author. 10 bis rue Jacques groslot 45000, Orleans, France.
E-mail address: tayeb.belhabib@gmail.com (T. Belhabib).

http://dx.doi.org/10.1016/j.jnucmat.2015.09.001
0022-3115/

Unlike fission products that require a larger space for their incorporation, helium should be easily introduced into a UO_2 matrix [10]. In general, three sites liable to accommodate helium atoms have been studied theoretically [10–14]: the octahedral interstitial site (IOS), the uranium (VU) and oxygen (VO) vacancy sites. The first atomistic modelling efforts which could provided an estimate of helium incorporation energies in UO_2 were performed in the early nineties by Grimes and al [14]. The development of *ab initio* methods has since allowed more precise estimates of the most stable sites for helium atoms in UO_2. Incorporation energies found in the literature vary substantially from one study to the other. Furthermore to our knowledge, all *ab initio* studies involving helium behaviour have been carried out using standard DFT which notoriously fails to provide an accurate description of the electronic structure of actinide oxides. This is a very important point because methods which go beyond standard DFT such as the DFT + U approximation provide extremely different defect formation energies and enable charged defect calculations to be carried out [15,16]. According to the study by Freyss et al. [12], the most stable site is the octahedral site which has a negative incorporation energy estimated at −0.1 eV. These values and those from other studies [10,11,17] should not be taken literally. Qualitatively however, they generally show that incorporation energies are low at IOS but they are even lower at uranium vacancy sites. From an experimental standpoint, we know little about helium incorporation sites in UO_2 since only one experimental study was conducted on this topic by Garrido et al. [7]. The authors analysed an as-implanted single crystal using channelling techniques. This work showed that He implanted at 100 keV and at a fluence of 10^{16} at cm^{-2} in UO_2 is predominantly located at octahedral sites. It is worth emphasizing that so far no experimental study has been conducted on the evolution of helium location in UO_2 as a function of temperature.

This paper focuses on the effects of temperature and annealing on the behaviour of helium in uranium dioxide. The characterization of the location of helium atoms and of damage on the uranium sublattice are performed using the ^{3}He (d,p) ^{4}He nuclear reaction and Rutherford Backscattering Spectrometry (RBS) respectively. Both techniques are applied in a channelling mode. Processes associated with damage induced through helium implantations and thermal annealing thereof are investigated. In two UO_2 single crystals implanted with low energy (50 keV) He^+ ions and further annealed at two different temperatures (600 and 800 °C) the location of helium was studied as a function of temperature. The results were quantified and interpreted by Monte-Carlo simulations. The crystal lattice was visualized using the Diamond software [6]. We first describe the experimental procedures which includes UO_2 single crystal preparation and implantation along with the procedure for crystal alignment along the main axes and planes. Results obtained on an as-implanted crystal are provided in the second part. Lastly helium lattice location as function of temperature is described and discussed based on simulations of the experimental data carried out with the McChasy software [18].

2. Experimental

Three good quality (O/U ~ 2.0) square shaped UO_2 single crystals with dimensions of 5 × 5 mm^2 and a thickness of approximately 220 μm, were cut from a large uranium dioxide single crystal block 15 mm long, 8 mm wide and 20 mm thick. They were oriented along the main <111> crystallographic axis. Samples were subsequently mechanically polished to a mirror finish on the face to be subsequently analysed and then annealed under Ar/H_2 for 24 h at 1700 °C at CEA Cadarache to restore the stoichiometric composition and to recover any damage left over from the polishing stage. Then, specimens were implanted with 50-keV ^{3}He ions at fluence of 10^{15} at cm^{-2} using the IRMA ion implanter located at CSNSM/CNRS, France. The implantations were achieved by focussing a ^{3}He + beam on a support, where the three samples were disposed, and by sweeping it over the entire surface to ensure homogeneously distributed helium fluence. The average implantation current is estimated at 13 μA with a flux of 5.2 × 1011 at cm^{-2} s^{-1}. In order to prevent overheating of the crystals the temperature throughout the implantation was maintained below 80 °C using a water cooling system.

The SRIM 2008 simulations [19] predict that the ^{3}He projected range is roughly 180 nm and that all ions are implanted at depths ranging from 0 to 400 nm. The maximum ^{3}He concentration, calculated at the maximum of the distribution is about 0.064 at % (see Fig. 1). Such a low concentration was chosen as a compromise between the need to avoid excess damage to the matrix, radiation induced migration and precipitation of He (as is observed above 1% atomic concentration [20]) and the requirement for satisfactory statistics in relation to the ^{3}He(d,p)^{4}He reaction in a reasonable timeframe. The maximum damage to the UO_2 lattice amounts as estimated from SRIM was 0.031 dpa at a depth of 170 nm.

The two crystals were subsequently annealed at 600 °C and 800 °C under vacuum in the DIADDHEM [21] setup at CEMHTI-Orléans, France. This device was also used to perform He-TDS (thermal desorption spectroscopy) measurement. The sample was introduced into the device to undergo a heat treatment to 1000 °C under high vacuum. During the annealing stage, helium atoms are likely to migrate to free surfaces when they are released from the samples. The concentration of helium atoms remaining within the sample is measured using the ^{3}He(d,p)^{4}He nuclear reaction. To this end, a 550 keV deuteron beam is used normal to the sample surface, 20 nA in intensity and covering an area of approximately 2 × 2 mm^2. The temperature at the sample surface was regulated using an infrared pyrometer. The protons forward emitted over 15 MeV have a sufficient energy to be transmitted through the samples and are collected by a large solid angle detector (1200 mm^2) located at 0° of the beam direction, at 90 mm from the rear of the sample. The relative He release rate is then deduced from the proton counting during annealing compared with the proton counting performed before annealing. The analysis time required to reach counting statistics with a relative error of 5% was 60 s.

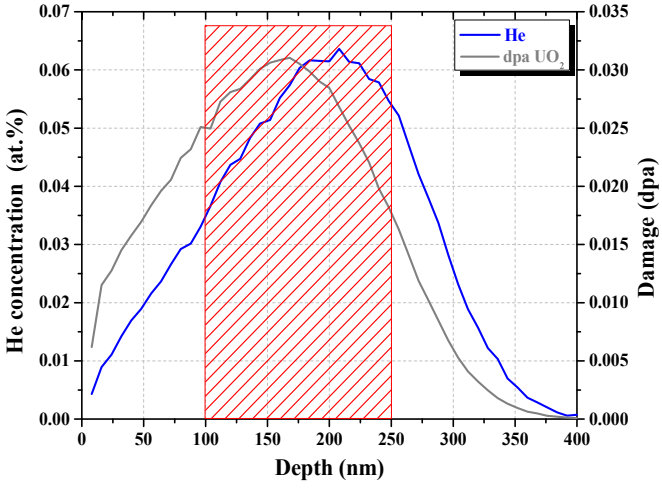

Fig. 1. He concentration and dpa depth profiles in uranium dioxide implanted with 50 keV ^{3}He ions at 1 × 10^{15} at cm^{-2} obtained by using SRIM software. The 'ion distribution and quick calculation of damage' mode has been utilized. (E_d(U) = 40 eV and E_d(O) = 20 eV [21]).