Krypton and Helium Irradiation Damage in Yttria-stabilised Zirconia

M. Gilbert¹, C. Davoisine², M. Stennett³, N. Hyatt³, N. Peng⁴, C. Jeynes⁴, W. E. Lee¹

¹Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, Exhibition Road, London, SW7 2AZ, UK.

²Laboratoire de Réactivité et Chimie des Solides, CNRS-UMR 6007, Université de Picardie Jules Verne, 33 rue Saint-Leu, 80039 Amiens, France.

³Immobilisation Science Laboratory, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield, S1 3JD, UK.

⁴Surrey Ion Beam Centre, Nodus Laboratory, University of Surrey, Guildford, Surrey, GU2 7XH, UK.

ABSTRACT

A candidate matrix material for inert matrix fuel (IMF), yttria-stabilised zirconia (YSZ) has been doped with Nd³⁺ as a surrogate for Pu³⁺. In order to simulate and assess the effects of fission gas accommodation and alpha decay on the microstructure, samples of (Y_{0.1425},Nd_{0.05},Zr_{0.8075})O_{1.904} have been irradiated with 2 MeV ³⁶Kr⁺ ions at fluences of 1×10¹⁴ and 5×10¹⁵ cm⁻² and 200 keV ⁴He⁺ ions at fluences of 1×10¹⁴, 5×10¹⁵ and 1×10¹⁷ cm⁻². TEM analysis of thin sections prepared by focussed ion beam (FIB) milling revealed damage was only observable at the highest fluence for both (5×10¹⁵ cm⁻² for ³⁶Kr⁺ ions and 1×10¹⁷ cm⁻² for ⁴He⁺ ions). Monte Carlo simulations using the TRIM code show that it is only at these fluences that the level of atomic displacements is sufficient to result in defect formation within the material.

INTRODUCTION

The use of inert matrix fuel (IMF) in either thermal or fast reactors has emerged as the most promising method of maximising plutonium burn-up within a reactor, and so gaining better control over waste stockpiles. IMF is certainly more competitive than mixed-oxide fuel (MOX), which will only produce sufficient plutonium burn-up in fast reactors [1], and although the increased plutonium burn-up will result in the increased production of minor actinides the overall radiotoxicity of the spent fuel cores would be significantly less than for UO₂ or MOX [2].

In such a fuel system, the plutonium carrier is an ‘inert matrix,’ that is, a neutron-inactive or neutron-transparent compound [3]. Candidate IMFs can be broadly divided into two categories: heterogeneous particle fuels, where the plutonium is embedded in the inert matrix, such as with molybdenum, ferritic steels and spinels; and homogeneous fuels, where the plutonium forms a solid solution with the inert matrix, such as with zirconium oxides and yttria-stabilised zirconia (YSZ) [4]. The inert matrix must give the fuel stable mechanical behaviour under irradiation and as such must display high thermal conductivity and good pile performance for swelling, fission gas release and pellet-cladding interaction.

Although development of such fuel is still at an early stage, LWR tests of Pu-IMFs have shown marked increases in the burn-up of plutonium compared to MOX. Zirconia-based Pu-IMFs have achieved plutonium consumption rates of up to 142 kg/TWhe, although the thermal conductivity of zirconia-based fuel is less than half that of UO₂ [5]. Stable behaviour of multi-

phase fuel based on (Y,Pu,Zr)O₂ solid solution (11.1 wt.% PuO₂), MgAl₂O₄ and Al₂O₃ has been demonstrated at burn-ups of 184, 192 and 237 GWd/m³ [6] and single-phase fuel based on (Er,Y,Pu,Zr)O_{2-x} solid solution has demonstrated behaviour under irradiation comparable to that of MOX [7].

As an IMF candidate, YSZ has demonstrated an exceptionally high resistance to radiation damage, remaining crystalline at doses well beyond those at which other ceramic materials become amorphous. Irradiation effects of I⁺, O⁺, Pt⁺, Sr⁺, Fe⁺, Ti⁺, Ag⁺, Cs⁺ and Xe⁺ ions have all been reported, with evidence of amorphisation observed only when the implanted ion forms precipitates [8-14]. Its excellent neutronic properties have lead to its use in the reflector segments of the Belgium MYRRHA accelerator driven system (ADS) for minor actinide transmutation [15]. Further work is now needed asses the effects of both helium and fission gas accommodation on the microstructure.

EXPERIMENTAL DETAILS

Sample Preparation

Samples of yttria-stabilised zirconia (YSZ), (Y_{0.1425}Nd_{0.05}Zr_{0.8075})O_{1.904}, doped with Nd³⁺ as a surrogate for Pu³⁺, were prepared at the Immobilisation Science Laboratory of the University of Sheffield in accordance with methods described by Stennett *et al* [16]. The samples were cut and polished to obtain a flat planar surface and then thermally annealed in air over a range of temperatures and dwell times in order to release the strain induced by the polishing and ensure sample stoichiometry.

Ex-situ Irradiation

Sample irradiation was performed at the Surrey Ion Beam Centre using a 2 MV High Energy Implanter. Samples were implanted with ³⁶Kr⁺ (2 MeV) ions at fluences of 1×10¹⁴ and 5×10¹⁵ cm⁻² using an implantation current of 0.2 μA/cm² and ⁴He⁺ (200 keV) ions at fluences of 1×10¹⁴ using an implantation current of 0.2 μA/cm² and at 5×10¹⁵ and 1×10¹⁷ cm⁻² using an implantation current of 1 μA/cm².

Characterisation

For TEM examination, sample sections were prepared by Focussed Ion Beam (FIB) milling using an FEI Helios Nanolab 600 dual beam FIB operating with a gallium beam at 30 keV. Samples were first coated with a gold layer (~ 30 nm) to avoid charging effects and to protect the surface from initial ion scanning. Inside the FIB chamber, a platinum layer of approximately 1.5 μm was deposited on the area of interest to protect the surface from damage induced by milling and scanning. The sample was then progressively milled until a ~100 nm thick electron transparent section was obtained. *Ex-situ* lift out was performed using a micromanipulator and a thin glass needle created by localised heating of a glass tube and the FIB sections were mounted onto copper grids covered with a holey carbon film for use in the microscope.

Microstructural characterisation and electron diffraction patterns were obtained through transmission electron microscopy (TEM) using a JEOL 2010 microscope operating at 200 kV.

TRIM Calculations

Ion and damage distributions were determined by Monte Carlo simulation using the Transport and Range of Ions in Matter (TRIM) code, included in the SRIM2008 package. All calculations were performed in “Detailed Calculation and full Damage Cascades” mode with a total layer depth of 1.5 μm and the displacement energies for all elements were fixed at 40 eV. The total vacancies created were then used to calculate the number of displacements per atom (dpa) at depth throughout the irradiated regions of the samples.

RESULTS

$^{36}\text{Kr}^+$ Irradiated YSZ

Figure 2 shows a TEM section of Nd-doped YSZ irradiated with 2 MeV $^{36}\text{Kr}^+$ ions at fluences of 1×10^{14} and $5 \times 10^{15} \text{ cm}^{-2}$. Whilst the sample irradiated at $1 \times 10^{14} \text{ cm}^{-2}$ shows no visible signs of damage, the sample irradiated at the higher fluence of $5 \times 10^{15} \text{ cm}^{-2}$ displays a region of damage resulting from atomic dislocations (a) extending to a depth of $\sim 1 \mu\text{m}$ from the surface, although not at sufficient level to cause any amorphisation of the material, as can be seen from the accompanying diffraction patterns.

Figure 1. TEM sections of Nd-doped YSZ irradiated with 2 MeV $^{36}\text{Kr}^+$ ions at fluences of 1×10^{14} (left) and $5 \times 10^{15} \text{ cm}^{-2}$ (right). Sample irradiated at higher fluence ($5 \times 10^{15} \text{ cm}^{-2}$) shows damaged region, a, extending to a depth of $\sim 1 \mu\text{m}$ from the surface, but no evidence of amorphisation.

TRIM simulations of the *ex-situ* irradiation show a good correlation with the experimental observations. Figure 2 shows the dpa vs. depth profile of Nd-doped YSZ irradiated with 2 MeV $^{36}\text{Kr}^+$ ions at a fluence of $5 \times 10^{15} \text{ cm}^{-2}$, showing a maximum dpa of 9.03 at a depth of 0.51 μm , compared to a maximum dpa of 0.18 at the same depth in the $1 \times 10^{14} \text{ cm}^{-2}$ sample, before dropping to a dpa of 0.55 at a depth of 1 μm , where the region of damage observed in the FIB sections ends.

Figure 2. dpa vs. depth profile of Nd-doped YSZ irradiated with 2 MeV $^{36}\text{Kr}^+$ ions at a fluence of $5 \times 10^{15} \text{ cm}^{-2}$, showing a maximum dpa of 9.03 at a depth of 0.51 μm .

$^4\text{He}^+$ Irradiated YSZ

Samples irradiated at the lower two fluences of 1×10^{14} and $5 \times 10^{15} \text{ cm}^{-2}$ show no observable signs of either damage or helium accumulation. Only in the sample irradiated with the highest dose of $^4\text{He}^+$ ions, a fluence of $1 \times 10^{17} \text{ cm}^{-2}$, is any change observed. TEM examination of the FIB section shows a dense cluster of defects at a depth of $\sim 0.37 - 0.73 \mu\text{m}$ from the sample surface, as shown in figure 3.

Figure 3. TEM sections of Nd-doped YSZ irradiated with 200 keV $^4\text{He}^+$ ions at a fluence of $1 \times 10^{17} \text{ cm}^{-2}$. Enlarged region, a, shows a dense defect cluster 0.37 – 0.73 μm from the surface.

TRIM simulations of the *ex-situ* irradiation are again in good correlation with the experimental observations, showing maximum dpa's of 0.003, 0.13 and 2.51 for irradiation with fluences of 1×10^{14} , 5×10^{15} and $1 \times 10^{17} \text{ cm}^{-2}$ respectively, all at a depth of 0.62 μm . Figure 4 shows the dpa

vs. depth profile of the sample irradiated at a fluence of $1 \times 10^{17} \text{ cm}^{-2}$, showing a dpa of ≥ 1 within the damaged region $0.37 - 0.73 \text{ }\mu\text{m}$ from the surface, beginning with a dpa of 0.98 at a depth of $0.37 \text{ }\mu\text{m}$, rising to the maximum of 2.51 at a depth of $0.62 \text{ }\mu\text{m}$ and returning to a dpa of 1.1 at a depth of $0.73 \text{ }\mu\text{m}$, where the damaged region ends.

Figure 4. dpa vs. depth profile of Nd-doped YSZ irradiated with 200 keV $^4\text{He}^+$ ions at a fluence of $1 \times 10^{17} \text{ cm}^{-2}$, showing a maximum dpa of 2.51 at a depth of $0.62 \text{ }\mu\text{m}$ and a dpa of ≥ 1 within the damaged region $0.37 - 0.73 \text{ }\mu\text{m}$ from the surface.

CONCLUSIONS

Ex-situ irradiation of Nd-doped YSZ with 2 MeV $^{36}\text{Kr}^+$ ions at a fluence of $1 \times 10^{14} \text{ cm}^{-2}$ causes no observable damage to the YSZ as the number of atomic displacements is minimal, with a maximum dpa of 0.18. At the higher fluence of $5 \times 10^{15} \text{ cm}^{-2}$ the number of atomic displacements is sufficient to result in damage to the top $1 \text{ }\mu\text{m}$ of the sample, although not high enough to cause any amorphisation of the material. Neither sample shows any evidence of the krypton gas accumulation within the material.

Likewise, *ex-situ* irradiation of Nd-doped YSZ with 200 keV $^4\text{He}^+$ ions at the lower fluences of 1×10^{14} and $5 \times 10^{15} \text{ cm}^{-2}$ produces no visible effects within the material, the irradiation at these fluences resulting in minimal elastic collisions leading to negligible atomic displacements, with maximum dpa's of 0.003 and 0.13 at the two fluences respectively. Only at the highest fluence of $1 \times 10^{17} \text{ cm}^{-2}$ is the level of atomic displacements sufficient to cause damage to the material, resulting in a dense cluster of defects where the dpa is ≥ 1 . It is thought that these defects are dislocation loops, primarily vacancy in nature, in line with those observed in other ion implantation studies [17], although further work is needed to characterise these.

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