Caesium isothermal migration behaviour in sintered titanium nitride: New data and comparison with previous results on iodine and xenon

S. Gavarini a,*, R. Bès a, C. Peaucelle a, P. Martin b, C. Esnouf c, N. Toulhoat a,1, S. Cardinal c, N. Moncoffre a, A. Malchère c, V. Garnier c, N. Millard-Pinard a, C. Guipponi a

a Université de Lyon, CNRS/IN2P3, UMR5822, IPNL, Université Lyon 1, F-69622 Lyon, Villeurbanne, France
b Centre d’études de Cadarache, DEN/DEC/SESC/LLCC Bâtiment 151, 13108 Saint-Paul-lez-Durance, Cedex, France
c Université de Lyon, CNRS/IN2P3, UMR5822, IPNL, Université Lyon 1, F-69622 Lyon, Villeurbanne, France

ABSTRACT

Titanium nitride has been proposed as a fission product barrier in fuel structures for gas cooled fast reactor (GFR) systems. The thermal migration of Cs was studied by implanting 800 keV 137Cs+ ions into sintered samples of TiN at an ion fluence of 5 × 1015 cm–2. Thermal treatments at temperatures ranging from 1500 to 1650 °C were performed under a secondary vacuum. Concentration profiles were determined by 2.5 MeV 4He+ elastic backscattering. The results reveal that the global mobility of caesium in the host matrix is low compared to xenon and iodine implanted in the same conditions. Nevertheless, the evolution of caesium depth profile during thermal treatment presents similarities with that of xenon.

1. Introduction

Within the framework of the Generation IV project, the gas cooled fast reactor (GFR) [1–4] fuel cycle has to be optimised to recycle actinides and to minimise waste production. (U, Pu)C carbides and (U, Pu)N nitrides are candidate fuels because of their high densities, decomposition temperatures and thermal conductivities [5,6]. Nitride fuel presents interesting thermal properties and a relative ease of reprocessing compared to carbides [7,8]. However a partial or total pre-enrichment in 15N is needed to prevent nitrogen activation according to the following nuclear reaction 14N(n, p)14C [9–11]. Several geometries for the fuel assembly have been proposed in which the fuel is surrounded by several coating layers and an inert matrix [12,13]. The principal criteria for the choice of the inert matrix are: chemical compatibility with the fuel, mechanical and irradiation resistance, thermal properties allowing high gas temperatures and total retention of fission products (FP) during the in-pile process. The ability of titanium nitride to act as a diffusion barrier in microelectronic applications [14–17] combined with its mechanical and thermal properties [18–22] make it relevant as an inert matrix.

In the past four decades, most of the existing studies have been focused on the behaviour of FP in UO2 fuel [23–25] and zirconia [26–29], but very few on nitride compounds [30–33]. Caesium is one of the most important fission products created during the irradiation of nuclear fuel. Due to its high chemical reactivity and the formation of the highly radioactive 137Cs (30.7 years half-life) [34,35], the caesium behaviour must be considered in all aspects of the nuclear cycle. Degueldre et al. [26] have compared caesium migration behaviour in zirconia with those of iodine and xenon in similar thermal conditions. These authors have shown that Cs mobility is globally higher than that of both other elements in ZrO2. This observation was interpreted as a consequence of Cs+ ion higher solubility in the host lattice, which would be the result...
of its lower ionic radius [27,28] compared to P and Xe (charge states identified by Pouchon et al. [27,28] after implantation in ZrO₂). On the other hand, many authors have pointed out possible similarities in the diffusional behaviour of Cs and the fission rare gases, Kr and Xe, in UO₂ [36], but also in metals [37]. The complex electronic bonding system of titanium nitride includes metallic, covalent and ionic components [18] and thus the behaviour of caesium in this structure is hard to predict. The aim of the present work is to study the isothermal migration of a non radioactive isotope of Cs implanted into sintered titanium nitride. The concentration profile was determined by Rutherford Backscattering Spectrometry (RBS) and its evolution was characterized as a function of temperature. The possible mechanisms at the origin of caesium isothermal migration are discussed and compared with those previously observed on xenon [31] and iodine [32] implanted in similar conditions.

2. Experimental

2.1. Sample preparation and thermal treatments

Samples are sintered TiN pellets of size 15 × 15 × 2 mm³ and density 5.18 g cm⁻³ (theoretical density of TiN = 5.39 g cm⁻³ [38]). Hot pressing (HP) was used as sintering process with an uniaxial pressure of about 50 MPa and a progressive increase of the temperature up to 1600 °C. The mean diameter of the grains after sintering was found to be about 18 μm. Classically the major impurities contained in titanium nitride are oxygen and carbon (about 2 at.% here). Minor impurities are principally Fe, Ni and Si at a concentration of a few hundreds of atomic ppm. Samples were polished down to the micron scale using diamond powders. The heating procedure was described extensively in a previous work [31,32]. The first step consists in a pre-implantation thermal treatment at 1000 °C for 10 h in order to anneal most of the damages induced by polishing near the surface [39]. The same treatment was also performed just after the ion implantation. In a second step, higher temperatures, ranging from 1500 to 1650 °C (for 1–6 h maximum), are achieved using a 12 kW induction heating system. For each thermal treatment, the sample is mounted in a silica tube under a vacuum of about 5 × 10⁻² mbar and the temperature is monitored using a bichromatic pyrometer (Fig. 1).

2.2. Ion implantation and RBS analysis

The ion implantation was performed at ambient temperature using the 400 kV accelerator of the Nuclear Physics Institute of Lyon (IPNL). The implantation energy was chosen to be 800 keV (maximum energy with doubly charged particles), to obtain a projected range of about 150 nm, and the targeted ion fluence was 5.0 ± 0.2 × 10¹⁵ cm⁻². Depth profiles after implantation were measured by using the 4 MV Van de Graaff accelerator of IPNL through Rutherford Backscattering Spectrometry (RBS). The incident “He⁺ ions energy, incident beam intensity and detection angle were respectively 2.5 MeV, 10 nA and 172°C. A typical RBS spectrum is presented in Fig. 2(a). The mean experimental ion projected range (Rp) and full width half maximum (FWHM) corresponding to as-implanted samples (Fig. 2(b)) were found to be 145 ± 5 nm and 120 ± 5 nm, respectively. These values are slightly different from those predicted by SRIM2008 code [40] (i.e. Rp ≈ 166 nm and FWHM ≈ 98 nm), probably because of unavoidable matter sputtering during implantation process. In these experimental conditions, the maximum caesium concentration was found to be about 0.27 at.%. Samples were observed after each step of the experimental procedure by Scanning Electron Microscopy (SEM), detecting the secondary electrons to determine the evolution of the surface morphology.

3. Results

3.1. Surface morphology

Fig. 3(a) and (b) shows secondary electron micrographs of the implanted surface after annealing at 1650 °C for 2 h. Large intergranular voids and square-like intragranular cavities are observed (Fig. 3(a)). The typical depth of these last intragranular cavities was evaluated to be a few hundreds of nanometers depending on the considered cavity. An image of a given square, obtained using Transmission Electron Microscopy (TEM), is represented in Fig. 3(d). As it can be seen, the edges of the cavity are well defined.

![Fig. 1. Cross sectional scheme of the induction heating system.](image)

![Fig. 2. (a) RBS spectrum corresponding to TiN implanted with 800 keV ¹³⁵Cs⁺ ions at an ion fluence of 5 × 10¹⁵ cm⁻² and (b) the corresponding caesium depth profile obtained using SIMNRA software [57].](image)
and aligned with the atomic planes of the fcc structure. These craters were not observed just after the implantation and could thus result from a rearrangement of defects and/or atoms during thermal treatment. In addition, after 1 h at 1600 °C, matter was observed inside some cavities as shown in Fig. 3(c). The nature of these phases still has to be determined (perhaps crystallites or traces left by gas bubbles bursting) but their presence seems to be temperature dependent since, in contrast, most of the observed cavities were empty at higher temperature.

3.2. RBS analysis

The modifications of caesium profile after thermal treatments are presented in Fig. 4 for temperatures ranging from 1500 to 1650 °C. Note that below 1500 °C, caesium profile is almost not modified (not shown here). After 6 h at 1500 °C (Fig. 4(a)), a slight shift of the profile is observed, coupled with a 7% release of caesium (Table 1). The magnitude of the shift increases with temperature, as shown in Fig. 4(b)–(d). After 3 h at 1600 °C (Fig. 4(c)), the Cs profile intercept the surface resulting in a truncation of the signal. The same truncation is observed after 1 h at 1650 °C (Fig. 4(d)) whereas at longer times Cs concentration strongly decreases. The mean transport rate (nm s⁻¹) of caesium was estimated considering the shift in the peak maximum position. The resulting values are summarized in Table 1 for each temperature and duration. The values measured for caesium transport rate vary from 6.0 × 10⁻⁴ nm s⁻¹ at 1500 °C to about 2.5 × 10⁻² nm s⁻¹ at 1650 °C. In the same time, the elemental loss was calculated using the integrated signal and vary from 4% after 1 h at 1500 °C to about 87% after 2 h at 1650 °C.

4. Discussion and comparison with previous results on xenon and iodine

In order to compare the retention of caesium with that of iodine and xenon, values measured for Xe and I in previous works have been reported in Table 1 (data extracted from [31,32]). As it can be seen, both transport rates and releases measured for Cs in the present study are lower than those reported for other elements up to 1650 °C. The global mobility of the three species (symbolized here by the term $v_i$, with i the considered species) could thus be represented using the following inequation: $v_1 > v_{Xe} > v_{Cs}$. This hierarchy does not follow the trend of the implanted species radii as proposed by Degueldre et al. [26] for implanted zirconia (i.e.: $r_{Cs} < r_{I} < r_{Xe}$, with r the ionic radius). Supposing the same charge
states here, ionic radius could thus not be the only parameter to be taken into account in our case. In addition, the important release of iodine compared to that of caesium (for example: 83 at.% after 1 h at 1600 °C instead of 2 at.% for caesium) seems to be in good agree-

Table 1

Elemental loss (%) and mean transport rate (nm s⁻¹) values as a function of temperature and heating duration for each implanted species (Cs, Xe and I).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Implanted species</th>
<th>Duration (h)</th>
<th>Elemental loss (%)</th>
<th>Mean transport rate (nm s⁻¹ × 10⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>Cs</td>
<td>1</td>
<td>4 ± 2</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>7 ± 2</td>
<td>0.6 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>7 ± 2</td>
<td>0.8 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>1</td>
<td>6 ± 2</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>10 ± 2</td>
<td>1.2 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>23 ± 2</td>
<td>1.9 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>Xe</td>
<td>1</td>
<td>&lt;2</td>
<td>3.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>&lt;2</td>
<td>2.5 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>&lt;2</td>
<td>2.0 ± 0.5</td>
</tr>
<tr>
<td>1550</td>
<td>Cs</td>
<td>1</td>
<td>&lt;2</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>&lt;2</td>
<td>2.1 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>0.5</td>
<td>34 ± 2</td>
<td>23.2 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>54 ± 2</td>
<td>16.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>58 ± 2</td>
<td>9.2 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>Xe</td>
<td>1</td>
<td>25 ± 2</td>
<td>19.1 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>60 ± 2</td>
<td>20.2 ± 0.5</td>
</tr>
<tr>
<td>1600</td>
<td>Cs</td>
<td>1</td>
<td>2 ± 2</td>
<td>3.1 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>8 ± 2</td>
<td>5.1 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>33 ± 2</td>
<td>9.2 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>0.25</td>
<td>49 ± 2</td>
<td>&gt;98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>83 ± 2</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Xe</td>
<td>0.5</td>
<td>7 ± 2</td>
<td>3.1 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>85 ± 2</td>
<td>34.2 ± 0.5</td>
</tr>
<tr>
<td>1650</td>
<td>Cs</td>
<td>1</td>
<td>29 ± 2</td>
<td>25.1 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>87 ± 2</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>0.25</td>
<td>90 ± 2</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Xe</td>
<td>0.5</td>
<td>&lt;0.01</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 4. Caesium depth profiles after thermal treatments at (a) 1500 °C, (b) 1550 °C, (c) 1600 °C and (d) 1650 °C.
ment with the results of Busker et al. [41] carried out on irradiated UO₂. In this last study, a better retention of caesium was evidenced and was interpreted as the consequence of the higher activation energy for this element, assuming the same release mechanism for both species [42]. In our case, however, the evolution of iodine depth profile at 1500 °C is very different from that of caesium as displayed in Fig. 5. Indeed, the shape of iodine profile (dotted line in Fig. 5) is significantly modified during thermal treatment with a visible narrowing of the distribution. This dissymmetrical evolution was interpreted in a previous work [32] as a consequence of the possible heterogeneous trapping of iodine atoms in vacancy-like defects near the surface. In comparison, xenon migration behaviour (dash-dotted line in Fig. 5) is dominated by a directed diffusion towards the surface while the concentration profile remains almost symmetrical. The amplitude of this transport was well fitted using a gas migration model in a previous work [31], however a complete modelling of the implied mechanism still has to be drawn as many complex driving forces could enter into account (stress, thermal and/or vacancy gradients near the surface [35,43,44]). Concerning caesium, a directed diffusion towards the surface is observed (dashed line in Fig. 5), as for xenon. The symmetry of the profile is preserved during thermal treatment but the shift in the peak position is less pronounced than for xenon which confirms the lower mobility of caesium. Our assumption to explain the similar evolution of caesium and xenon profiles is that common mechanisms could be involved in each case. Note that this last assertion was already proposed by Walker et al. [36] in the case of UO₂ fuel. These authors have shown that similar percentages of Cs and Xe were released from UO₂ pellets above 1200 °C. It was therefore suggested that the effective diffusion coefficient for xenon was also valid for Cs above 1200 °C. However at the rim of high burn-up fuel where the temperature is lower, caesium appears to be retained completely, although a high percentage of fission gas is released. This difference in the release behaviour of xenon and caesium at the rim was explained by xenon being a gas, whereas caesium was liquid below 1200 °C. Note however that, in our case, neither xenon nor caesium gas (or liquid) bubbles were evidenced using transmission electron microscopy until this article (work still in progress), perhaps because of their presumably small size [30]. In any case, the high threshold temperature needed to observe a notable transport of xenon atoms (about 1500 °C, see Table 1) may suggest a particular and strong interaction between this species and the host matrix. Complementary experiments are needed at this stage to determine if this interaction is purely chemical, purely physical or if it results from a mixture of these effects. More generally, an influencing parameter could be the surface oxidation during thermal treatment since the slightest increase in oxygen content is known to increase species release dramatically for many metals [45] and oxide compounds [46,47]. For example, it was shown that the oxidation of UO₂ to U₂O₅ by steam generally enhance caesium releases [48]. Indeed, the oxidation of U₂O₅ causes an increase in the U vacancy concentration, which results in enhancement of diffusion of fission products in the fuel grain. Thus, it has become clear that diffusion of rare gases, but also other fission products, is highly sensitive to the stoichiometry of the U₂O₅, which is probably a major reason for the very high scatter in release measurements in literature. Titanium nitride is known to be very sensitive to oxidation [49–51] and the incorporation of a small amount of oxygen can hardly be avoided, even under secondary vacuum. The oxygen content near the surface after each thermal treatment was estimated to be lower than 5 at.% which did not result in any visible change of colour for the considered samples. However, even a slight change in the surface stoichiometry could play a role on implanted species mobility depending on species reactivity [52]. In order to highlight this point, a complementary experiment was thus performed under a vacuum of 10⁻³ mbar (instead of 5 × 10⁻⁶ mbar). After a treatment at 1500 °C for 1 h, the surface was clearly oxidised with a change of colour from gold yellow to clear brown. An oxide layer of approximately fifty nanometres was formed on the surface which composition nearly corresponds to TiO₂. Beneath this layer, the oxygen concentration decreases gradually until a depth of about 300 nm from which the composition corresponds to the bulk material. The inverse gradient of concentration was observed for nitrogen. This oxidation was associated with a complete removal of caesium atoms from the sample. Similar results were obtained on samples initially implanted with Xe and I, respectively. It is worth noting that a more systematic study is needed (currently in progress) to complete these first results and to establish more refined correlations between each species mobility and the external partial pressure of oxygen. However, at this stage, it is already confirmed that a massive oxidation of titanium nitride during annealing globally increases species release.

The formation of submicrometric square-like cavities on the surface of TiN after thermal treatment was already observed after Xe implantation [32], and also to a lower extend after I implantation [31]. It was first interpreted in terms of possible traces left on the surface by xenon (or iodine) gas bubbles but the large size of these shapes appeared hardly compatible with Xe or I bubbles (bubbles of some nanometres could be awaited [30,53]). On the other hand, these shapes present similarities with faceted blisters observed on the surface of TiN films deposited by reactive magnetron sputtering in mixed Ar/N₂ discharges [39,54–56]. According to Hultman et al. [39,55,56], these blisters could be due to the formation of nitrogen gas bubbles during ion irradiation. To confirm this hypothesis in our case, SEM-EDS analysis was carried out in regions rich in cavities but these measurements did not reveal any variation of the superficial composition, perhaps because of the too superficial thickness concerned (typically a few hundreds of nanometres in depth). Until this article, the origin of these shapes was not clearly demonstrated but the most probable explanation could be the formation of nitrogen gas bubbles which would be evacuated through grain boundaries (intergranular voids) or grains (square-like cavities) during thermal treatment. TEM experiments on transversal sections are still in progress to highlight this point as well as nuclear microprobe analysis in order to study more precisely the role played by the microstructure on this phenomenon.

5. Conclusion

The thermal migration of Cs in titanium nitride was investigated by implanting 800 keV ¹³³Cs⁺ ions into sintered samples of

Fig. 5. Comparison of caesium, iodine and xenon depth profiles after implantation at an ion fluence of 5 × 10¹⁵ cm⁻² and a subsequent heating at 1500 °C for 6 h.
TiN with an ion fluence of $5 \times 10^{15}$ cm$^{-2}$. Isothermal treatments were performed at temperatures ranging from 1500 to 1650 °C and concentration profiles were determined by 2.5 MeV $^4$He$^+$ elastic backscattering. Caesium depth profile evolution presents similarities with that of xenon implanted in the same conditions, with a dominant transport component towards the surface in both cases. However, in the case of caesium, the transport starts to become significant above 1500 °C, instead of 1400 °C for xenon. This difference in the threshold temperature could be due to a liquid to gaseous phase transition in the case of caesium which is known to be gaseous above 1200 °C. An additional and undefined interaction (chemical and/or physical) between caesium and the nitride matrix is suggested to explain the very low transport rates measured for caesium below 1500 °C. Both xenon and caesium exhibit a lower mobility than iodine implanted in the same conditions. Moreover, the dissymmetrical evolution of iodine depth profile suggests a different and specific migration mechanism. The potential role played by the oxidation during annealing has been underlined since the incorporation of oxygen in the material, correlated with nitrogen departure, was shown to enhance the global mobility of the implanted species. More generally, the apparition of square-like intragranular cavities and large intergranular voids on the surface after implantations and thermal treatments could result from the formation of nitrogen gas.

**Acknowledgments**

The authors thank all the people who contributed to this work and especially A. Perrat-Mabilon, A. Gardon, Y. Champelovier and R. Fillof from the “accelerator group” of the IPNL. Please note that J. Vincent, L. Thomé, F. Garidio, O. Kaitasov, Nucl. Instr. and Meth. B 257 (2005) 249.

**References**