



Letter to the Editors

Concentration-triggered fission product release from zirconia: consequences for nuclear safety

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Abstract

Crystalline oxide ceramics, more particularly zirconia and spinel, are promising matrices for plutonium and minor actinide transmutation. An important issue concerning these materials is the investigation of their ability to confine radiotoxic elements resulting from the fission of actinides. This letter reports the study of the release, upon annealing or irradiation at high temperature, of one of the most toxic fission product (Cs) in zirconia. The foreign species are introduced by ion implantation and the release is studied by Rutherford backscattering experiments. The results emphasize the decisive influence of the fission product concentration on the release properties. The Cs mobility in zirconia is strongly increased when the impurity concentration exceeds a threshold of the order of a few atomic per cent. Irradiation with medium-energy heavy ions is shown to enhance Cs outdiffusion with respect to annealing at the same temperature. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The management of high-level radioactive waste arising from the nuclear fuel cycle or nuclear weapon dismantling is a decisive challenge for the industrialized world over the next decades. Reprocessing of the spent fuel and vitrification of radiotoxic elements in borosilicate glasses or direct disposal in geological repositories are the main options selected nowadays in countries using nuclear technology. In the future, a foreseeable solution for reducing the excess of plutonium and other actinides is their burning in specifically devoted nuclear reactors. To that purpose, the concept of advanced nuclear fuels based on non-fertile matrices has been re-

cently proposed [1–4]. Crystalline oxide ceramics, more particularly zirconia and spinel, were identified as the most promising matrices for actinide transmutation due to their high melting point, their reasonable thermal conductivity and their strong resistance to irradiation [2–7].

The final qualification of materials with respect to safety criteria requires an extensive study of their physico-chemical properties. For instance, a crucial issue of research on inert matrix fuel is the evaluation of their ability to confine the radiotoxic elements resulting from the fission of actinides. To that purpose, it is essential to investigate the influence of various parameters (concentration and location of foreign atoms in the host material, substrate temperature, radiation damage production, . . .) on the mechanisms of fission product diffusion. The fission products may be introduced into the host matrix by ion implantation. This technique offers decisive advantages for diffusion studies. Firstly, any

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element may be introduced in any solid target in a wide range of concentration; secondly, since the doping can be performed at room temperature, the diffusion processes may be studied starting from low temperatures; and finally, the radiation damage produced in the nuclear fuel can be easily simulated by inert gas irradiation. The characterization of the disorder created in the crystal by the implantation process, the identification of the lattice site and of the depth distribution of fission products following various treatments (annealing or high-temperature irradiation) may be performed by using the Rutherford backscattering and channeling (RBS/C) technique implemented with a MeV ion accelerator [8].

The present paper focuses on the important role of the fission product (Cs) concentration towards migration and release in yttria-stabilized zirconia single crystals. Actually, in a polycrystalline material such as inert matrix fuel pellets, both diffusion mechanisms within crystalline grains and through grain boundaries occur, making difficult the identification of their individual contribution to the release process. This work provides useful data regarding the first step of this process. The choice of caesium is mainly dictated by its high volatility, making this element particularly dangerous for the environment.

2. Experimental

Various concentrations (from ~ 1 to ~ 10 at.%) of caesium ions were introduced into yttria-stabilized zirconia (ZrO_2) and spinel (MgAl_2O_4) single crystals by 300 keV room-temperature ion implantation (fluences ranging from 5×10^{15} to 5×10^{16} at. cm^{-2}) at the CSNSM Orsay facility. Implanted samples were then either annealed in vacuum (10^{-6} Torr) during 1 h, or irradiated (also during 1 h) with 360 keV Ar ions (total fluence: $\sim 10^{15}$ cm^{-2}) at temperatures ranging from 300 to 1000 °C. Irradiation with Ar ions simulates the damage created in a fuel matrix by the various nuclear reactions. In order to avoid the overlapping of Cs- and Ar-rich regions, the ion energies were chosen to ensure a much larger implantation depth for Ar ions (~ 250 nm) than for Cs ones (~ 60 nm).

The modifications of the Cs ion depth distribution due to thermal annealing or high-temperature ion irradiation were investigated by RBS experiments at the ARAMIS accelerator of the CSNSM in Orsay [9]. The RBS analysis was made using He ions with incident energies of 3.07 MeV.

3. Results and discussion

Fig. 1 shows a typical RBS spectrum recorded on a ZrO_2 single crystal implanted with Cs ions at a fluence of

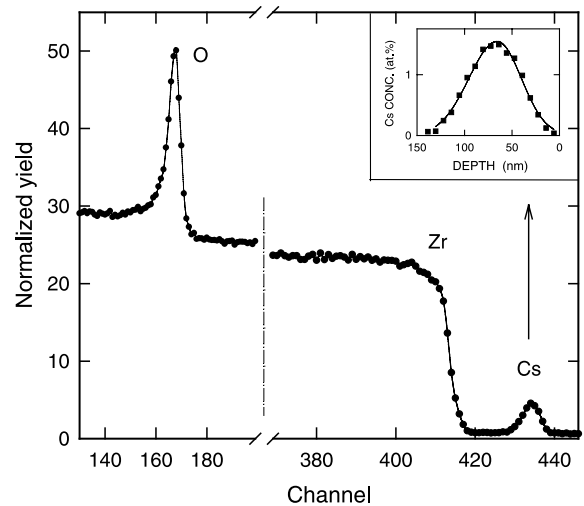


Fig. 1. RBS spectrum recorded on a ZrO_2 single crystal implanted with Cs ions at a fluence of 10^{16} at. cm^{-2} . The inset presents a zoom of the Cs peak (after Hf background subtraction) in atomic concentration vs. depth scales.

10^{16} at. cm^{-2} . The signals arising from the various atoms present in the targets (Zr, O and Cs) are labelled in the figure. The inset is a zoom of the Cs depth distribution (atomic concentration vs. depth) calculated from the analysis of the Cs peak (appearing at channels 430–440). It exhibits a gaussian-like shape with a mean depth and a depth straggling in agreement with Monte-Carlo computer simulations for implanted ions [10].

The modifications of the Cs depth distributions upon annealing or irradiation at high temperatures are shown in Fig. 2 for ZrO_2 single crystals implanted at two Cs fluences (10^{16} and 3×10^{16} at. cm^{-2}), i.e. for samples containing two initial concentrations of Cs atoms (~ 1.5 and 5 at.%) at the maximum of the distribution. The Cs depth profile is almost unaffected upon annealing (up to the highest temperature used in this study) when the initial Cs concentration is low (open symbols). Moreover, high-temperature irradiation has no significant effect on the Cs mobility for the samples having a low Cs content. The situation is markedly different when the initial Cs concentration is high (filled symbols). The concentration of Cs atoms has decreased dramatically down to ~ 2 at.% upon annealing at 650 °C (filled circles). The effect of high-temperature ion irradiation is an enhancement of the mobility of Cs atoms; the concentration of 2 at.% is reached at a temperature as low as 500 °C (cross-haired triangles), where annealing is almost ineffective (filled triangles).

Fig. 3 presents a summary of the results obtained on Cs-implanted ZrO_2 samples submitted to thermal treatments. It shows the variation of the Cs concentration at the maximum of the distribution as a function of

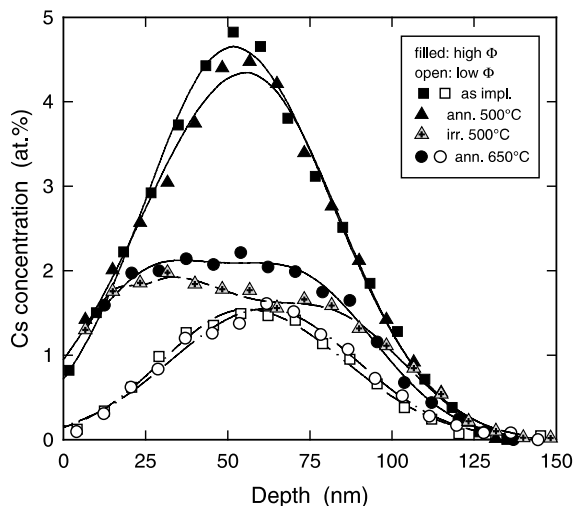


Fig. 2. Depth distributions of Cs ions implanted into ZrO_2 single crystals at fluences of 3×10^{16} at. cm^{-2} (filled symbols) and 10^{16} at. cm^{-2} (open symbols), before and after annealing or irradiation with Ar ions at the indicated temperatures.

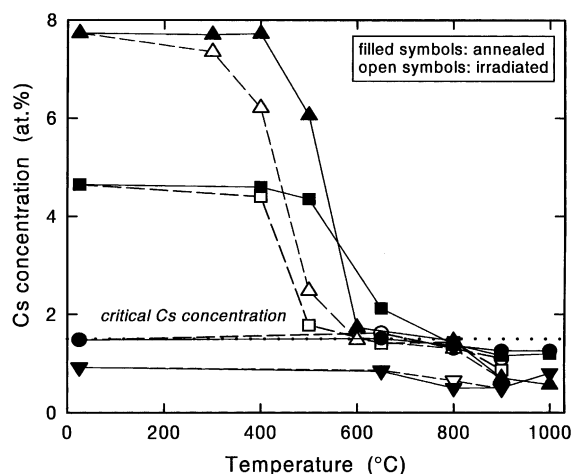


Fig. 3. Maximum Cs concentration vs. annealing (filled symbols) or irradiation (open symbols) temperatures for ZrO_2 single crystals implanted with Cs ions at fluences of 5×10^{16} at. cm^{-2} (right triangles), 3×10^{16} at. cm^{-2} (squares), 10^{16} at. cm^{-2} (circles) and 5×10^{15} at. cm^{-2} (inverted triangles).

the annealing or irradiation temperature for various implantation fluences. For crystals implanted at low (below 1.5 at.%) atomic concentrations (hereafter referred to as *low-c* samples), no release of Cs atoms occurs up to the highest temperature investigated in this study. In this concentration range, high-temperature Ar irradiation has essentially no influence on the mobility of implanted species. For crystals implanted at medium

(~5 at.%) and high (~8 at.%) atomic concentrations (hereafter referred to as *high-c* samples), release of Cs atoms occurs upon annealing at ~550 °C. The result is a decrease in the Cs concentration down to a critical value (c_c) of the order of 1.5 at.% (hereafter noted *high-c* → *low-c* transition). In this concentration range, Ar ion irradiation increases the mobility of Cs atoms, since the release starts at ~450 °C to reach the same final concentration as upon annealing. Furthermore, once the Cs concentration has dropped down to the critical concentration, the Cs depth profile remains almost unaffected up to the highest annealing temperature, revealing a high stability of the phases formed below c_c . Very similar results were obtained in MgAl_2O_4 samples with the difference that the Cs release occurs at a higher temperature than in ZrO_2 for heavily doped samples, namely ~800 °C for annealing and ~700 °C for high-temperature ion irradiation.

Out of equilibrium doping processes, such as ion implantation or nuclear fuel fission reactions, favour the introduction of high concentrations of foreign atoms which may largely exceed the solubility limit for a given material. Supersaturated phases are thermally unstable, so that annealing at moderate temperature may cause drastic changes in the impurity depth distribution. The consequence is the release of impurity atoms from highly concentrated regions, leading to a flattening of the depth profile similar to that exhibited in Fig. 2. Argon ion irradiation causes a further enhancement of the Cs diffusion *via* ballistic effects due to elastic collisions between incoming ions and target atoms.

The stability of implanted systems may be related to the local atomic configuration of foreign species. Previous RBS and channeling data on ZrO_2 single crystals implanted with various ions showed that a large fraction of Cs atoms occupy substitutional lattice sites at *low-c* (i.e. below ~2 at.%) [11,12]. A Cs ion has an effective radius ranging from 0.174 to 0.188 nm (8-fold coordinated) or from 0.188 to 0.202 (12-fold coordinated) [13,14], and the ZrO_2 fluorite structure can accommodate only cations smaller than 0.124 nm [15]. Thus, the straightforward replacement of a Zr cation by a Cs ion is very unlikely. The stress caused by the introduction of large Cs ions into cationic positions can be efficiently released by the formation of anionic vacancies in the vicinity of impurities. In such stable atomic arrangements, Cs ions occupy positions only slightly displaced from the original locations of Zr atoms, leading to a high value of the substitutional fraction, f_s . When the Cs concentration exceeds c_c , the value of f_s falls to zero, indicating randomly distributed lattice positions for Cs atoms. The solubility limit of Cs in ZrO_2 (at 2000 K) was estimated to be 1.5 at.% [16,17]. The decrease of f_s at high Cs concentration is thus very likely due to either the precipitation of Cs atoms in metallic inclusions, or the

formation of ternary compounds (such as Cs_2ZrO_3 [15–17]). The atomic configurations built up in high-*c* samples are less stable than Cs-vacancy complexes, thus leading to the increased Cs mobility observed in the case of highly doped samples. After thermal treatment, the substitutional fraction measured in channeling experiments remains unchanged for both types of samples. This result reveals that random positions of Cs atoms are observed in high-*c* samples even when these samples are annealed at temperatures above the high-*c* → low-*c* transition. Thus, despite the fact that the final concentration is the same after annealing for low-*c* or high-*c* samples, the local environment of implanted species is obviously different. The most likely atomic configurations are thus: isolated atoms surrounded by vacancies in the case of low-*c* samples and precipitates in the case of high-*c* samples (before and after annealing). Physico-chemical analyses of the samples, more particularly X-ray diffraction and transmission electron microscopy, are in progress in order to gain information about the nature of the phases formed upon ion implantation and annealing. Similar conclusions can be drawn in the case of spinel for which RBS and channeling data also showed that a large fraction of Cs atoms occupy substitutional lattice sites at low concentration and random positions at high concentration [18].

4. Conclusion

The results presented in this article show for the first time that the release of fission products (Cs) in potential candidates for nuclear waste matrices (zirconia and spinel) is strongly dependent on their concentration. In both materials the Cs release increases when its concentration exceeds a threshold of the order of a few atomic per cent. Further enhancement of the Cs out-diffusion is observed when the temperature rise is accompanied by radiation damage production. All three conditions, high fission-product concentration, elevated temperature and atomic collisions, are combined in inert matrix fuel irradiated in a nuclear reactor. It is thus of great importance to consider the effects described here when developing innovative nuclear fuels, in order to decrease the risk of accidental release of radiotoxic elements into the geosphere.

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