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Behavior of cesium implanted in zirconia based inert matrix fuel

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Abstract

Retention of cesium in yttria stabilized zirconia (YSZ) was studied experimentally and discussed on the basis of its solubility estimated on a thermodynamic basis. The retention was investigated experimentally by determination of the temperature dependence of diffusion and the cesium release. Cesium was introduced using 1 MeV ions or by chemical reaction in yttria stabilized zirconia. The distribution of the implanted cesium was evaluated by using TRIM computer calculation and measured by Rutherford backscattering spectroscopy (RBS) using 5 MeV ^{4}He ions. The cesium profile was quantified after successive annealing up to 1373 K. Cesium release was rather weak up to 1173 K. The retention of Cs chemically introduced by Cs_2ZrO_3 was also experimentally investigated for different calcination temperatures. The chemically introduced cesium followed similar release behavior as the implanted one. Thermodynamic modelling of the system cesium, zirconium and oxygen was performed in a comprehensive way and as a function of temperature. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Yttria stabilized zirconia (YSZ) is studied at the Paul Scherrer Institute as an inert matrix for an advanced nuclear fuel [1]. This new fuel generation is foreseen for burning plutonium excesses in light water reactors. For radiological-protection safety reasons the retention behavior of specific fission products such as Xe and I in YSZ fluorite material was recently studied [2,3]. Radiocesium is also a safety relevant fission product, and both its solubility and retention must be assessed in the fuel. The condition of formation of specific phases such as zirconate must also be investigated. Cesium is known as a volatile fission product which diffuses from the UO_2 pellets towards the gap between the fuel and cladding [4].

In this study, the retention behavior of cesium in YSZ was investigated after Cs implantation in zirconia. The sample was subsequently studied by Rutherford Backscattering Spectroscopy (RBS) to determine the cesium distribution. The effect of temperature on the diffusion of the cesium was measured after heating up the sample to progressively higher temperatures and by repeating the RBS investigations. For comparison, retention tests were also performed by introducing cesium chemically into the stabilized zirconia matrix. Annealing at different temperatures was again tested. Thermodynamic modelling was performed as a function of temperature to identify the cesium zirconium oxide phases.

2. Physical and chemical background

2.1. Distribution after implantation

For the calculation of the implantation profiles, i.e., dopant concentration (C) as a function of depth (x), the simulation code TRIM-95 (Transport of Ions in Matter) [5] was used. The implantation of 1 MeV cesium ions was simulated. For this incident ion energy the implantation profile followed a Gaussian distribution.

2.2. Diffusion

The distribution of cesium as a function of time changes according to the equation [6]

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$$C(x,t) = \frac{\phi}{2\sqrt{\pi\left(D\cdot t+\frac{\sigma_0^2}{2}\right)}} \exp\left\{-\frac{(x-x_0)^2}{4\cdot D\cdot t+2\cdot\sigma_0^2}\right\}, \tag{1}$$

where σ_0 in m is the initial variance, ϕ in m^{-2} is the ion fluence, x_0 in m is the mean depth of the Gaussian distribution in the sample, t in s is the time of diffusion after initiation and D in $m^2\ s^{-1}$ is the diffusion coefficient. Diffusion increases the variance of the Gaussian distribution. The variance is consequently a function of time and temperature. For a given temperature (i.e. D constant) the variance variation with time is given from Eq. (1) by

$$\sigma(t) = \sqrt{2\cdot D\cdot t+\sigma_0^2}. \tag{2}$$

This results in a diffusion coefficient as a function of temperature. Its variation is generally given by the function

$$D = D_0 \cdot e^{-E_0/k_B\cdot T}, \tag{3}$$

where E_0 in J is the activation energy, D_0 in $m^2\ s^{-1}$ a diffusion precoefficient, k_B the Boltzmann constant and T in K the absolute temperature.

2.3. Study of the thermodynamic system Zr–Cs–O

Multi compound phase diagram calculations were performed using the software package THERMO-CALC [7]. The principle of a thermodynamic equilibrium calculation is the minimization of the Gibbs free energy function. The thermodynamic database used for these calculations is Nuclear Materials Databases for THERMO-CALC from Mike Mignanelli, AEA Technologies Harwell UK (1986).

This allows calculations of isothermal sections in the system Zr–Cs–O for a given pressure e.g. 0.1 MPa.

3. Experimental

3.1. Preparation of samples for cesium implantation studies

The specimen used in the implantation tests was an yttria stabilized zirconia pellet. It was produced by coprecipitation. The starting compounds $ZrO(NO_3)_2$ (purum, Fluka™) and $Y(NO_3)_3$ (puriss, Fluka™) were diluted separately in Milli Q water and mixed together to produce a solution with 15 at.% Y for the Zr–Y ratio. The solution was then precipitated by adding NH_4OH in drops. The resulting hydroxide cake was filtered, dried and milled. By calcination at 1073 K the product became $(Zr_{0.85}, Y_{0.15})O_{1.925}$. The material was subsequently milled, pelletized and sintered at 1473 K for 4 h in a first step and at 1873 K for 4 h in a second step. The heating rate was 5 K min^{-1}. The sample was then cooled to room temperature over a period of about 10 h by shutting down the furnace. The resulting pellet of 10 mm diameter was cut into a 1 mm slice. The relative density of the entire pellet was 85% with a theoretical density of 6.0 g cm^{-3}, determined from lattice parameter measurements. The $ZrO(NO_3)_2$ product contained 1.06 at.% hafnium; consequently, the end product was contaminated with hafnium which was taken into account for the RBS spectra simulations.

3.2. Preparation of samples containing cesium

For the chemical introduction of cesium the base material was a powder produced by the internal gelation process [8]. The internal gelation process is used at PSI for several years to fabricate UO_2 and uranium plutonium mixed oxide fuel, it was applied here for the fabrication of zirconia microspheres. The principle of this process is a conversion of a mixture of nitrate solutions (Zr–Y–Ce-nitrate feed solution) to oxides, based on the coprecipitation of metal hydroxides. Additives like hexamethylentetramine and urea are used to keep the feed solution stable. Spherical particles are formed after the feed solution (which is cooled down to 273 K) has been given drop by drop into a heat carrier. Then these particles are washed, dried and calcinated leading to a dense oxide product of the formula $(Zr_{0.8}, Y_{0.1}, Ce_{0.1})O_{1.95}$.

3.3. Cesium implantation in YSZ and RBS analysis after annealing

The cesium implantation and the RBS analyses were both performed with the PSI/ETH Tandem accelerator [9]. The implantation energy was 1 MeV and the implantation fluence was $M = 6\times10^{19}\ m^{-2}$. The ions were implanted under normal incidence at room temperature. An area of $4\times10^{-6}\ m^2$ was irradiated using a beam current of 5 nA. The resulting cesium depth profile was measured by 5 MeV ^4He RBS. This energy was selected in order to improve the resolution of the RBS spectrum. The analysis was performed under standard conditions [10].

After implantation the sample was heat-treated at different temperatures. RBS analysis was performed after each thermal treatment. Thermal treatments were performed at 773, 873, 1073 and 1173 K for 2 h with a heating rate of 17 K min^{-1}. A final temperature step was performed at 1373 K for 2 h with a heating rate of 10 K min^{-1}. All thermal treatments were performed on the same sample. Consequently, previous annealing cycles have to be taken into account for correct interpretation of the results.

3.4. Chemical introduction of cesium and calcination of the mixture

The calcined (773 K) Zr–Y–Ce oxide powder obtained by internal gelation was mixed with cesium zirconate (Cs_2ZrO_3) powder. Different annealing temperatures (4 h, respectively, at 873, 973, 1073 and 1173 K) were applied with a similar effect to the different thermal treatments for the cesium implanted sample.

After thermal treatment the samples were dissolved in HCl with a small amount of HF, this was heated in a microwave oven. The leaching solution was analyzed by induced coupled plasma-atomic emission spectroscopy (ICP-AES) utilizing an ARL 3410 Minitorch spectrometer.

4. Results and discussion

4.1. Cesium implantation

After cesium implantation the YSZ specimen remained white. However, after ^4He irradiation for RBS analysis the sample was covered with a dark gray/brown spot. The dark spots generated by the He ion disappeared after each thermal treatment, this indicates that the coloration was not due to any carbon contamination. The implantation profile was calculated by TRIM, the initial result was a Gaussian at a depth of $x_0 = 195$ nm and a variance of $\sigma_0 = 65$ nm.

4.2. Analyses of the implanted cesium by RBS

Fig. 1 shows the RBS spectra of the irradiated and the non-irradiated parts of the pellet. These are compared with a RUMP [11] simulation for the implanted cesium profile. For the simulation, the depth of the Gaussian x_0 and the fluence M were kept constant. The reason for keeping the depth constant was the assumption that asymmetric diffusion was negligible. The variance σ was fitted. However, the presence of hafnium has to be taken into account in the RBS spectra simulation. This element is responsible for a shoulder on the high energy side of the spectra (see Fig. 1).

Fig. 1 shows the spectra of the sample before thermal treatment and after annealing at 773 K for 2 h. It is striking to find no significant release of cesium at this temperature. Fig. 2 shows RBS spectra after the last thermal treatment at 1373 K for 2 h. At this temperature a significant cesium displacement is observed and may be quantified. Cesium diffusion starts to be measurable at a temperature of 873 K. The fitted variances after the thermal treatments are shown in Fig. 3. In this figure the crosses are the values of σ obtained from the calculated diffusion coefficient, obtained by substituting Eq. (3) into Eq. (2) and integrating for the real temperature function, e.g. heating and cooling. The estimated error on the variance is ±20%.

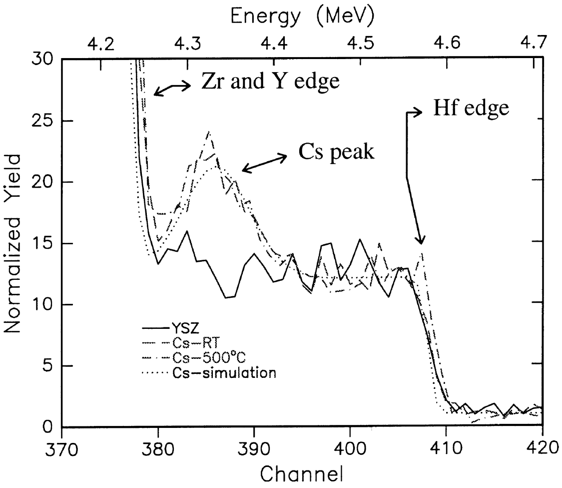

Fig. 1. YSZ irradiated with cesium before heat treatment and after 2 h at 773 K. (——) non irradiated YSZ. (– –) YSZ irradiated with cesium before heat treatment. (– · –) YSZ irradiated with cesium after 2 h at 773 K. (· · ··· ·) simulation by RUMP with Gaussian variance: 78 nm.

The final diffusion coefficient result is given by the Eq. (3) with an activation energy E_0 of $(2.0 \pm 0.2) \times 10^{-19}$ J ((1.25 ± 0.1) eV) and a D_0 of $(4.66 \pm 0.6) \times 10^{-14}$ m^2 s^{-1}.

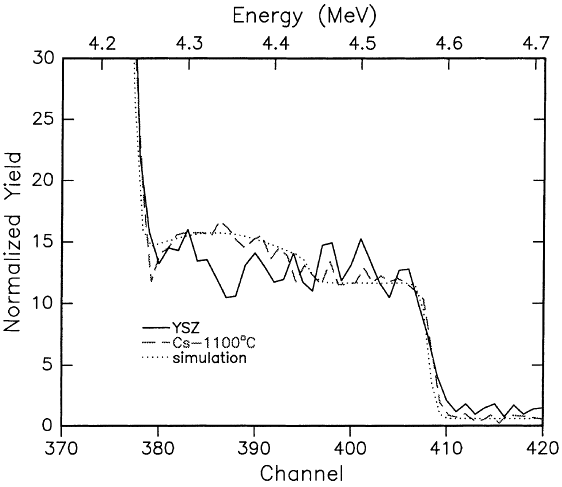

Fig. 2. YSZ irradiated with cesium after 2 h at 1373 K. (——): non irradiated YSZ. (– – –) YSZ irradiated with cesium after 2 h at 1373 K. (· · ··· ·) simulation by RUMP with Gaussian variance: 180.5 nm.

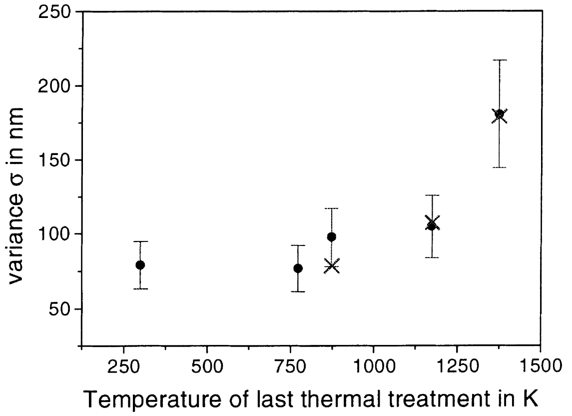

Fig. 3. Variance of the Gaussian distribution as a function of the last thermal treatment temperature. The crosses represent the values determined from the calculated diffusion coefficient.

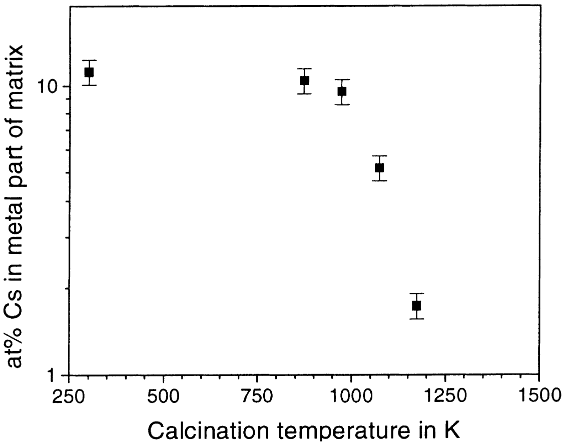

Fig. 4. Cs determined in the oxide mixture after annealing.

4.3. Behavior of the chemically introduced cesium

Samples obtained by mixing and calcinating ($Zr_{0.8}$, $Y_{0.1}$, $Ce_{0.1}$)$O_{1.95}$ and Cs_2ZrO_3 powder were analyzed after a second calcination step at different temperatures. Cesium and the other metals were analyzed by ICP-AES after acid dissolution. Fig. 4 shows the cesium concentration determined in the calcinated samples as a function of increasing thermal treatment temperature. The calcination step was always performed for 4 h each with separate samples. It is striking to observe a similar release behavior versus temperature as depicted in Fig. 3.

4.4. Thermodynamic study of the Zr–Cs–O system

The Zr–Cs–O system was calculated using the THERMO-CALC code (thermodynamic data given in Table 1) and by extrapolation to the investigated temperature when necessary. The calculations predict that one ternary phase Cs_2ZrO_3 (orthorhombic) exists even at 1000 K (see Fig. 5(a)). Further calculations with ideal solution model integrated in THERMO-CALC show slight solubility of Cs in ZrO_2 creating a ternary phase. The solubility of the ternary phase Cs_2ZrO_3 in ZrO_2 (at 1000 K) and the solubility of Cs in ZrO_2 (at 2000 K), respectively, are estimated up to 1.5 at.%. According to these calculations cesium zirconate does not exists at 2000 K (see Fig. 5(b)). It is also interesting to note that for both temperatures, there are no binary compounds existing in the system Zr–Cs.

Calculations of the system ZrO_2–Cs_2O confirm the stability of Cs_2ZrO_3 up to a temperature of 1173 K.

From these calculations it can be assumed that the phase found in the cesium implanted zirconia can be a solution of cesium in zirconia or a local formation of cesium zirconate. Further experimental tests are required to identify the actual phase in which cesium occurs in IMF (inert matrix fuel).

5. Conclusion

Progress has been made to understand the retention behavior of Cs in IMF material. The retention of implanted cesium in YSZ is significant up to 1000 K. Cesium from a cesium zirconate mixed with a ceria doped YSZ showed a similar behavior and no significant cesium release below 1000 K.

Table 1
Thermodynamic data of binary and ternary compounds in the systems Zr–Cs–O

Phase	$\Delta_f H^0_m$ (kJ mol^{-1})	$\Delta_f G^0_m$ in (kJ mol^{-1})	S^0_m (J mol^{-1} K^{-1})	$C_{p,m}$ (J mol^{-1} K^{-1})	Reference
ZrO_2 (mcl.) [a]	−1097.50	−1039.70	50.36	42.80	[12]
ZrO_2 (tetra.) [b]	−1043.55	−1380.80	138.08	78.10	[12]
ZrO_2 (cub.) [c]	−953.68	−1346.85	196.59	80.00	[12]
Cs_2O (hex.) [a]	−345.77	−308.16	318.08	55.40	[13]
Cs_2ZrO_3 (orth.) [a]	−1748.20	−1647.20	197.60	132.05	[14]

[a] Reference temperature 298.15 K.

[b] Reference temperature 1000 K.

[c] Reference temperature 2000 K.

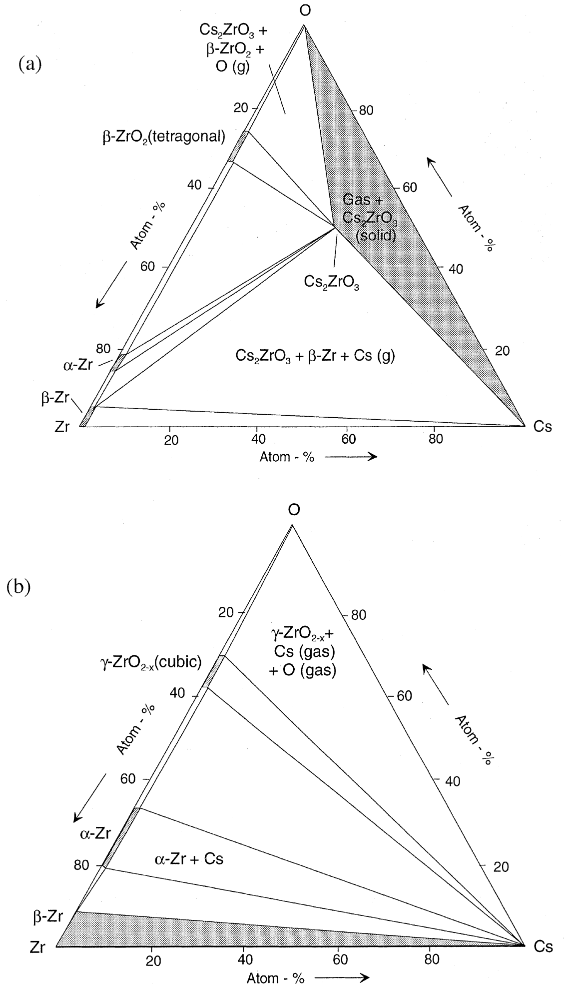

Fig. 5. Calculated isothermal section of the system Zr–Cs–O at 1000 (a) 2000 K (b) and 0.1 MPa.

Thermodynamic modelling showed that the formation of ternary phases in the Zr–Cs–O systems e.g. Cs–Cs_2O in ZrO_2 (solution) and Cs_2ZrO_3, are possible between room temperature and 1173 K. These phases may be taken into account to justify the retention behavior of implanted Cs in zirconia based IMF.

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