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USE OF FISSION PRODUCT IMPLANTATION IN NUCLEAR WASTE MANAGEMENT

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Abstract

1. Introduction

The large uranium fission cross section leading to long lived fission products like iodine, cesium or technecium and the behaviour of these elements in the cladding tube during energy production and afterwards during waste storage is a crucial problem [1, 2]. During the reactor processing, fission products are implanted by recoil inside the zircalloy cladding tube at different energies ranging from keV to some tens of MeV. This corresponds to implanted depths varying respectively from 10 nm to several μm [3-5].

Let us first remind that in France, nuclear wastes are classified into 4 categories depending on the type and on the importance of radioactivity (α, β, γ , high, medium, low activities). They are then specifically deposited. High level nuclear wastes belong to the C category made of fission products, actinides and activation products. Among fission products, iodine lies a real problem first since it is a volatile element and also because of ^{129}I which is a very long half life isotope ($T=1.59 \times 10^7$ years). At the moment two storage options are opened : the closed cycle for which wastes are reprocessed and the open cycle for which no reprocessing is performed. In the open cycle, the spent fuel UO_2 is directly the first barrier to radionuclide migration surrounded by a second barrier which is the zircalloy cladding tube. In the closed cycle, fission products and minor actinides are separated from uranium and plutonium and then vitrified to constitute the wastes glasses. Before chemical separation, the cladding tubes are sectioned into pieces called hulls in order to release the UO_2 pellets which are rendered soluble in nitric acid. The hulls are collected as solid wastes and embedded inside a concrete structure. In the perspective of geological storage, radionuclides could migrate through the geosphere using water as migration vector. Hence a great interest is given to migration processes in order to model diffusion data and to extrapolate them to large time scales [6].

We have focused this study on iodine migration into zirconia (zirconium oxide) since a natural oxidation of the internal face of the zircalloy tube occurs during reactor processing simply by contact with the UO_2 fuel on a thickness ranging between 5 and 10 μm [7]. Hence fission products are implanted in the superficial ZrO_2 layer. The mean energy of emitted fission products from UO_2 is 73 MeV and their maximum range inside the cladding tube is of about 7 μm . However, most of them are distributed in the first 2 μm . For these reasons it is of primary importance to study phenomena occurring at the surface of the cladding tube. The aim of this work is then to study iodine diffusion into zirconia by using ion implantation. This

method allows to introduce impurity atoms in a solid with an excellent control of depth and concentration by adjusting incident energy and fluence [8,9].

2. Experimental conditions

The zirconia samples were obtained by air oxidation of zircalloy foils on a typical thickness of 4 μm . Two energy fields have been chosen that we will call low energy : $E = 50$ keV ($R_p = 16$ nm, $\Delta R_p = 6$ nm) and high energy : $E = 800$ keV ($R_p = 164$ nm, $\Delta R_p = 52$ nm), and $E = 6.5$ MeV ($R_p = 1270$ nm, $\Delta R_p = 500$ nm), where R_p and ΔR_p are respectively the mean range and the standard deviation (straggling) of the distributions. The predicted distributions given by the TRIM code [10] are presented on figure 1 as a function of the different energies.

FIGURE 1 : TRIM distributions for the 50, 800 keV and 6.5 MeV implantations energies

Two types of implantation have been carried out using either stable or radioactive isotopes. Rutherford Backscattering Spectrometry (RBS) was used in order to determine distribution profiles of stable species with a depth resolution of about 12 nm. In case of radioactive iodine, release of radioactivity was measured by γ -ray spectroscopy using a Ge(H.P) detector of 2 keV resolution. For each implantation condition, successive annealings were carried out in air in the temperature range 700-900°C and either the iodine profile (for stable element) or the activities (for radioactive ones) were determined after each annealing step.

The 50 and 800 keV implantations were performed on the isotope separator of the 'Institut de Physique Nucléaire' of Lyon (IPNL). For 50 keV implantations, both radioactive ^{131}I ($T = 8$ days) and stable ^{127}I were implanted. The ^{131}I implanted dose was deduced from activity measurements of the 364 keV γ ray. It was found to be approximately 10^9 at.cm $^{-2}$ which corresponds to a maximum iodine concentration of 8×10^{-7} at %. The 800 keV ^{127}I implantations were performed at a fluence of 2×10^{16} at.cm $^{-2}$ which corresponds to a maximum iodine concentration of 1.8 at %.

The 6.5 MeV implantations were realised by using the Lohengrin spectrometer at ILL from the neutronic fission of ^{239}Pu . The Lohengrin spectrometer allows to select the 133 isobaric chain at an energy of 65 MeV and an ionic charge of 24 which corresponds to the highest intensity. The use of a 8 μm thick aluminium absorber allows to reduce the incident

energy down to 6.5 MeV. This layer thickness was checked by using α emission from ^{241}Am at 5.486 MeV.

The 133 isobaric chain which is the following [11] :

Activities of the different radionuclides were followed by γ spectroscopy :

^{133m}Te : $E_\gamma = 913$ keV and 334 keV, ^{133g}Te : $E_\gamma = 312$ keV, ^{133}I : $E_\gamma = 530$ keV,

^{133}Xe : $E_\gamma = 81$ keV.

3. Results and discussion

3.1. At low energy

In order to determine experimentally the distribution of the 50 keV implanted ions, ^{127}I ions were implanted at a fluence of 8×10^{15} ions cm^{-2} . The RBS profile is displayed in **figure 2**. **Figure 3** presents the amounts of desorbing iodine versus annealing times at 700, 800 and 900°C.

FIGURE 2 : Distribution profile of the 50 keV implanted iodine

FIGURE 3 : Iodine release versus time for the 50 keV implanted samples.

In general, experimental data are interpreted on the basis of models derived from Fick's second law. Solutions vary depending on limiting conditions. The law is given by :

$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$ where C is the concentration of the diffusing species and D is the diffusion coefficient. Considering the experimental profiles, it can be deduced the existence of a flux from the right to the left at $x=0$. Let us assume that $C_0(x) = C_0$ is the mean iodine concentration in the as-implanted layer and is considered as constant for simplification. The C_0 value is taken at half height of the distribution and considered as constant on the thickness $R_p + \Delta R_p$ as shown on **figure 2**. As described in [12], the solution is : $C = C_0 \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$.

$$\text{The flux } J \text{ is equal to : } J(x, t) = -D \frac{\partial C}{\partial x} = \frac{-DC_0 \exp\left(-\frac{x^2}{4Dt}\right)}{\sqrt{\pi Dt}}$$

It can be deduced that at $x = 0$, the flux through the surface in the direction opposite to x is $J(0, t) = \frac{DC_0}{\sqrt{\pi Dt}}$. $M(t)$ is the total amount of iodine which migrates through the surface per surface unit. $M(t) = \int_0^t J(0, t') dt'$, which leads to $M(t) = 2C_0 \sqrt{\frac{D}{\pi}} \sqrt{t}$. The different $M(t)/C_0$

values have been plotted on **figure 4** as a function of the square root of time in case of the various annealing temperatures.

FIGURE 4 : $M(t)/C_0$ values as a function of the square root of time in case of the various annealing temperatures for the 50 keV implanted samples.

The experimental data can be fitted by a straight line, the slope of which is proportional to D . The so determined D values are listed in table 1. It is then possible to determine an activation energy of 1.5 ± 0.3 eV at¹ from the arrhenius plot displayed on **figure 5**.

T (°C)	700	750	800	850	900
D (cm ² s ⁻¹)	1.02×10^{-18}	2.38×10^{-18}	5.14×10^{-18}	1.03×10^{-17}	1.96×10^{-17}

Table 1 : Diffusion coefficients deduced from the experiments at 50 keV

FIGURE 5 : Arrhenius plot corresponding to the 50 keV experiments.

3.2. At high energy

The activities of ^{133}I , ^{133}Xe and ^{105}Ru were followed at the same time. ^{105}Ru ($T=4.44\text{h}$, $E_\gamma=724.30\text{ keV}$) is a refractory element and was also implanted together with the 133 isobaric chain because of a similar M/Q ratio. This implantation allows to compare the evolution of volatile products to that of a refractory one. The evolution of the ^{133}I activity has been determined by integrating the filiation equations. Measurements of γ rays have been normalised from these calculated activities taking as a reference the activities of non annealed samples. **Figure 6** represents the radioactive decrease versus time in the case of a 800°C annealing for ^{133}I , ^{105}Ru and ^{133}Xe which activity is much lower due to its large period. In order to optimise accuracy, each γ radioactivity measurement was performed during 30 minutes.

Figure 6 : Iodine , ruthenium and xenon activity evolution versus time at 800°C .

The full lines plotted on this figure represent the reference activities. The dots are the experimental data. The desorption of volatile products (I, Xe) can be determined from the activity loss observed by comparison to the calculated activity using the filiation laws. It can be noticed that ^{105}Ru follows the theoretical exponential decrease. ^{133}I fed by the ^{133}Te decrease also fits the filiation law (continuous line). However from a 90 minute annealing time, a significant variation to this law is observed. A similar evolution is noticed for Xe despite a lack of precision due to a large statistical error.

Iodine release is plotted on **figure 7**. For annealing temperatures lower than 800°C, no desorption is observed in the studied time scale whatever the sample nature.

Figure 7: Quantities of desorbed iodine versus annealing time for 800 keV and 6.5 MeV implantations.

These results cannot be interpreted as it was done previously in case of the 50 keV implantation since iodine profiles are distributed deeper in the samples. The iodine concentrations are then not constant from the surface. In order to obtain intermediate data, implantations at 800 keV with stable atoms have been thus performed. The evolution of desorbed iodine concentrations versus time is presented on **figure 7** together with a comparison between 800 keV and 6.5 MeV results. In order to understand these results, we propose the following analysis : The diffusion coefficients deduced from the Arrhenius plot of 50 keV experiments are identical at 800 keV and 6.5 MeV.

Let us consider the Fick's second law $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$ with non dimensioned variables. For a given experiment :

$$\bar{x} = \frac{x}{\sigma}, \quad \bar{C} = \frac{C}{C_0}, \quad \text{and} \quad \bar{t} = \frac{t}{\tau}, \quad \text{therefore} \quad \frac{\partial^2 \bar{C}}{\partial \bar{x}^2} = \frac{\sigma^2}{D\tau} \frac{\partial \bar{C}}{\partial \bar{t}}$$

where σ is the straggling, τ the time necessary to observe iodine desorption and C_0 the mean iodine concentration.

Then, for two different experiments numbered 1 and 2, the law can be written as :

$$\frac{\partial^2 \bar{C}}{\partial \bar{x}^2} = \frac{\sigma_1^2}{D_1 \tau_1} \frac{\partial \bar{C}}{\partial \bar{t}} \quad \text{and} \quad \frac{\partial^2 \bar{C}}{\partial \bar{x}^2} = \frac{\sigma_2^2}{D_2 \tau_2} \frac{\partial \bar{C}}{\partial \bar{t}}, \quad \text{hence} \quad \frac{\sigma_1^2}{D_1 \tau_1} = \frac{\sigma_2^2}{D_2 \tau_2} = \text{constant}$$

If we compare the experiments performed at ILL with the 800 keV ones for an annealing temperature of 800°C. We can write : $D_1 = D_2$. Hence $\frac{\sigma_1^2}{\tau_1} = \frac{\sigma_2^2}{\tau_2}$

Since $\sigma_1 = 500$ nm, $\sigma_2 = 52$ nm and that 90 minutes were necessary at ILL to observe a desorption ($\tau_1 = 90$ min), we can deduce that only one minute is necessary at 800 keV to observe iodine release ($\tau_1 = 1$ min). The technique sensitivity does not allow to determine such a short time and it is why the iodine release appears to be immediate. The same evaluation can be done at 700°C. It is there found that 92 hours would have been necessary to observe a desorption. This could explain why nothing was seen at this temperature at ILL.

4. Conclusion

An extrapolation of 50 keV experiments to an annealing temperature of 100°C, which roughly corresponds to real disposal conditions, would lead to a diffusion coefficient of 10^{-32} cm² s⁻¹. The energies available at ILL correspond to realistic simulation of reactor conditions. The first results obtained there tend to show a good agreement with low energy ones. They have pointed out that for future irradiations, it would be necessary to implant the iodine isobaric chain more superficially in order to be able to observe desorptions in reasonable times for temperatures below 800°C. Plateau distributions have now to be considered.

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