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Letter to the Editors

First study of uranium self-diffusion in UO_2 by SIMS

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Abstract

Uranium self-diffusion coefficients were measured in UO_2 single crystals through an original methodology based on the utilization of 235U as tracer and depth profiling by secondary ion mass spectrometry (SIMS). The values of the self-diffusion coefficients measured in this work, between 1498 and 1697°C, in H_2 atmosphere, can be described by the following Arrhenius relation: D (cm^2/s) = 8.54×10^{-7}exp[−4.4(eV)/kT], and are lower than those previously determined by other authors in 'nearly stochiometric' UO_2 in the same temperature range. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

UO_2 is a material which presents a great technological interest because of its utilization as nuclear fuel. The properties of this material have been intensively studied in the last few decades. In particular, uranium self-diffusion has been the object of a number of investigations. The interest in uranium diffusion in UO_2 has lain in the fact that many important processes like, for example, sintering, creep, grain growth in-reactor densification and others, are controlled by uranium diffusion. Many methods – direct and indirect – have been used for the determination of cation self-diffusion in UO_2. All the direct methods have applied radioactive techniques, while the indirect methods are based on data from sintering kinetics. In general, the published results present a significative spread. Reviews about uranium diffusion in UO_2 have been made in previous papers [1,2].

The present work deals with new measurements of uranium diffusion in UO_2 single crystals through an original methodology based on the utilization of ^{235}U as tracer and depth profiling by secondary ion mass spectrometry (SIMS). The results of these measurements are described, and compared to earlier results obtained by other authors.

2. Experimental procedures

The crystals were supplied by IPN *Groupe de Radiochimie, Universite de Paris-Sud* (Orsay–France). The metallic impurities were (in ppm) Fe(70), Ca(45), Cr(43), Al(15), Mg(14), Ni(12), Mo(<30) and Co (<3). Samples of $4 \times 2 \times 4$ mm^3 were polished with diamond paste, pre-annealed under the same conditions of temperature and atmosphere of the diffusion annealing, and then packed in a UO_2 powder into alumina crucible. The uranium of the UO_2 powder was enriched (~18.5%) with the isotope ^{235}U. This powder was supplied by *Comissão Nacional de Energia Nuclear/Brazil.*

The diffusion experiments were performed from 1498°C to 1697°C, in a H_2 atmosphere. The diffusion times varied between 4.4 and 48.3 h. The schematic of the heat-treatment arrangement used for the diffusion experiments is shown in Fig. 1. After the diffusion annealings the samples were carefully cleaned in order to ensure that no powder remained in contact with the surface of the samples. The polished surface was not damaged during the diffusion annealing.

The depth profiles of ^{235}U were determined by means of a SIMS-Cameca 4F using a 10 keV primary ion beam

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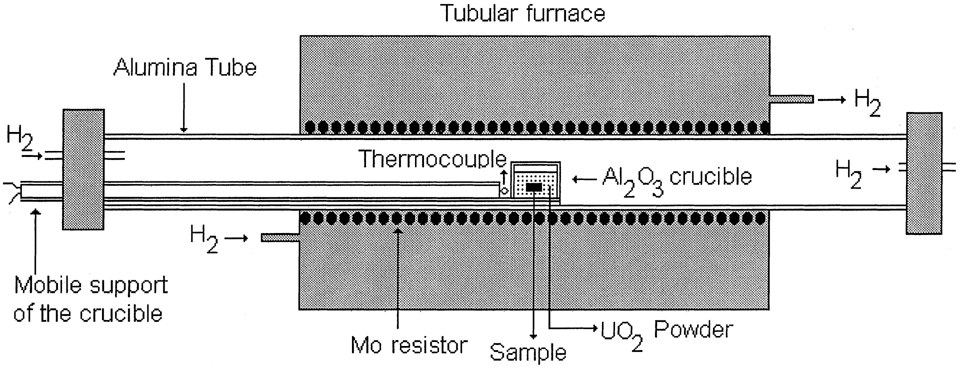

Fig. 1. Schematic drawing of the heat-treatment set used for the diffusion annealings.

of O^+. These analysis were performed on *Laboratorie de Physique des Solides*/CNRS (Meudon/Bellevue, France). The analysis were performed at an area of 250 μm × 250 μm, and the signals of the ions $^{235}U^-$, $^{234}U^-$ and $^{238}U^-$ were taken from a zone of 62 μm in diameter. The concentration of ^{235}U was determined through the expression

$$C(^{235}U) = \frac{I(^{235}U^-)}{I(^{234}U^-) + I(^{235}U^-) + I(^{238}U^-)}.$$

The penetration depths were obtained assuming a constant sputtering rate and measuring the depth of the crater by means of a Tencor profilometer or by laser interferometry in the case of shallow craters of a few nanometers depth.

3. Results and discussion

The concentration of ^{235}U at the surface of the samples was similar to that of the ^{235}U in the UO_2 powder. Therefore, the following Ficks' second law solution has been used for the determination of the diffusion coefficients [3]

$$\frac{C_s - C}{C_s - C_o} = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right), \tag{1}$$

where C_s is the concentration of the tracer at the surface, C is the concentration as a function of position, C_o is the natural abundance of tracer in sample, x is the depth, D is the diffusion coefficient, and t is the annealing time.

Eq. (1) has been fitted very well to the diffusion profiles obtained at 1498°C as shown in Fig. 2, but, for higher temperatures, the diffusion profiles have not corresponded to those given by Eq. (1). The shape of the profiles has indicated that some matter had been deposited on the surface. Evaporation–condensation from the powder to the crystal surface may be responsible for the shape of the profiles, a point that is discussed in Appendix A. In such cases, the diffusion coefficients were estimated using Fick's second law solution derived for the case of an evaporating medium and given by [4]

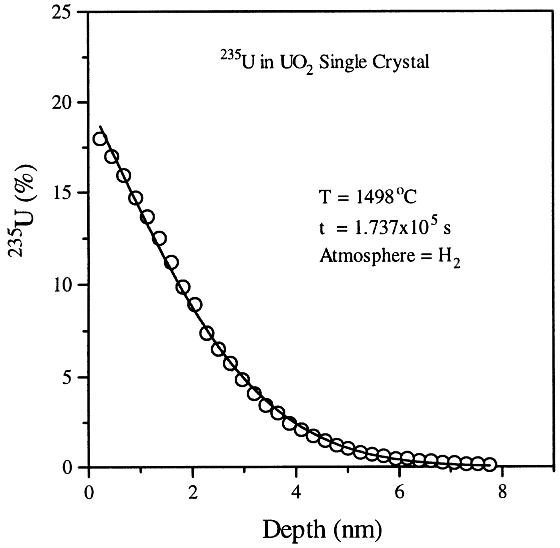

Fig. 2. Diffusion profile for the isotope ^{235}U in UO_2 single crystal at 1498°C.

$$C(x', t) = \frac{1}{2} C_{ss} \left[\mathrm{erfc}\left(\frac{x' + vt}{2\sqrt{Dt}}\right) + \exp\left(-\frac{vx}{D}\right) \mathrm{erfc}\left(\frac{x' - vt}{2\sqrt{Dt}}\right) \right], \tag{2}$$

where C_{ss} is the concentration at the separation surface between the sample and the involving medium, x' is the depth from the new surface, and v is the evaporating velocity.

In Eq. (2), $v > 0$ for the loss of material from the sample and $v < 0$ for the deposit of material on the surface, the latter being the case here. In plot of Fig. 3 is shown a fitting of Eq. (2) to a diffusion profile at

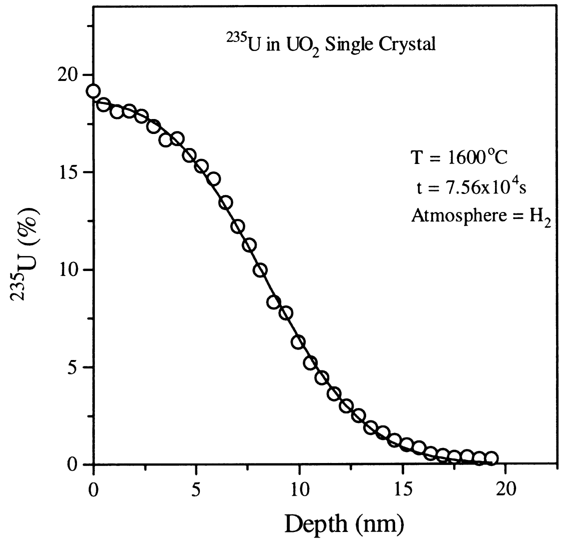

Fig. 3. Diffusion profile of ^{235}U in UO$_2$ single crystal at 1600°C.

1600°C. The variation of v with the temperature is illustrated in Fig. 4, and can be described by the following relation:

$$v\ (\mathrm{nm/s}) = 2.3 \times 10^{10} \exp[-5.4(\mathrm{eV})/kT]. \tag{3}$$

The new methodology used in this work was able to measure uranium diffusion coefficients as small as 1.91×10^{-19}cm^2/s at 1498°C. The diffusion coefficients measured in the present work, between 1498 and 1697°C, can be described by the following Arrhenius relation

$$D\ (\mathrm{cm^2/s}) = 8.54 \times 10^{-7} \exp[-4.4(\mathrm{eV})/kT]. \tag{4}$$

Fig. 5 shows an Arrhenius diagram, that contains the uranium diffusion coefficients measured in this work and those determined by other authors in 'nearly stoichiometric' UO$_2$ [2,5–9] and also in ThO$_2$ [10]. The activation energies for uranium volume diffusion in UO$_2$ of the earlier works have ranged from 3.0 to 5.6 eV. (Our value is 4.4 eV.) Activation energy for uranium diffusion obtained by Jackson et al. [11], using theoretical calculations, is 12.5 eV, and, consequently, very different from those obtained experimentally.

The order of magnitude of the uranium self-diffusion coefficients measured in this work seems to be well established. Our results for uranium diffusion in UO$_2$ are lower than those of previous works, but they are in reasonable agreement with those for uranium diffusion in ThO$_2$ [10]. The reliability of the present data can be corroborated by the following arguments:

- Our single crystalline samples had no defect (porosity, breaks,...). So, the artifact contribution to the diffusion profiles were eliminated.
- The results of the diffusion coefficients were reproducible.
- The values obtained for the fitted parameters had correct physical meaning.
- Very low diffusion of U in UO$_2$ is not surprising. Matzke [12], for example, using data of Marin et al. [13], has roughly estimated the 'true' uranium diffusion coefficient, at 1500°C, as 10^{-19}cm^2/s, which is similar to the present data.

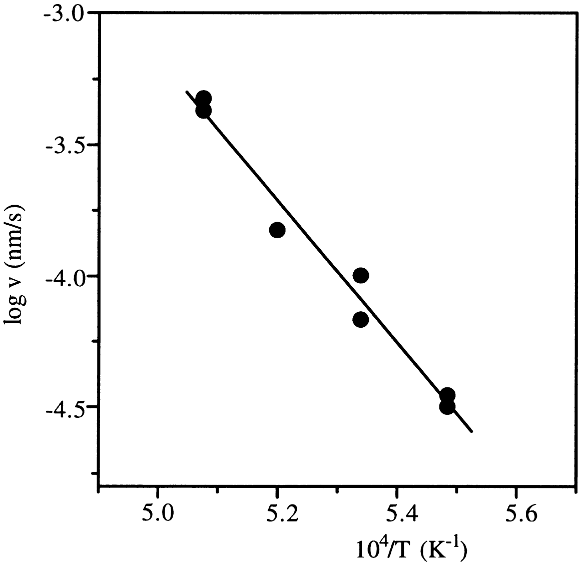

Fig. 4. Variation of the parameter v as a function of the temperature.

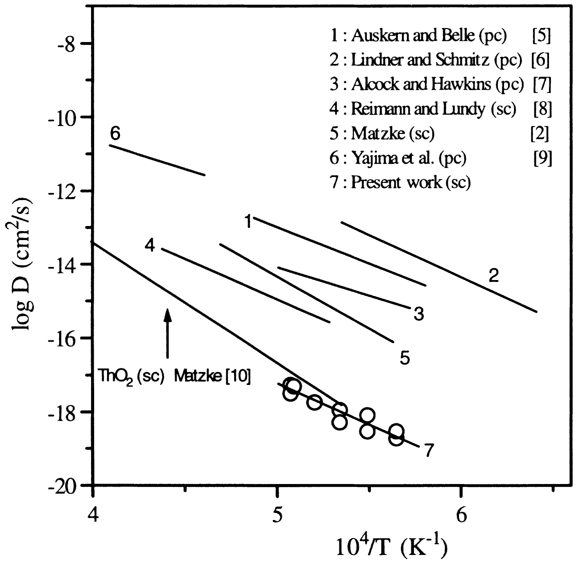

Fig. 5. Arrhenius diagram comparing the present data with results previously published for uranium diffusion in UO$_2$ and ThO$_2$ (sc = single crystal; pc = polycrystal).

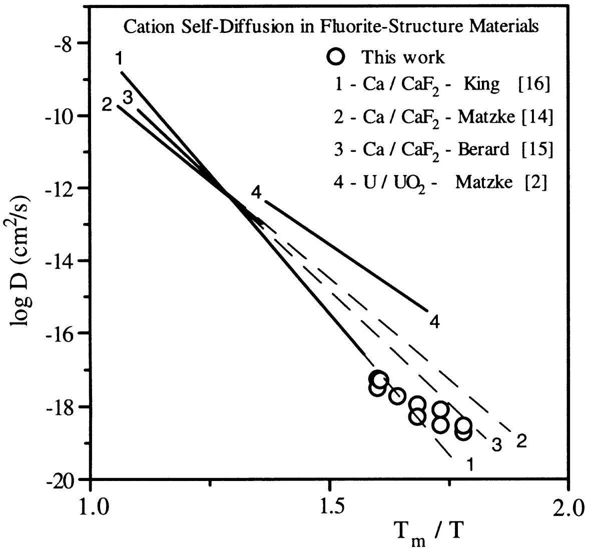

Fig. 6. Arrhenius diagram comparing the cation self-diffusion in different fluorite-structure materials.

Finally, according to some authors [14,15] cation self-diffusion in fluorite-structure materials ($UO_2, ThO_2, CaF_2, HfO_2, \ldots$) should be similar in a normalized Arrhenius diagram (log$D$ versus T_m/T, where T_m = melting temperature in kelvin). As shown in Fig. 6, the values of the present work fall inside the region defined by the extrapolation of the results for Ca self-diffusion in CaF_2 [14–16].

In the discussion above, our UO_2 samples were assumed to be stoichiometric. Other authors have also performed diffusion experiments in hydrogen atmosphere, and have assumed a stoichiometric behavior for the UO_2 [2,5–8]. But, it is expected that uranium dioxide may be hypostoichiometric at high temperature, in a reducing atmosphere. This possible deviation from the stoichiometry of the UO_2 was estimated for our experimental conditions, and its influence on the results is discussed below.

In the diffusion annealings, pure hydrogen was used, and the amount of H_2O in the gas, according to the supplier, was less than 5 ppm. In order to discuss the effect of a possible deviation from stoichiometry on the uranium diffusion in UO_2, we have assumed 5 ppm of H_2O in the H_2 atmosphere. Probably, there was no penetration of oxygen from outside to inside the alumina tube, during the diffusion annealings, because it was also externally involved by hydrogen as shown in Fig. 1.

Using thermodynamical data of Pattoret et al. [17], and considering that the oxygen partial pressure is defined by the amount of the water impurity in H_2, values of x were estimated for UO_{2-x}. These x-values and also the calculated uranium-defect concentration in stoichiometric and hypostoichiometric UO_2, between 1500°C and 1700°C, are shown in Table 1. The point-defect concentration was calculated using Lidiard Model [18,19] for the defect structure of $UO_{2\pm x}$.

Table 1 shows that uranium vacancy is the predominant metal-defect in stoichiometric UO_2, while the total amount of uranium defects (vacancies and interstitials) in hypostoichiometric UO_{2-x} is much lower than the uranium vacancy concentration in stoichiometric UO_2. It means that uranium diffusion in UO_{2-x} should be much lower than in UO_2 in the same temperature range. So, an hypostoichiometric behavior of the UO_2 may have affected the present results, but it is not the only reason able to explain why our results are lower than those of previous works. It is worth remembering that several of the previous works were also performed in H_2 atmosphere [2,5–8], sometimes even at higher temperatures, and the samples used may eventually have had an hypostoichiometric behavior.

In fact, it is not very simple to explain the scattering of the earlier results, and the difference between them and the results of the present work. Besides the possible deviation from stoichiometry, which is very sensitive to small variations of the oxygen pressure, many other parameters should be considered, such as, for example, the nature and amount of the impurities, the characteristics of the samples, and the experimental procedures and techniques used to measure the diffusion coefficients. New experiments are planned in order to study the uranium diffusion in UO_2 as a function of the oxygen pressure, or in other words, as a function of x in $UO_{2\pm x}$. Only such a study may allow us to draw a conclusive interpretation of the uranium diffusion mechanism in uranium dioxide and to establish how the deviation from the stoichiometry affects the magnitude of the diffusion coefficients.

Table 1
Calculated uranium-defect concentrations for uranium dioxide

T (°C)	Stoichiometric UO_2		Hypostoichiometric UO_{2-x}		
	$[V_U]$	$[U_i]$	x	$[V_U]$	$[U_i]$
1500	6.0×10^{-9}	1.7×10^{-19}	0.010	1.5×10^{-14}	7.0×10^{-14}
1600	1.7×10^{-8}	1.7×10^{-18}	0.019	3.9×10^{-14}	8.0×10^{-13}
1700	4.4×10^{-8}	1.3×10^{-17}	0.030	1.2×10^{-13}	5.0×10^{-12}

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Appendix A

The deposition of ^{235}U enriched UO_2 on the surface of the sample during the diffusion experiments for the higher temperatures of this study implies that some transport mechanism of UO_2 is operative during the diffusion mechanism which allow transferring matter from the UO_2 powder to the UO_2 single crystal. Estimation of UO_2 transport from the powder to the single crystal by an evaporation–condensation mechanism based on different vapor pressures at the surfaces of the UO_2 powder and single crystal can be made by using the Gibbs–Thompson relation given by

$$\mathrm{RT}\ \ln\frac{p_{\text{powder}}}{p_{\text{crystal}}}=2\gamma\frac{V}{r},\tag{5}$$

where $\gamma = 600$ dyne/cm is a mean surface tension value for UO_2 [20], V is the molar volume of UO_2, and r is the mean radius of the hypothetically spherical powder ($r = 1.25$ μm).

With these numbers, we have $p_{\text{powder}}/p_{\text{crystal}} = 1.0016°\mathrm{C}$, at 1600°C, and this difference of pressure induces a net flux of gaseous uranium bearing species from powder to crystal

$$J_{\mathrm{U}}=-D_{\mathrm{U}}\nabla C_{\mathrm{U}}=D_{\mathrm{U}}\frac{(p_{\text{powder}}-p_{\text{crystal}})}{r\mathrm{RT}},\tag{6}$$

where the interdiffusion coefficient, D_{U}, of uranium gaseous species in hydrogen could be of the order of 1 cm^2/s. Although approximative, this value is reasonable on account of the empirical comparisons among various experimental cases (see for instance Ref. [21]).

The rate of increase of the thickness v of the UO_2 single crystal is therefore

$$v=\alpha VJ_{\mathrm{U}},\tag{7}$$

where α is the percentage of surface porosities measured on a plane cut into the powder ($\alpha = 0.5$ can be chosen for an uncompacted powder).

In order to estimate the value of v, we need an input value of the vapour pressure of $UO_2^{(\mathrm{gas})}$, the only gaseous specie able to realize an approximate congruent transport. From Pattoret et al.'s work [17], we have at 1600°C, $p = 1.35 \times 10^{-8}$ atm, and, consequently, $v = 1.4 \times 10^{-13}$ m/s. This value is in a reasonable agreement with that given by Eq. (3), viz. 8.5×10^{-14} m/s on account of the approximations involved in the model. The temperature dependence of v is related to its activation energy ($E_v = 5.4$ eV, see Eq. (3)) and is comparable with the enthalpy of vaporization of $UO_2^{(\mathrm{gas})}$ (6.1 eV following Ref. [17]). On account of the previous calculations, the transport of UO_2 from powder to crystal by the gas phase seems a reasonable hypothesis which comforts the choice of Eq. (2) to describe the diffusion experiments.

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