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Letter to the Editors

Effect of grain-boundaries on uranium and oxygen diffusion in polycrystalline UO_2

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Abstract

The influence of grain-boundaries on uranium and oxygen diffusion in polycrystalline UO_2 has been investigated. Our results show that between 1498°C and 1697°C, in H_2 atmosphere, uranium diffusion in UO_2 grain-boundaries is about five orders of magnitude greater than uranium volume diffusion, in the same experimental conditions. Between 605°C and 750°C, in $H_2/N_2/H_2O$ atmosphere, the oxygen diffusion coefficients measured in polycrystalline and single crystalline UO_2 are similar, and correspond to the volume diffusion. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Uranium-dioxide is a material of great technological interest due to its utilization as nuclear fuel in power reactors. Uranium and oxygen diffusion have been extensively studied in this material due to their importance for the nuclear fuel fabrication and in-pile performance analysis. Uranium is the slowest mobile atomic specimen, and its diffusion controls the kinetics of processes such as sintering, creep, grain growth, in-pile densification among others. The knowledge of oxygen diffusion, which diffuses faster than uranium, is important, principally, in nuclear fuel oxidation and reduction processes.

Most previous works on uranium diffusion in UO_2 dealt with the determination of volume diffusion coefficients in single crystalline and polycrystalline samples, and, in general, the results show poor agreement. These results have been reviewed in Refs. [1–3].

There are only two works [4,5] concerned with uranium diffusion in nearly stoichiometric UO_2 grain-boundaries and, even so, their results are questionable as shown by Matzke in Ref. [6]. Therefore more grain-boundary diffusion experiments must be performed to provide reliable data for uranium diffusion in UO_2 grain-boundaries.

Recently, Sabioni et al. [3] measured uranium volume diffusion coefficients in UO_2 single crystals through an original methodology based on utilization of the isotope ^{235}U as tracer and depth profiling by secondary ion mass spectrometry (SIMS).

This new methodology is used in this work to measure uranium grain-boundary diffusion coefficients in UO_2 polycrystals. The knowledge of uranium intergranular diffusion in UO_2 is important, because the UO_2 nuclear fuels used in power reactors are polycrystalline, and the intergranular diffusion may become significant in diffusion controlled processes, principally, at lower temperatures.

In this paper the possible effect of the grain-boundaries on oxygen diffusion in UO_2 is also investigated. Marin et Contamin [7] proposed that oxygen diffusion in UO_2 polycrystals has no dependence on grain size, which means that the grain-boundaries should not play any important role on oxygen diffusion in UO_2.

In order to check these previous results related to the oxygen diffusion, new measurements of oxygen diffusion were performed in UO_2 single crystals and polycrystals, in the same experimental conditions, using modern techniques for this type of study.

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The effect of the grain-boundaries on oxygen and uranium diffusion in UO_2 was determined by comparing the uranium and oxygen diffusivities measured in polycrystalline samples with those measured in single crystalline samples, in the same experimental conditions.

2. Experimental procedures

2.1. Material

Sample fabrication. The uranium dioxide used as nuclear fuel in nuclear reactors has a density of ca. 95% of its theoretical value. The volumetric porosity of 5% in this material unables it inadequate to be used in diffusion experiments, because the porosity is a fast path for the penetration of the tracer, which affects the diffusion profile.

Therefore, UO_2 samples of high density were specially fabricated for this work at CDTN/CNEN Laboratories (Brazil). The high density UO_2 samples were fabricated by using UO_2 powder prepared by sol–gel method, cold pressing of the powder and sintering at 1700°C, for 2 h in H_2 atmosphere.

Characterisation of the samples. The density of the sintered UO_2 polycrystals was ca. 99.3% of the theoretical value and the average grain size was about 12 μm. A typical microstructure of the UO_2 polycrystals is shown in Fig. 1.

The chemical analysis of the UO_2 polycrystals showed about 200 ppm of metallic impurities with the following distribution: Ni (12), Fe (70), Si (31), Al (15), Mg (14), Cr (43), Co (<3), Mo (<30).

The UO_2 single crystalline samples used in the oxygen diffusion experiments were supplied by the IPN Groupe de Radiochimie, Université Paris XI (Orsay, France). These single crystalline samples were identical to those used for the determination of the uranium volume diffusion [3]. The impurity content of the single
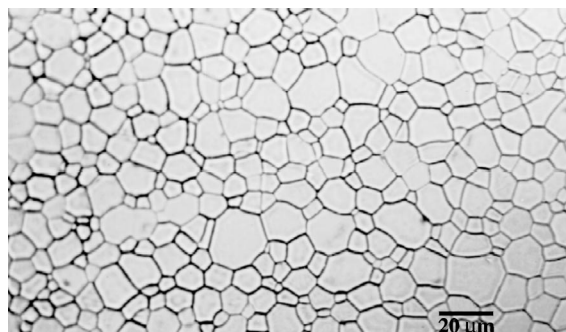

Fig. 1. Typical microstructure of a UO_2 polycrystal used in this work.

crystals is similar to that of the polycrystals. The characteristics of the single crystals are described in Ref. [3].

2.2. Diffusion experiments

Sample preparation. The UO_2 polycrystals and single crystals were cut with the dimensions 2 mm × 5 mm × 5 mm, polished with diamond paste, and submitted to a pre-annealing in order to equilibrate the samples with the temperature and atmosphere to be used in the diffusion annealings.

Oxygen diffusion. Oxygen diffusion experiments were performed by means of the gas–solid isotopic exchange method, using the isotope ^{18}O as oxygen tracer. The diffusion experiments were performed from 605°C to 750°C, in an atmosphere of the gaseous mixture: 98.4% N_2: 1% H_2: 0.6% $H_2^{18}O$, where the water vapor was enriched with the isotope ^{18}O (40% ^{18}O). Detailed description of the solid–gas exchange apparatus used in our experiments is given in Ref. [8].

Uranium diffusion. In the uranium diffusion experiments, the UO_2 polycrystalline samples were placed in a UO_2 powder in an alumina crucible. The uranium of the powder was enriched with the isotope ^{235}U (18.5%) used as uranium tracer. This powder was supplied by Comissão Nacional de Energia Nuclear/Brazil.

The diffusion annealings were performed from 1498°C to 1697°C, in H_2 atmosphere, in a molybdenum resistance furnace. The annealing times ranged from 4.8 to 240 h.

After the diffusion annealings, the samples were removed from the powder, cleaned, and carefully examined to be sure that the surfaces had no powder particles.

2.3. Depth profiling by secondary ion mass spectrometry (SIMS)

The uranium and oxygen diffusion profiles were determined by SIMS. The SIMS analyses were performed by using a CAMECA 4F apparatus at Laboratoire de Physique des Solides–CNRS/Meudon-Bellevue, France.

The analyses of the uranium isotopes were performed by using a primary ion beam of O^+ with energy of 10 keV, while the analyses of the oxygen isotopes were performed with a primary ion beam of Cs^+ with 10 keV energy.

The diffusion profile of the isotope ^{235}U was determined through the expression

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

where the Is represent the signals of the ions $^{234}U^-$, $^{235}U^-$ and $^{238}U^-$. The diffusion profiles of the isotopes ^{18}O were determined by using the following expression:

$$C(^{18}O) = \frac{I(^{18}O^-)}{I(^{18}O^-) + I(^{16}O^-)}$$

where the Is represent the signals of the ions $^{16}O^-$ and $^{18}O^-$.

In all cases, the SIMS analyses were performed on an area of 250 μm×250 μm. The signals of the ions $^{235}U^-$, $^{234}U^-$ and $^{238}U^-$ for the case of the uranium, and the signals of the ions $^{18}O^-$ and $^{16}O^-$ in the oxygen analysis, were collected from a central zone of the crater of 62 μm in diameter.

The depth profiles were obtained assuming a constant sputtering rate and measuring the depths of the craters by means of a profilometer Tencor.

3. Results and discussion

3.1. Uranium diffusion in UO₂ grain-boundaries

Fig. 2 shows a diffusion profile of ^{235}U in a polycrystalline UO₂ after diffusion at 1697°C, during 1.71×10^4 s, in hydrogen atmosphere. In the same figure, it is shown, for comparison, the diffusion profile of the isotope ^{235}U in a single crystalline UO₂ [3] obtained in the same experimental conditions. In the detail of Fig. 2 the diffusion profile of the ^{235}U in the single crystalline UO₂ in a more appropriate scale to be visualized is shown.

Fig. 2 shows an evident difference between the diffusion profiles measured in single crystalline and polycrystalline samples in the same experimental conditions.
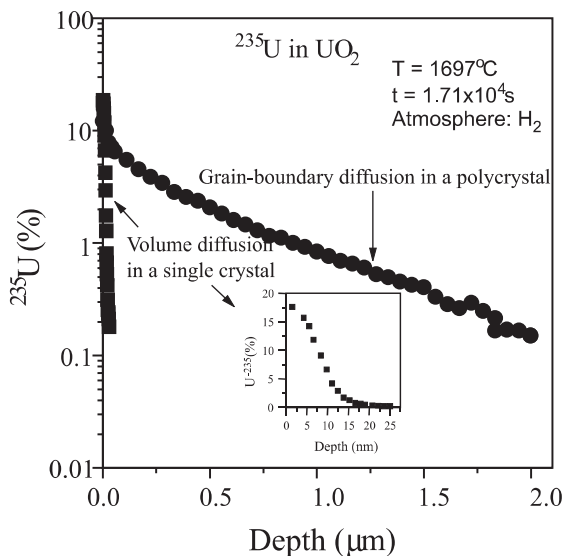
The depth penetration of the tracer in the polycrystal is much greater than in the single crystal. The long tail of the profile in the polycrystal is a characteristic of the diffusion in the grain-boundaries.

In our experimental conditions, the uranium diffusion in UO₂ grain-boundaries corresponds to the B-type intergranular diffusion, which, according to Harrison's conditions [9], is defined by the relation
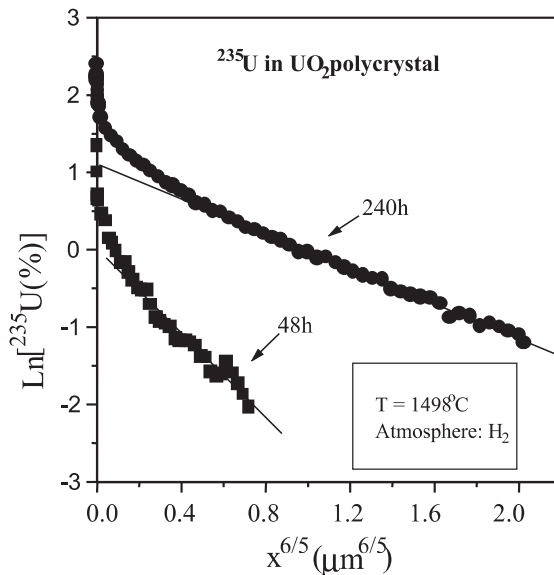

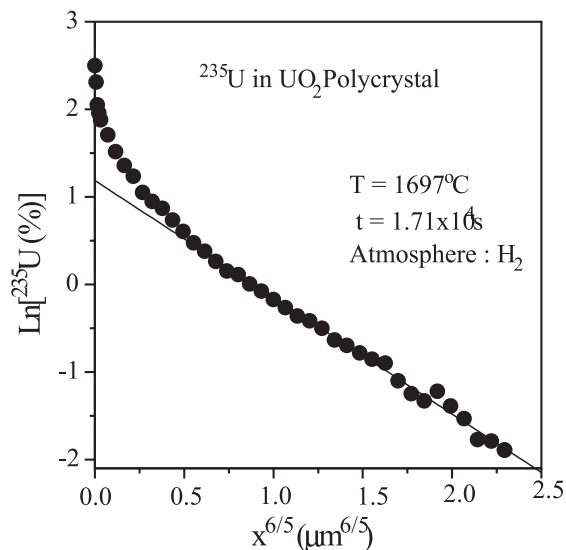Fig. 3. Comparison of uranium diffusion profiles obtained in UO₂ at 1498°C for different annealing times.

Fig. 2. Comparison of uranium diffusion profiles obtained in UO₂ single crystal and polycrystal in the same experimental conditions.

Fig. 4. Uranium diffusion in UO₂ polycrystal at 1697°C.

Table 1
Experimental conditions and results obtained for uranium grain-boundary diffusion in UO_2 polycrystals

T (°C)	t (s)	D (cm²/s)	D' (cm³/s)	D'/D[a]
1498	1.737×10^5	2.7×10^{-19}	2.9×10^{-21}	1.1×10^5
1498	8.640×10^5	2.7×10^{-19}	5.9×10^{-21}	2.2×10^5
1600	7.560×10^4	1.3×10^{-18}	4.2×10^{-20}	3.2×10^5
1697	1.710×10^4	4.9×10^{-18}	1.4×10^{-19}	2.8×10^5

[a] Using $\delta = 1$ nm.

$$\delta \ll (Dt)^{1/2} < \Phi/2$$

where δ is the grain-boundary width, D is the volume diffusion coefficient, t is the diffusion time, and Φ is the grain size.

In B-type integranular diffusion experiments it is not possible to determine the grain-boundary diffusion coefficient (D'), but only the product $D'\delta$. Le Claire [10] showed that the product $D'\delta$ may be calculated through the following expression:

$$D'\delta = 0.661 \left[-\frac{\partial(\ln C)}{\partial x^{6/5}} \right]^{-5/3} \left(\frac{4D}{t} \right)^{1/2}. \quad (1)$$

Figs. 3 and 4 show other diffusion profiles of ^{235}U in polycrystalline UO_2, but in plots of $\ln C$ versus $x^{6/5}$, which enable the calculation of the gradient $d(\ln C)/dx^{6/5}$ used in Eq. (1).

Fig. 3 shows two diffusion profiles of ^{235}U in polycrystalline UO_2 at 1498°C. The difference between these profiles is due to the different diffusion times used in these experiments (48 and 240 h).

In order to determine the product $D'\delta$, through Eq. (1), we have used D-values previously measured in UO_2 single crystals [3], in the same experimental conditions of this work.

The experimental conditions used in our experiments and the results obtained for the uranium diffusion in UO_2 grain-boundaries are listed in Table 1. The similarity of the data obtained at 1498°C, for diffusion times of 48 and 240 h, shows the consistency of our results.

In the Arrhenius diagram of Fig. 5 the uranium volume diffusion coefficients (D) determined by Sabioni et al. [3] in UO_2 single crystals [3] are compared to the uranium grain-boundary diffusion coefficients (D') determined in this work. In this comparison, it was assumed a typical value of 1 nm for δ in Eq. (1).

The data of Table 1 and the Arrhenius diagram of Fig. 5 show that the uranium grain-boundary diffusion coefficients in UO_2 are ca. 5 orders of magnitude greater than the volume diffusion coefficients [3] in the same experimental conditions.

Fig. 5 also shows that the grain-boundary diffusion coefficients determined in this work are comparable to most of volume diffusion coefficients previously
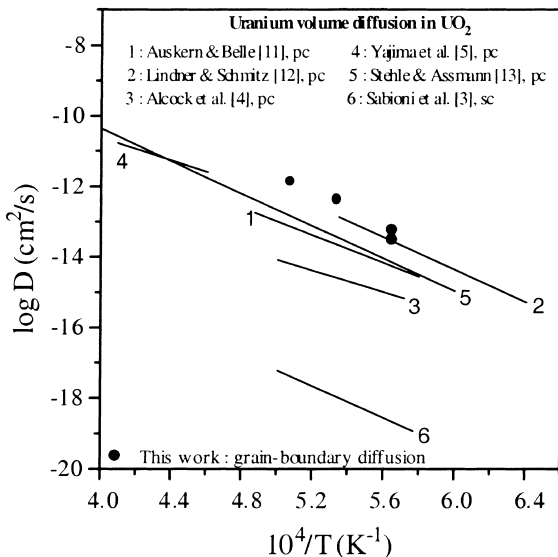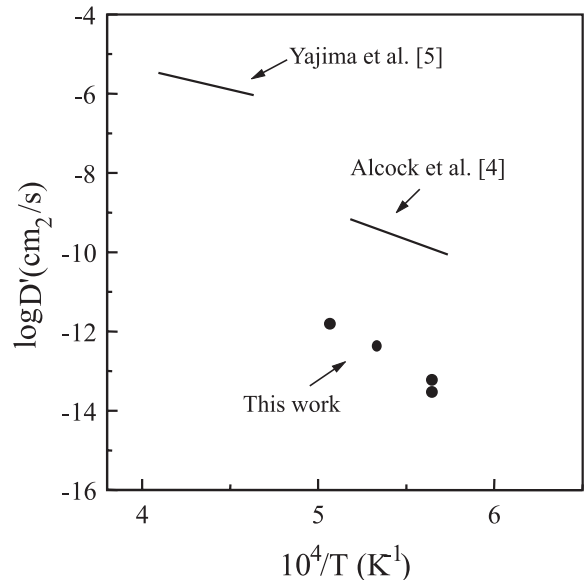

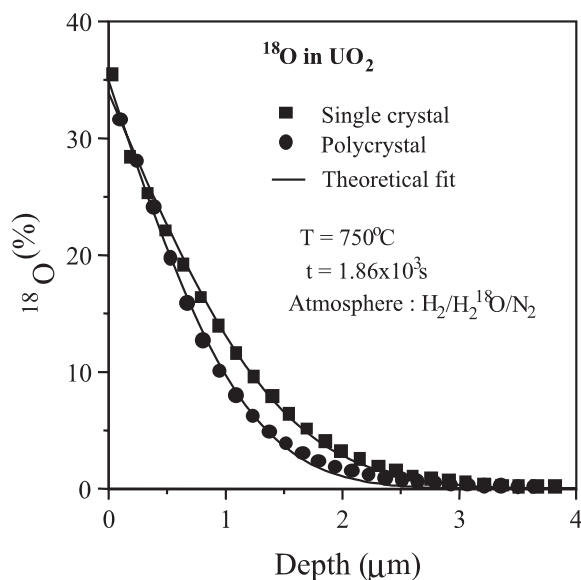Fig. 5. Comparison of grain-boundary diffusion coefficients determined in this work with volume diffusion coefficients measured in UO_2 single crystals [3] and in UO_2 polycrystals [4,5,11–13] (pc = polycrystal, sc = single crystal).

Fig. 6. Uranium diffusion in UO_2 grain-boundaries.

Fig. 7. Comparison of oxygen diffusion profiles measured in polycrystalline and single crystalline UO$_2$.

Fig. 8. Arrhenius diagram for oxygen diffusion in UO$_2$ single crystals and polycrystals.

determined in polycrystalline UO$_2$ [4,5,11–13]. It agrees with Reimann and Lundy [14] who have already shown that the volume diffusion coefficients determined in Refs. [5,11,12] are not representative of the true volume diffusion, but they correspond to the apparent values due to some short-circuiting mechanism.

Fig. 6 compares uranium grain-boundary diffusion coefficients, measured in this work, with the previous results determined by Alcock et al. [4], and by Yajima et al. [5]. Our results are lower than those of the previous works. This difference was expected, because the grain-boundary diffusion coefficients determined in the previous works [4,5] were calculated using very high values for the volume diffusion coefficients (apparent values), as shown in Fig. 5.

3.2. Oxygen diffusion in UO$_2$ polycrystals and single crystals

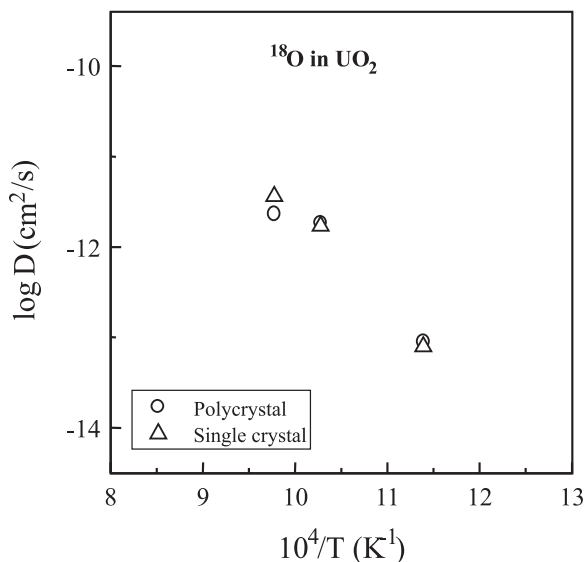In Fig. 7 diffusion profiles of oxygen in a UO$_2$ single crystal and in a UO$_2$ polycrystal, obtained in the same experimental conditions, are compared. The diffusion profile in the polycrystalline UO$_2$ does not show the typical tail that characterizes the grain-boundary diffusion such as that shown in Fig. 2 for uranium diffusion. Therefore, Fig. 7 shows the similarity between the oxygen diffusion in polycrystalline and single crystalline samples of UO$_2$.

The oxygen diffusion coefficients in single crystalline and polycrystalline UO$_2$ were determined through a solution of the diffusion equation, for diffusion in a semi-infinite medium from a constant surface concentration. This solution is given by [15]

$$\frac{C_s - C}{C_s - C_0} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right), \tag{2}$$

where C_s is the concentration of the tracer at the surface, C is the concentration as a function of position, C_0 is the natural abundance of tracer in the UO$_2$ (0.204%), x is the depth, D is the diffusion coefficient, t is the annealing time, and erf is the error function.

Table 2
Results obtained for oxygen diffusion in UO$_2$

Sample	Type	T (°C)	t (s)	D (cm^2/s)
1	Single crystal	605	6.060×10^4	7.91×10^{-14}
2	Single crystal	700	3.841×10^3	1.69×10^{-12}
3	Single crystal	750	1.860×10^3	3.61×10^{-12}
4	Polycrystal	605	6.060×10^4	8.92×10^{-14}
5	Polycrystal	700	3.841×10^3	1.84×10^{-12}
6	Polycrystal	750	1.860×10^3	2.30×10^{-12}

Fig. 7 also shows the fitting of Eq. (2) to the experimental diffusion profiles of ^{18}O measured in polycrystalline and single crystalline UO_2, in the same experimental conditions. As Eq. (2) is only applied for volume diffusion, and as it fits well to the oxygen diffusion profile in polycrystalline UO_2, it shows that the oxygen diffusion in UO_2 polycrystal essentially corresponds to the volume diffusion.

The experimental conditions used in this work, as well as the results obtained for the oxygen diffusion coefficients in UO_2, are listed in Table 2.

The Arrhenius diagram of Fig. 8 shows that oxygen diffusion coefficients measured in polycrystalline and single crystalline UO_2 are similar in the same experimental conditions. It means that the grain-boundaries are not preferential ways for oxygen diffusion in UO_2. This result agrees with previous work of Marin et Contamin [7].

It is worth noting, by comparing Figs. 5 and 8, that oxygen diffusion coefficients in UO_2 are much greater than the uranium volume diffusion coefficients extrapolated to the temperature range used in the oxygen diffusion experiments.

4. Conclusions

Uranium and oxygen diffusion coefficients were determined in uranium dioxide by using modern techniques. The aim of this study was to establish the role of the grain-boundaries on the uranium and oxygen diffusion in UO_2.

Between 1498°C and 1697°C, in H_2 atmosphere, uranium diffusion in UO_2 grain-boundaries is ca. five orders of magnitude greater than uranium volume diffusion, in the same experimental conditions. These results show that grain-boundaries are fast ways for uranium diffusion in polycrystalline UO_2.

The uranium grain-boundary diffusion coefficients determined in this work are comparable to most of uranium volume diffusion coefficients previously determined in polycrystalline samples, which confirms that most of previous data of uranium volume diffusion

coefficients determined in UO_2 polycrystals are in fact apparent diffusion coefficients due to some short-circuiting diffusion mechanism.

Between 605°C and 750°C, in $H_2/N_2/H_2O$ atmosphere, the oxygen diffusion coefficients measured in polycrystalline and single crystalline UO_2 are similar, and correspond to the volume diffusion. It means that the UO_2 grain-boundaries do not play an evident role on oxygen diffusion processes in UO_2.

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