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LETTER TO THE EDITORS

THE DIFFUSION OF URANIUM IN U_3O_8

1. Introduction

During oxidation of UO_2 in air, U_3O_8 (or U_3O_{8-x}) is the final product. U_3O_8 is not being used as nuclear fuel, but it is a material of interest for both basic and applied research. For instance, it is used as starting material for various reactions and also as standard for determining O/U-ratios of uranium oxides. The motivation for the present study of uranium self-diffusion was a technological problem. While oxidizing (U, Pu)C in air to facilitate solubility in HNO_3, a segregation of Pu between the MO_2 and the M_3O_8 phases formed is observed (M = U and/or Pu). The M_3O_8 is rich in U and the MO_2 phase becomes enriched in Pu, even if the oxidation is performed at relatively low temperatures, say at < 800°C [1–3]. Since Pu-rich MO_2 is not easily soluble in HNO_3, this causes difficulties in dissolving the oxidation product.

Oxygen diffusion is known to be fast in MO_2 and MO_{2+x}, but metal atom diffusion is very slow in UO_2 and MO_2 [4]. No data exist for U_3O_8. Transport of metal atoms, however, is needed for the observed segregation. To fill this gap, the self-diffusion of uranium in U_3O_8 was measured. Most experiments were performed at constant composition and some attempts were made to study diffusion during oxidation or reduction.

U-233 was used as a tracer, applying the thin layer condition and high resolution α-spectroscopy to measure the U-penetration profiles following different annealing steps. This non-destructive method of high resolving power has been described before [5–7].

2. Sintering of U_3O_8 diffusion samples

Sintered pellets of U_3O_8 are not commercially available. Some literature exists about sintering of U_3O_8. Fogaça and Falleiros [8] achieved densities of in average 7.6 g cm^{-3} (or ~ 90% of theoretical) at 1050°C in air. The temperature dependence of the sintering rate yielded an activation enthalphy of ~ 376 kJ mol^{-1}.

To produce suitable specimens for the present diffusion studies, green pellets of U_3O_8 were pressed, degased at 300°C for 2 h and sintered in air at temperatures between 800 and 1300°C. The densities achieved are summarized in table 1. At or above densities of 91%, sintering was apparently very slow. Based on these results, the diffusion specimens were sintered at 1200°C for 24 h and densities of 7.66 ± 0.03 g cm^{-3} or 91.4 ± 0.3% of theoretical were achieved.

U_3O_8 ($= UO_{2.667}$) is known to loose oxygen on annealing in air at temperatures above ~ 700°C [9–11]. Following sintering, substoichiometric specimens U_3O_{8-x} would thus be expected. The present samples were, however, all orthorhombic. Table 1 contains the lattice parameters of three batches. The specimens sintered at 850°C have lattice parameters of the orthorhombic cell in good agreement with literature values [11]. With decreasing oxygen content in U_3O_{8-x}, a is known to increase, b to decrease and c to remain constant, again in agreement with the results of table 1. In addition, annealing the as-sintered specimens for up to 5 d at 700°C did not change their density, but caused the weight to increase. Based on such weight increases,

Table 1
Densities achieved by sintering U_3O_8 in air

T (°C)	t (h)	ρ (g cm^{-3})	ρ (% of theor.) [a]	Lattice parameter (nm)		
				a	b	c
850	1	4.93	58.9	0.6717	1.1961	0.4149
1100	3	7.59	90.6	0.6736	1.1886	0.4145
1200	6	7.65	91.3	0.6740	1.1912	0.4147
1300	27	7.63	91.1	nd [b]	nd	nd

[a] A theoretical density of 8.38 g cm^{-3} was used.
[b] nd = not determined.

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the compositions at 1000 and 1200°C, respectively, were calculated to have been $UO_{2.658}$ and $UO_{2.655}$, respectively, corresponding to x-values in U_3O_{8-x} of 0.026 and 0.035. This again is in agreement with typical literature results [10,11]. Note also that the composition determined following annealing in air depends on the cooling rate [10] and is usually slightly higher than that actually occurring at temperature.

3. Results

Since the α-energy degradation method [5–7] is non-destructive, the samples could be used to measure the penetration profiles of the U-233 tracer at different times (0.5 to 160 h) at constant temperature. Three temperatures were used, i.e. 800, 1000 and 1200°C. To convert the measured α-energy spectra into the desired concentration-depth profiles, an energy loss of α-particles of U-233 in U_3O_8 of 245 keV/μm was calculated as described in ref. [12]. Two specimens were always annealed together in air such that two values of the square mean tracer penetration, $4 \cdot Dt$, in μm^2, could be deduced for each annealing step. Here, D is the diffusion coefficient. Fig. 1 shows that the expected straight lines were obtained in a plot of $4 \cdot Dt$ versus t. Open and full symbols represent the two specimens of the diffusion sandwich. At 800 and 1200°C, good agreement was achieved between the two specimens, whereas at 1000°C, one specimen showed consistently a slightly smaller tracer penetration than the other one. This difference, however, amounted to only a factor of 1.4 in D. The D-values obtained at the three experimental temperatures are plotted as squares in the form of an Arrhenius diagram in the lower part of fig. 2. These results represent diffusion coefficients for constant compositions (O/M-ratios), which, however, were different between the three temperatures used.

Attempts were also made to study U-diffusion during oxidation of UO_2 and during reduction of U_3O_8 since the observed segregation of U and Pu between MO_2 and M_3O_8 could tentatively also be assumed to be connected with enhanced atomic mobilities during phase

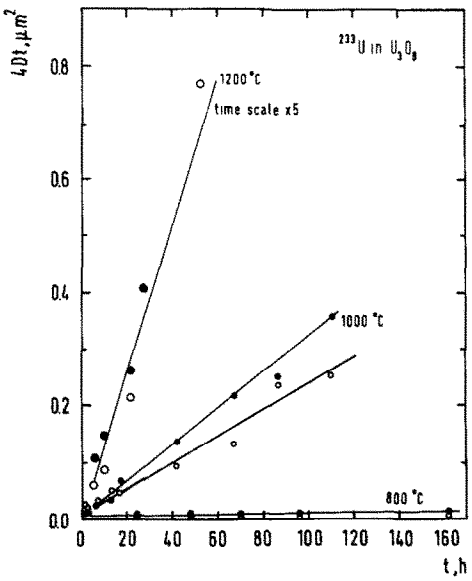

Fig. 1. Diffusional penetration of U-233 in U_3O_8 at 800, 1000 and 1200°C.

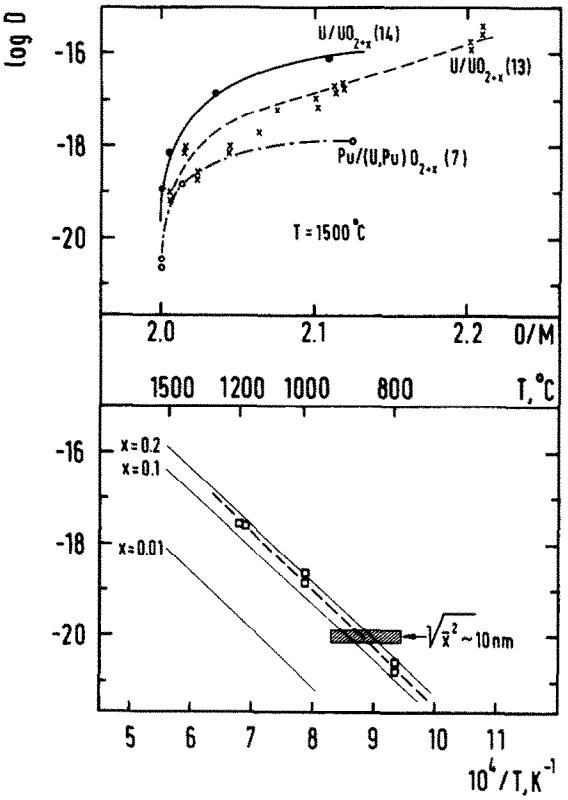

Fig. 2. Diffusion coefficients (in $m^2\ s^{-1}$) for U-233 in U_3O_8 in an Arrhenius diagram (lower part). The full lines show extrapolations from high temperature data [7,13,14] of uranium and plutonium diffusion in overstoichiometric UO_{2+x} and MO_{2+x} (see also upper part). The dashed area corresponds to a mean square displacement of 10 nm within 2 h and indicates the minimum mobility necessary for an observable Pu-segregation between the fluorite phase of MO_2 and the orthorhombic phase of M_3O_8.

changes or due to the pronounced mechanical, chemical, and vacancy gradients during oxidation (or reduction). For this latter possibility, pellets of U_3O_8 containing (U-233)-oxid tracer layers were annealed in a reducing atmosphere of CO and CO_2 ($CO : CO_2 = 10 : 1$) at 800°C for various periods of time (totals of 0.5, 3, 18, 21 and 24 h). The reduction proceeded fast, i.e. within the first annealing period. Since the total annealing time was only 1 d, only an upper limit of the diffusion coefficient for uranium of $D^U \leqslant 3 \times 10^{-20}$ m^2 s^{-1} was obtained. Attempts to measure diffusion during oxidation of UO_2 to U_3O_8 failed because the oxidation led to powder formation. Diffusion profiles could therefore not be measured under these conditions.

4. Discussion

As shown in fig. 2, diffusion of uranium in U_3O_8 is very slow at temperatures below 1000°C. Fig. 2 contains a dashed area which indicates the diffusion coefficient needed to achieve a mean atomic mobility of 10 nm within 2 h that might be thought to be necessary for an observable segregation. Obviously, diffusion at constant O/M-ratio cannot explain any Pu-enrichment or depletion below 800°C. The attempts to measure diffusion during reduction did not lead to diffusion coefficients essentially higher than without reduction; thus, enhanced diffusion during reduction does not occur. A tentative explanation could still be an activation of diffusion by the chemical and mechanical processes taking place during the formation of M_3O_8 from MO_{2+x}. Tracer diffusion experiments with a semi-infinite sample and the thin layer condition are not suitable to study this alternative.

The squares in fig. 2 could be described with an activation enthalpy ΔH of 240 kJ mol^{-1}. However, since different O/M-ratios existed at the different temperatures used, this value represents the activation enthalpy for constant oxygen pressure and not necessarily for constant composition. Fig. 2 contains also tracer diffusion data for UO_{2+x} and (U, Pu)O_{2+x} for 1500°C (upper part) which show a pronounced increase in both D^U and D^{Pu} with increasing oxidation within the MO_{2+x} phase. Extrapolation to lower temperatures, using the suggested migration enthalpy of uranium vacancies of $\Delta H^m_{M,v} \approx 2.4$ eV (≈ 230 kJ mol^{-1}) as the dominant metal defect in this O/M-range is shown for three O/M-ratios by thin lines in the lower part of fig. 2. The uranium self-diffusion in orthorhombic $U_3O_{8(-x)}$ proceeds at rates similar to those in cubic $UO_{2.2}$.

There are no other diffusion data for U_3O_8 with which to compare the present data except investigations of rare gas release (e.g. [15–17]). The rare gases were violently introduced into U_3O_8 by fission (Kr, Xe), or by ion bombardment (Xe, Rn). U_3O_8 is known to be rendered amorphous at fairly low ion doses [16,17]. It therefore shows a quite complex release behavior depending on the bombardment conditions used. Data attributed to crystalline U_3O_8 show diffusion coefficients of the same order of magnitude, but slightly larger, than the present D^U-values. This would be expected on the basis of the available knowledge on rare gas and self-diffusion in oxides [18]. These data can thus be regarded as being in agreement with the present results.

5. Summary and conclusions

The diffusion of U in orthorhombic $U_3O_{8(-x)}$ proceeds at rates similar to those in cubic $UO_{2.2}$. It is thus much faster than U diffusion in UO_2, but not fast enough to explain the observed segregation of metal atoms during the oxidation of (U, Pu)C or (U, Pu)O_2 to MO_2 and M_3O_8 for temperatures below 800°C. Though no enhanced diffusion was observed while reducing U_3O_8 to UO_{2+x}, the mechanical and chemical processes taking place during the oxidation of MO_{2+x} to M_3O_8 might enhance metal atom diffusion. Tracer experiments with the thin layer condition are not suitable to verify this hypothesis because of disintegration of the diffusion specimens into powder under oxidizing conditions.

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