

Letter to the Editors

Cation self-diffusion in $(\text{Th}-5\% \text{U})\text{O}_2$

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The utilization of thorium-based materials as nuclear fuels for pressurized water reactors was investigated in a joint Brazilian–German programme [1]. The present work was realized in the framework of that programme for the purpose of the determination of the cation volume self-diffusion in the nuclear fuel $(\text{Th}-5\% \text{U})\text{O}_2$.

In the actinide oxides of the fluorite type structure as ThO_2 , UO_2 , PuO_2 , etc., the cation is the more slowly moving species and is rate-determining in diffusion-controlled high temperature kinetic processes. In order to interpret the processes such as creep, grain growth, sintering and in-reactor densification it is necessary to know the cation diffusion coefficients in those oxides.

In $(\text{Th}-5\% \text{U})\text{O}_2$ there are two cations: thorium and uranium. According to the data published by Matzke [2] and King [3], the Th and U volume diffusion coefficients measured in ThO_2 single crystals have approxi-

mately the same values. Thus, in this work, the diffusion coefficients of Th and U in $(\text{Th}-5\% \text{U})\text{O}_2$ are assumed to have also the same values.

The Th and U volume diffusion coefficients were measured in $(\text{Th}-5\% \text{U})\text{O}_2$ polycrystals using Assmann and Stehle's model [4] for the thermal densification in the final-stage sintering, which is given by

$$\frac{\Delta V}{V_0} = \frac{6\gamma\Omega Dt}{kT} \sum_i (P_{0i}/r_{0i}^3), \quad (1)$$

where $\Delta V/V_0$ is the relative volume change of a sintered sample after a resintering test, γ the surface tension, Ω the vacancy volume, D the volume diffusion coefficient of the more slowly moving species, k Boltzmann's constant, t the annealing time of the resintering, T the absolute temperature, r_{0i} the initial radius of the i th class of pores in the sintered sample, and P_{0i}

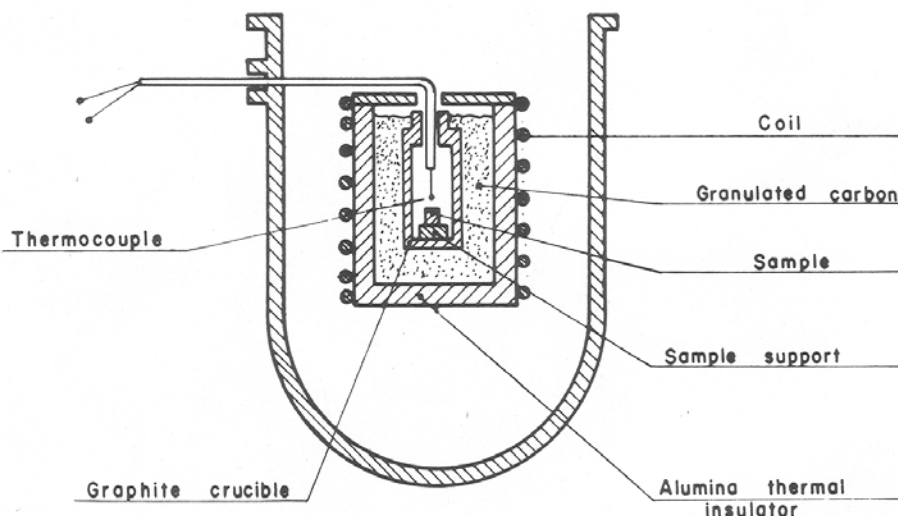


Fig. 1. Scheme of the heat-treatment arrangement used for resintering tests.

the volume fraction of the i th class of pores in the sintered sample.

In this model, described in detail in ref. [4], the basic mechanisms for shrinkage of the residual porosity are the generation of an excess vacancy concentration around the pores and the migration of vacancies to the grain boundaries by volume diffusion. This model was

successfully used by Assmann and Stehle [4] to evaluate the thermal densification in UO₂ pellets.

To determine the volume self-diffusion coefficient of the cations in (Th-5%U)O₂, using eq. (1), the factor $\sum_i (P_{0i}/r_{0i}^3)$ was calculated from the spatial pore distribution measured in the sintered samples through Saltykov's method [5]; the surface tension γ was taken

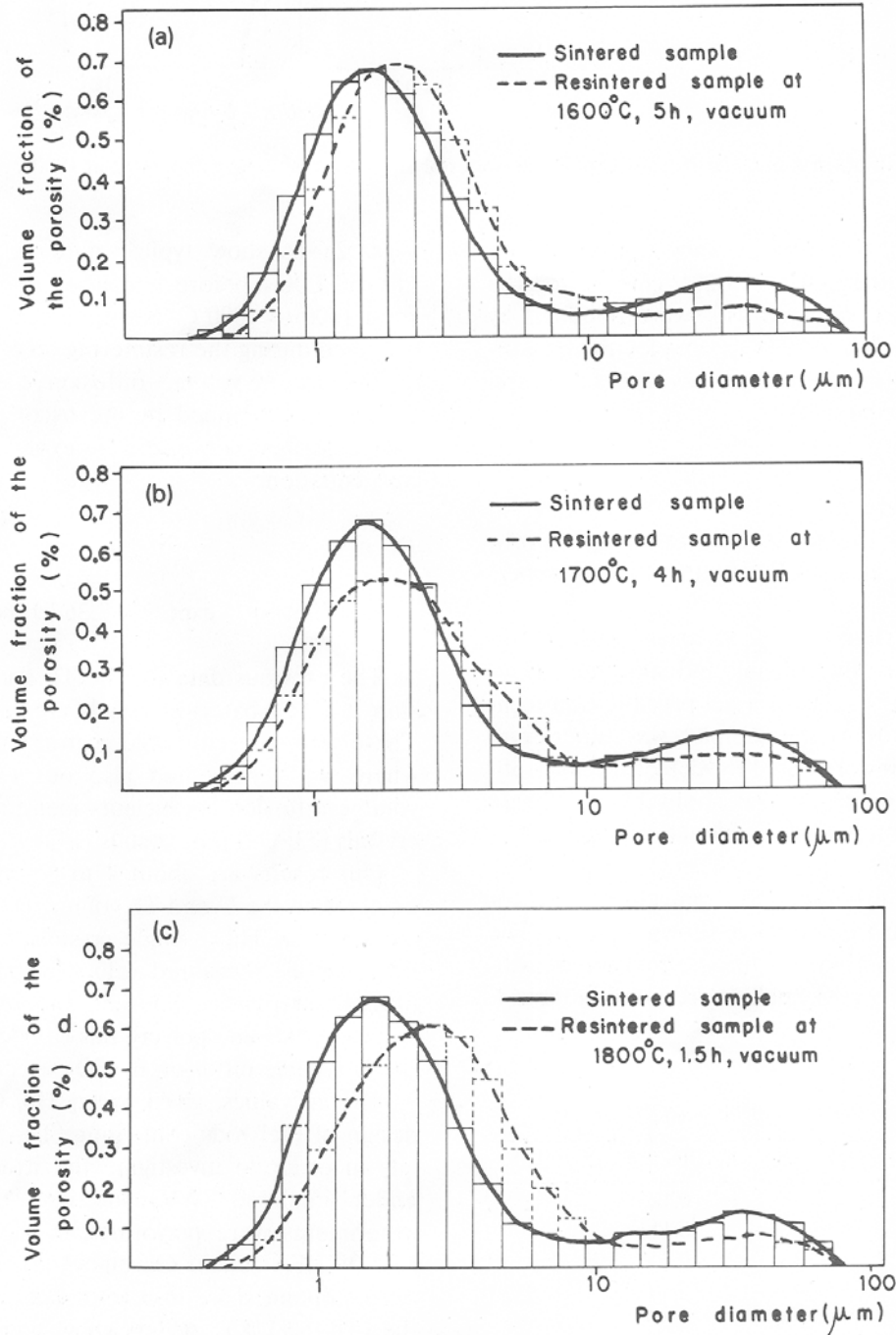


Fig. 2. Pore size distributions in (Th-5%U)O₂ pellets as-sintered and after resintering tests at (a) 1600°C, (b) 1700°C and (c) 1800°C.

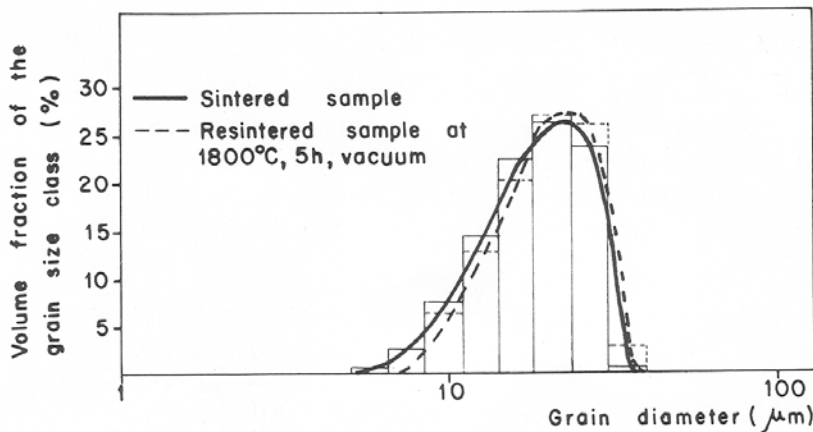


Fig. 3. Grain size distributions in a (Th-5%U)O₂ pellet as-sintered and after resintering annealing at 1800°C, 5 h under vacuum.

equal to 1.15 J/m² [6]; the vacancy volume Ω for (Th-5%U)O₂ is equal to 4.37×10^{-23} cm³ [7] and the thermal densification data $\Delta V/V_0$ were obtained by subjecting sintered (Th-5%U)O₂ samples to resintering tests. The relative volume changes were calculated through the expression

$$\Delta V/V_0 = \rho_s/\rho_r^{-1},$$

where ρ_s and ρ_r are the densities of the sample as-sintered and after the resintering test, respectively, both measured by means of the penetration-immersion method [8].

The sintered (Th-5%U)O₂ samples used in this study were produced by pressing and sintering microspheres obtained by means of a gel precipitation technique [1]. The purity of the samples was superior to 99.9%; the densities were equal to 95% of the theoretical value and the grain size was about 13 μ m. These samples were resintered in an induction furnace between 1600 and 1800°C under vacuum (1.3×10^{-2} Pa). The scheme of the experimental arrangement used for the resintering heat treatments is shown in fig. 1. The experimental results obtained for the thermal densification of the (Th-5%U)O₂ pellets are listed in table 1.

Table 1
Experimental results of the resintering tests

Sample	Temperature (°C)	Time (h)	Densification (%)
1	1600	5.0	0.126
2	1600	5.0	0.113
3	1700	4.0	0.270
4	1700	4.0	0.361
5	1700	5.0	0.377
6	1800	1.5	0.360
7	1800	5.0	0.614

Figs. 2a-2c show typical pore size distributions in (Th-5%U)O₂ before and after thermal densification from 1600 to 1800°C. No significant grain growth was observed during the resintering tests as shown in fig. 3.

The cation volume diffusion coefficients in (Th-5%U)O₂ determined by means of eq. (1), using the data described above, can be expressed by the Arrhenius equation

$$D(\text{cm}^2/\text{s}) = 5.47 \times 10^{-3} \exp(-367.36 \text{ kJ mol}^{-1}/RT). \quad (2)$$

The previous data for the Th and U volume diffusion in ThO₂-based materials are resumed in table 2. These data present large scatter as shown in fig. 4, where are represented also our results and the U volume diffusion coefficients measured in UO₂ single crystals [13] and polycrystals [14].

Our results are about 4 to 5 orders of magnitude higher than the U and Th volume diffusion coefficients measured in ThO₂ single crystals, but fall within the range of the measured values in polycrystalline samples. Discrepancies between the results obtained in single crystals and polycrystals can be observed also for the U volume diffusion in UO₂ as shown in fig. 4.

The D values, given by eq. (2), were used for the design of fuel rods containing (Th-5%U)O₂ fuel pellets in order to investigate the irradiation behaviour under simulated PWR conditions [1]. The irradiation experiments were performed in the research reactor FRJ-2 (KFA-Jülich, Germany) [1]. The experimental results obtained for in-reactor dimensional changes of the (Th-5%U)O₂ pellets show good agreement with the theoretical values calculated using the cation volume diffusion coefficients given by eq. (2).

Table 2
Parameters of cation lattice self-diffusion in thorium-based materials

Material ^{a)}	Diffusing element	Temperature range (°C)	Atmosphere	D_0 (cm ² /s)	Activation energy (kJ/mol)	Method ^{c)}	Ref.
ThO ₂ (SC)	U	1600–2000	Vacuum	0.5	627.9	A	[2]
ThO ₂ (SC)	Th	1924–2045	Ar	0.35	625.807	D + E	[3]
ThO ₂ (PP)	Th	1300–1600	Air	1.3×10^{-1}	389.298	B	[6]
ThO ₂ -2.31% CaO (PP)	Th	1300–1600	Air	4.02×10^{-6}	234.416	B	[6]
ThO ₂ -4.25% CaO (PP)	Th	1300–1600	Air	4.35×10^{-7}	196.742	B	[6]
ThO ₂ -8.8% CaO (PP)	Th	1300–1600	Air	3.43×10^{-7}	188.370	B	[6]
ThO ₂ (PC)	Th	925–1480	–	4×10^{-8}	133.022	C	[9]
ThO ₂ (PC)	Th	1600–2100	b)	1.25×10^{-7}	246.137	D	[10]
ThO ₂ (PC)	U	1800–2000	Ar	1.1×10^{-4}	319.577	E	[11]
ThO ₂ -50% UO ₂ (PC)	U	1800–2300	Ar	7.59×10^{-4}	359.577	E	[11]
ThO ₂ -5% UO ₂ (PP)	Th	950–1075	Air	7.26×10^{-2}	528.025	F	[12]
ThO ₂ -5% UO ₂ (PP)	Th	1050–1175	Ar + 4% H ₂	8.88×10^{-8}	449.155	F	[12]

a) SC = single crystal; PC = polycrystal and PP = pressed powder.

b) The experiments were conducted under air, CO/CO₂, vacuum and H₂. The Th diffusion in ThO₂ was found to be independent on oxygen pressure (10^{-20} to 0.2 atm) in the temperature range investigated.

c) Experimental methods:

A: α -energy degradation method.

B: Coble's model of intermediate stage sintering kinetics.

C: Determination of isotopic concentration gradients by mass spectrometry analysis.

D: α -ray spectrometry.

E: Sectioning method.

F: Johnson's model of initial stage sintering kinetics.

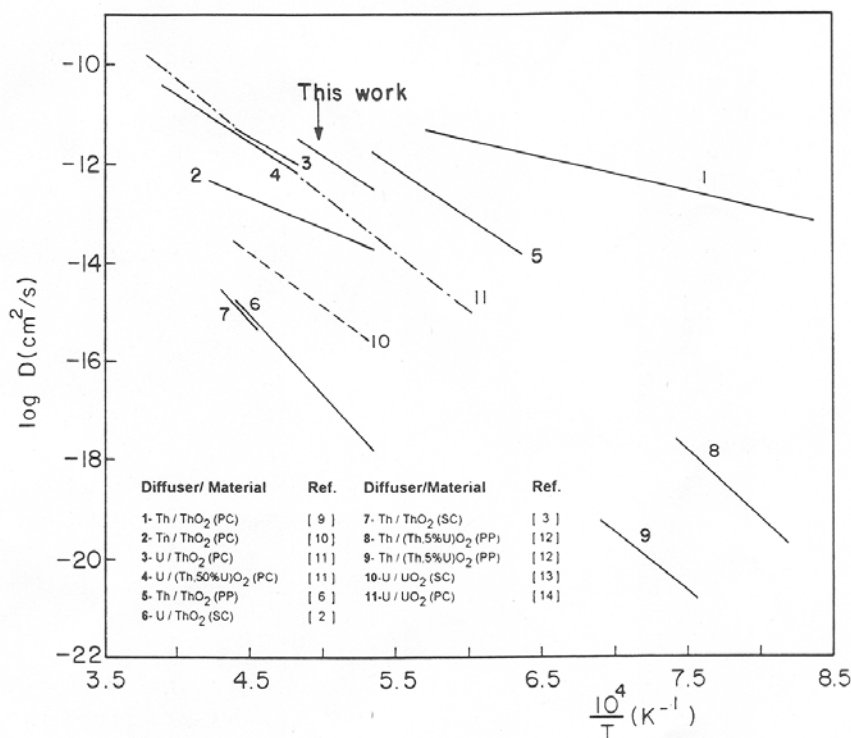


Fig. 4. Arrhenius plot of the Th and U diffusion coefficients D of the present results and the data of other authors. The solid lines are concerned to volume diffusion in ThO₂-based materials; (-----) U volume diffusion in UO₂ single crystals and (-·-·-) U volume diffusion in UO₂ polycrystals.

References

- [1] KFA, NUCLEBRAS, KWU, NUKEM – Program of Research and Development on the Thorium Utilization in PWRs, Final Report (1979–1988) Jül-Spez. 488 (1988).
- [2] H.J. Matzke, J. Phys. Colloque C7, 37 (1976) 452.
- [3] A.D. King, J. Nucl. Mater. 38 (1971) 347.
- [4] H. Assmann and H. Stehle, Nuc. Eng. Des. 48 (1978) 49.
- [5] S.A. Saltykov, Stereometrische Metallographie (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974).
- [6] S.N. Laha and A.R. Das, J. Nucl. Mater. 39 (1971) 285.
- [7] A.C.S. Sabioni, M.S. Thesis, Univ. Fed. de Minas Gerais, Brazil, 1985.
- [8] W. Dörr, H. Assmann, G. Mayer and J. Steven, J. Nucl. Mater. 81 (1979) 135.
- [9] C.S. Morgan and C.S. Yust, USAEC Rep. ORNL-3313 (1962) p. 142.
- [10] R.J. Hawkins and C.B. Alcock, J. Nucl. Mater. 26 (1968) 112.
- [11] H. Furuya, J. Nucl. Mater. 26 (1968) 123.
- [12] W.B. Ferraz, P.E. Cardoso and F.S. Lameiras, Anais do 34° Congresso Brasileiro de Cerâmica, May 1990, Blumenau, Brazil.
- [13] D.K. Reimann and T.S. Lundy, J. Am. Ceram. Soc. 52 (1969) 511.
- [14] H. Assmann, G. Maier and H. Stehle, Deutsches Atomforum, Proc. Reaktor-Tagung, Nürnberg, 1975, p. 391.