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PLUTONIUM DISTRIBUTION AND DIFFUSION IN UO_2-PuO_2 CERAMICS*

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Abstract

PLUTONIUM DISTRIBUTION AND DIFFUSION IN UO_2-PuO_2 CERAMICS. For the fabrication of UO_2-PuO_2 ceramics, a process combining economy with a sufficient degree of homogeneity is highly desirable. A good knowledge of the phase distribution after sintering of these ceramics and the determination of the maximum diameter of pure PuO_2 particles is necessary for the evaluation of the compatibility of the ceramic fuel with the canning material, the diffusion of the fission products, and the effect of the distribution on the Doppler coefficient of reactivity. Furthermore, the presence of pure PuO_2 particles complicates chemical dissolution during recycling. For this reason UO_2-PuO_2 pellets sintered in the temperature range from 1400 to 1600°C and for increasing periods from 1 to 32 h were examined by metallographic, autoradiographic and by quantitative electron microprobe analysis. The difference in relative amount and distribution of the constituents UO_2, PuO_2 and mixed oxide, observed by autoradiography and microprobe scanning pictures, is explained. The mean diameter of the pure PuO_2 particles and the frequency of the different particle diameters were computed from linear electron-microprobe scannings with the aid of an IBM 7074. From ultra-slow linear scannings the interdiffusion parameters in UO_2-PuO_2 ceramics were estimated.

INTRODUCTION

Segregation of plutonia in UO_2-PuO_2 has been up to now an unclearly defined, though necessary, evaluation parameter for fabrication procedures and in-pile performance of plutonium-containing ceramics [1, 2]. In a previous publication [3] it was shown that in reactor operation conditions, segregation occurs due to thermal diffusion, even for originally homogeneously mixed oxides.

The electron microprobe is an ideally suited instrument to analyse the following characteristics of sintered UO_2-PuO_2 pellets:

(1) Homogeneity of uranium and plutonium distribution, with determination of the resulting percentage of pure $PuO_{2\pm x}$, mixed $(U_a Pu_b)0_{2\pm x}$ and the pure UO_2 remaining

(2) Maximum diameter of the pure PuO_2 particles and distribution of the PuO_2 particle diameter

(3) Diffusion kinetics during sintering and influence of the sintering atmosphere.

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** EURATOM, Brussels, delegated to the Karlsruhe Fast Breeder Project.

MATERIALS AND METALLOGRAPHIC PREPARATION OF PLUTONIUM-CONTAINING CERAMICS

The available mechanically mixed UO_2-PuO_2 materials from three different laboratories – Institute of Radiochemistry, Kernforschungszentrum Karlsruhe (Dr. Dippel), Alkem, Alpha-Chemie und Metallurgie GmbH, Karlsruhe (Dr. Stoll), and BelgoNucléaire, Mol-Belgium – were generally sintered under comparable conditions; as can be seen from Table I.

TABLE I. CHARACTERISTICS OF MICROANALYSED UO_2-PuO_2 SAMPLES

Source	Composition (wt.% PuO_2)	Sintering conditions			Density (% TD)	O/M ratio
		Atmosphere	Temperature (°C)	Time (h)		
Inst. Radiochemistry	15	Ar + 6% H_2 > 200 ppm H_2O	1600	1	95.5	1.99 ± 0.01
	15		1600	2	96.1	
	15		1600	4	96.0	
	15		1600	8	93.1	
	15		1600	16	92.1	
	15		1600	32	90.5	
Alkem	25	Ar + 5% H_2 > 200 ppm H_2O	1450	2	ca. 93.0	1.99
	25		1450		93.0	2.00
Belgo-Nucléaire	20	Ar + 5% H_2 + 1500 ppm H_2O	1600	3	97.6	1.97
Belgo-Nucléaire	18	Ar + 5% H_2	1600	2.5	68.8	1.998
	18	Ar + 5% H_2 + 2500 ppm H_2O	1600	2.5	74.2	1.98
	18	Ar + 2% Air	1600	2.5	77.1	2.04

The pellets provided by the Institute of Radiochemistry were specially produced for these diffusion studies. Therefore the processing of the initial powders and the sintering conditions were absolutely comparable for these specimens. The results for the BelgoNucléaire pellets, demonstrating the influence of the sintering atmosphere on the plutonium distribution, are described in another paper to this Symposium [4].

The following steps are necessary to avoid possible α-contamination of the electron microprobe by plutonium-containing specimens. With the exception of the surface, which receives metallographic preparation, the specimen is enclosed in a conventional mounting resin (Struers conducting mounting resin or plexigum) or, even better, in a eutectic lead-bismuth alloy ($t_m \sim 120°C$). With this metallic mounting alloy existing cracks are filled and loose plutonia particles are retained. Furthermore geometrical and gross absorption effects are reduced. The diamond polishing includes a final treatment with 1/4 μm diamond paste. After ultrasonic cleaning in benzene, the specimen is submitted to optical microscopic examination and autoradiography. The surface is cleaned by repeated triafol replication – the last replica being checked for activity as well as the specimen. If necessary, a second ultrasonic decontamination precedes the vacuum evaporation of a 50-80 Å thick gold layer onto the polished and cleaned surface. This film has a three-fold purpose:

(1) To prevent α-contamination of the electron microprobe by retaining the loose activity of α-particles on the only open surface

(2) To increase the electrical conductivity of ceramics and prevent the deflection of the electron probe by electrostatic charging

(3) To increase the thermal conductivity and prevent a local rise in temperature of the specimen and a possible reaction of the specimen with the hydrocarbon deposits which result from the cracking of residual diffusion oil vapours.

EXPERIMENTAL AND ANALYTICAL PROCEDURES

For the microanalytical determinations a Cameca 46 D electron microprobe with four vacuum X-ray spectrometers was used. To minimize errors in the interpretation of results due to porosity or other geometrical irregularities of the surface of the ceramics, the plutonium and uranium concentrations were measured simultaneously by two independent fully focussing spectrometers on directly opposite sides of the specimen to be analysed. The plutonium concentrations were computed from the intensities of the $PuL\alpha_1$ line in a vacuum spectrometer equipped with a quartz (1120) monochromator and a sealed proportional counter, and the uranium concentrations by evaluation of the $UM\beta$ intensity in a spectrometer equipped with a (1010) quartz monochromator and a flow counter. Ultra-slow or slow mechanical linear scanning for several traverses over the whole specimen under a static electron beam (the spectrometers satisfying permanently the fully focussing conditions) in the direction perpendicular to the axis relating the two reflecting monochromators, with registration of the uranium and plutonium intensities, were necessary for the determination of the relative amounts of pure PuO_2 or UO_2 and mixed $(U, Pu)O_2$, as well as the distribution of the pure PuO_2

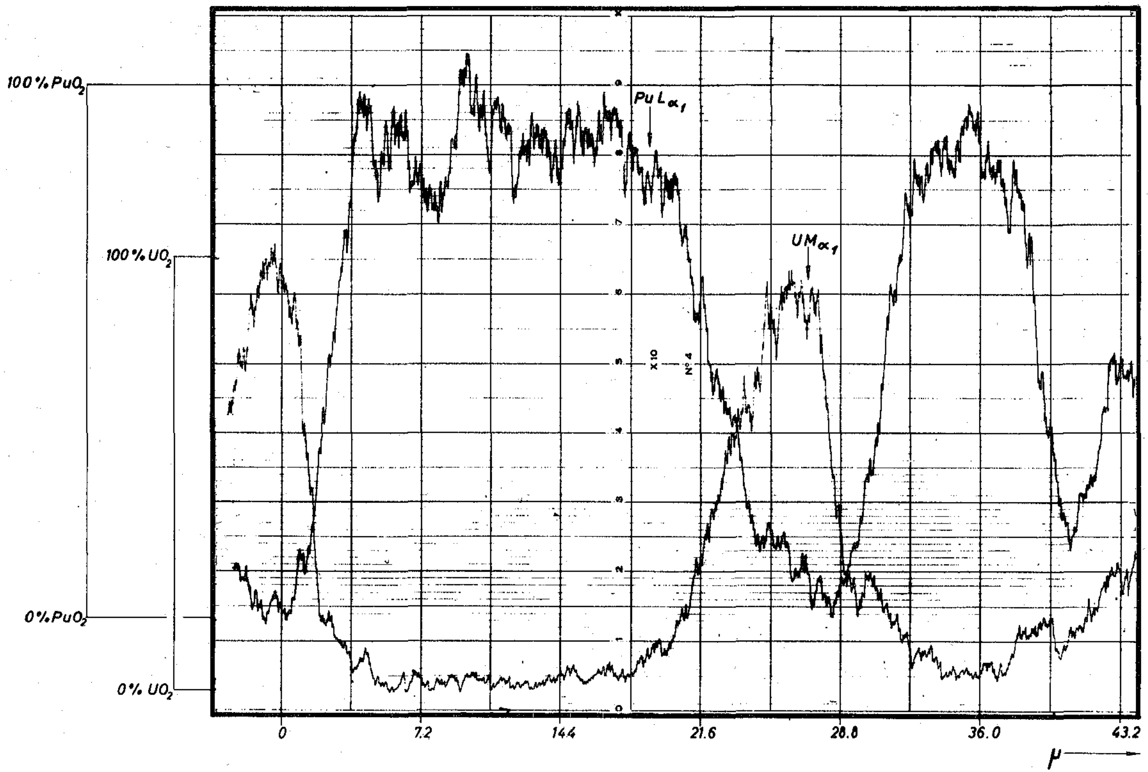
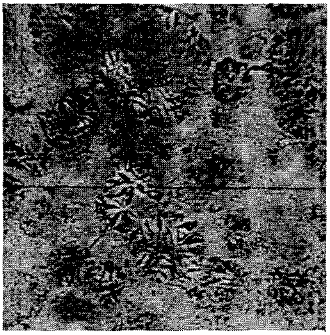


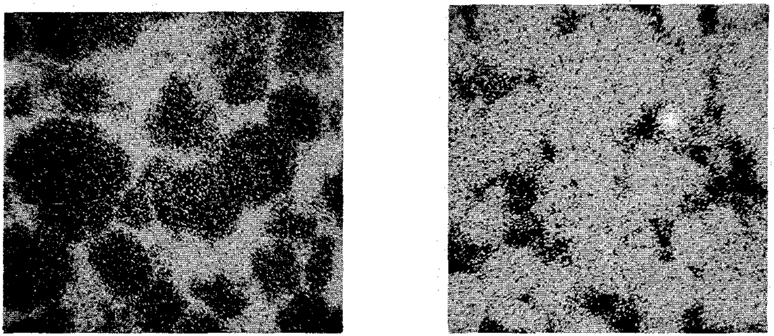
FIG. 1. Linear X-ray scan

segments. An extract of such a scan is seen in Fig. 1. Plutonium intensities corresponding to 85-100% PuO_2 combined with a background intensity for uranium are obtained over the whole section of a pure PuO_2 particle and, vice versa, about 100% UO_2 with background intensity for $PuL\alpha_1$ for pure UO_2.

The effective diameter of the electron probe could be reduced to 1 μm, as the focussed electron beam is about 0.5 μm and the penetration of electrons in the U, Pu ceramics down to the critical excitation voltage is only about 0.2 μm due to the high mean atomic number of these ceramics



electron optical *200μ x 200μ*

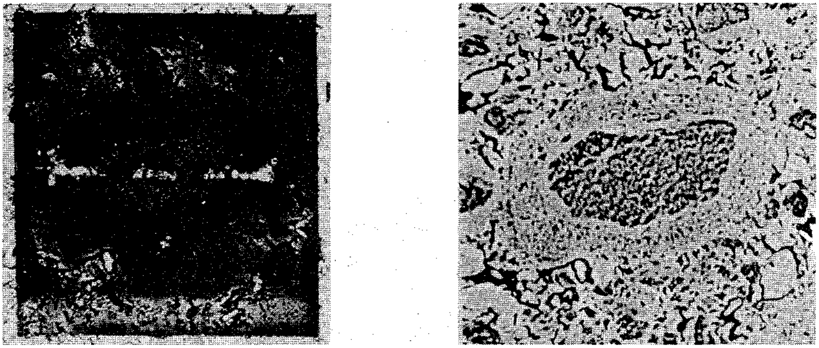


X-Ray *Pu Lα₁* *X-Ray* *UMα₁*

FIG. 2. Sintered UO_2-25PuO_2 (1450°C, 2 h, Ar + 5% H_2)

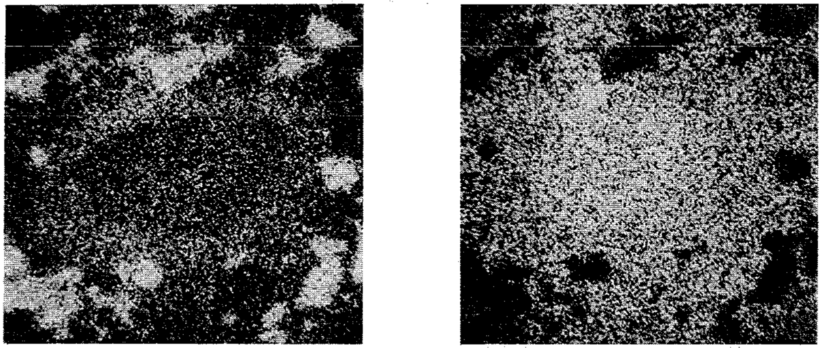
and the choice of a relatively low electron acceleration voltage (X-ray excitation range corresponding to an over-voltage of about 1.5 V/V_c). As the central part of concentration versus penetration plots give the most reliable data for the calculation of diffusion coefficients with the Gaussian error integral, investigations of very small interdiffusion zones (down to about 4 μm) were still possible.

It must be underlined that when recording these concentration versus penetration plots it is absolutely necessary that the direction of the linear X-ray scanning across the diffusion zone is parallel to the reflecting plane of the monochromators. Only if this condition is fulfilled is a differential absorption due to the Pu-concentration gradient avoided. Furthermore, during the final polishing steps, the intersected diameter of several larger PuO_2 particles was continuously observed. When the particles observed attained a maximum diameter, polishing was stopped.



Optical Micrograph

electron optical
300μ x 300μ



X-Ray $PuL\alpha_1$ *X-Ray* $UM\alpha_1$

300μ x 300μ

FIG. 3 a. Sintered UO_2-20 PuO_2(1600°C, 3 h)

Semi-quantitative survey studies are obtained by electronic surface scans (300 μm × 300 μm), Fig. 2. Plutonia particles (bright regions in the $PuL\alpha$ scanning image) surround the UO_2 particles (bright regions in the $UM\beta$ scan) with intermediate small interdiffusion zones. As will be shown later, Pu diffuses more rapidly in UO_2 than the U cation in PuO_2. The Kirkendall effect, with pores condensing in microcracks generally perpendicular to the interface, is observed in the absorbed electron scanning picture. Exceptionally, after sintering in very dry Ar + 5% H_2, microcracks surrounding the original interface appear (Fig. 3). The circumferential cracks can be observed clearly in the X-ray and ab-

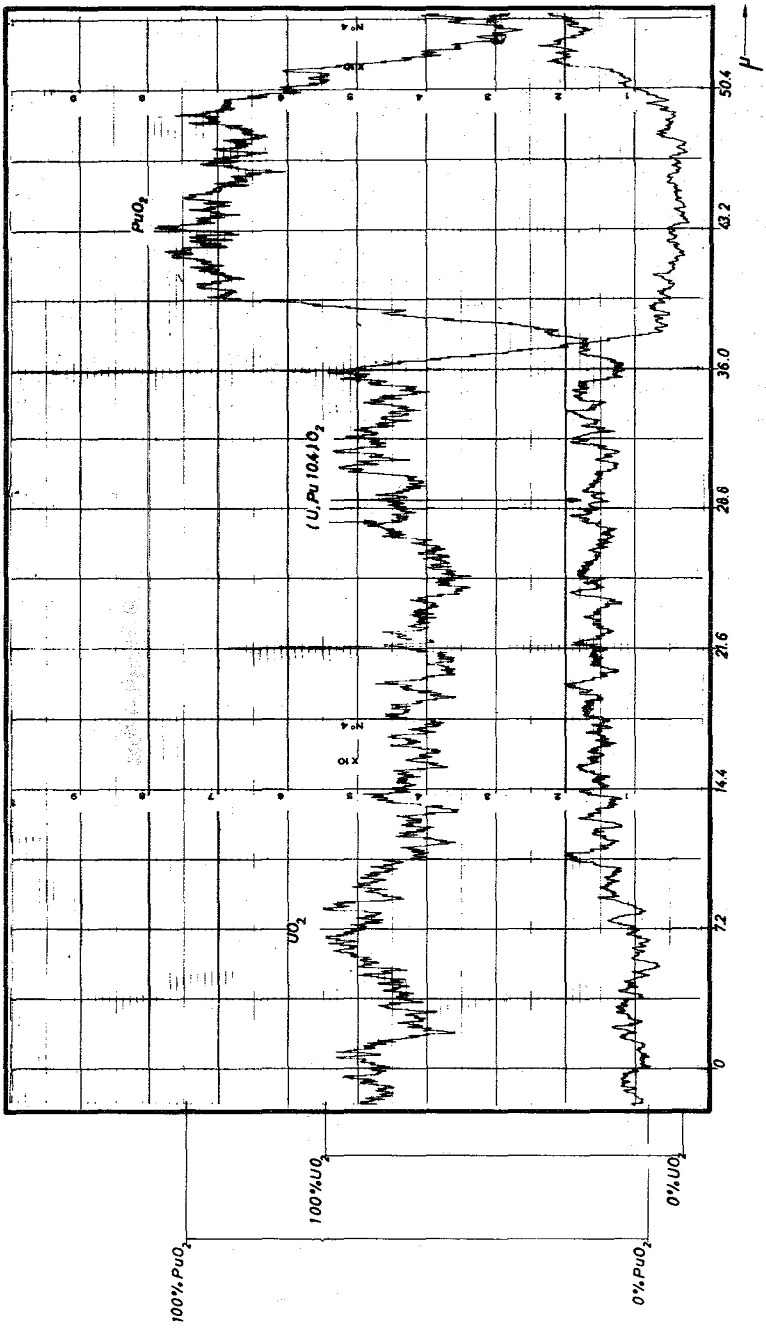


FIG.3b. Sintered UO$_2$-20PuO$_2$ (1600°C, 3 h)

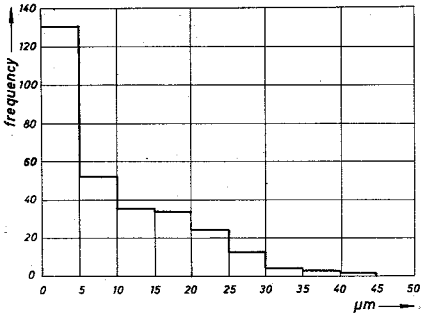
sorbed electron pictures. The corresponding linear scan (concentration versus penetration plot) demonstrates that the cracks must have formed during sintering. Their formation hampered further plutonium diffusion into the UO_2 particle and the original normal diffusion profile levelled out in the greater part of the diffusion zone.

The linear-scanning registration charts obtained with the microprobe were evaluated in the following manner to obtain a survey of the particle diameter distribution of incompletely dissolved PuO_2:

The length of the segments of pure PuO_2 were measured over the complete recorded diagram with the exception of those parts where the total amount of UO_2-PuO_2 did not add up to 100% as a consequence of geometrical irregularities of the surface (porosity). These segments were divided into different classes and the frequency of each fraction was counted. The segment distribution was converted to the spherical particle diameter distribution following a recently published procedure by Oel [5]. The primary condition for this method – the probability for a section is independent of its position – is fulfilled for a polishing procedure of small grain material. From the distribution of segment w(l) using the relation

$$w(l) = \int_{l}^{R} q(\rho)\, \frac{1\ d\rho}{(\rho^2 - l^2)^{\frac{1}{2}}} \tag{1}$$

the distribution $q(\rho)$ of circle segments (2 dimensions) is obtained. The next step leads to the calculation of the distribution of spherical diameters p(r) by



Autoradiographic determination measured by B.N. at Mol/Belgium

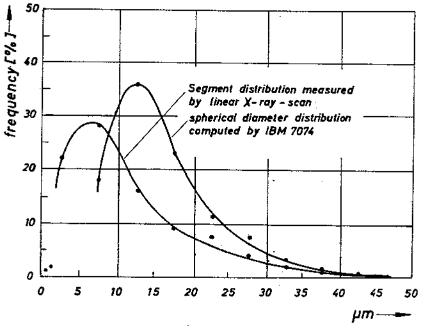


FIG. 4. Sintered $(U_{80}Pu_{20})O_2$ (1600°C, 2 h, Ar = 5% H_2)

$$q(\rho) = \int_{\rho}^{R} p(r) \frac{\rho \ d_r}{(r^2-\rho^2)^{\frac{1}{2}}} \quad (2)$$

Equations (1) and (2) are Abel integral equations which can be easily solved numerically by substituting the integrals by summation.

For the numerical solution of this problem a FØRTRAN programme was developed. In Fig.4 the calculated spherical diameter distribution of PuO_2 particles is indicated with the corresponding original, experimentally determined distribution of segments. Comparison with an autoradiographically determined particle distribution for the same specimen is of particular interest. The shift to smaller particle dimensions is probably explained by the absorption of α-particles in the specimens.

The relative amount of the sum of PuO_2 segments, the UO_2 and the segments of mixed $(U, Pu)O_2$ determined by the linear scan correspond to the volume fractions of these phases in the ceramics analysed.

The amount of $(U, Pu)O_2$ detected by this microanalytic procedure is in good agreement with chemical (nitric acid dissolution) studies by Bähr and Dippel [6].

INTERDIFFUSION IN SINTERED UO_2-PuO_2 PELLETS

Preliminary results of ^{239}Pu in sintered pellets of UO_2 by α-radiation absorption and sectioning by Schmitz and Lindner after annealings in the temperature range 1280 to 1575°C of UO_2 coated with a film of metallic Pu are described in Ref.[7]. Using a new radiochemical differential method, the temperature dependence of the diffusion coefficient is given by the equation

$$D = 0.34 \exp(-97\,300/RT) \quad (cm^2/sec)$$

The resulting energy for plutonium diffusion is 6.0 kcal/mol less than that of uranium diffusion measured by the same authors.

Evaluation of our ultra-slow linear scanning concentration versus penetration plots (an example is given in Fig.5) using either the formula indicated by Jost [8] taking into account the spherical geometry of the particles

$$\frac{c-c_b}{c_i-c_b} = \frac{6}{\pi 2} \exp(-t/\tau) \quad (3)$$

with

$$\tau = r_0^2/\pi^2 D$$

or the conventional solution by the Gaussian error integral results in a diagram (Fig.6) showing the diffusion coefficients of plutonium in UO_2 and uranium in PuO_2 for the temperature range 1450 to 1600°C. The extrapolation of the diffusion coefficients obtained for the temperature of 2400°C, gives reasonable agreement with the diffusion coefficients measured by

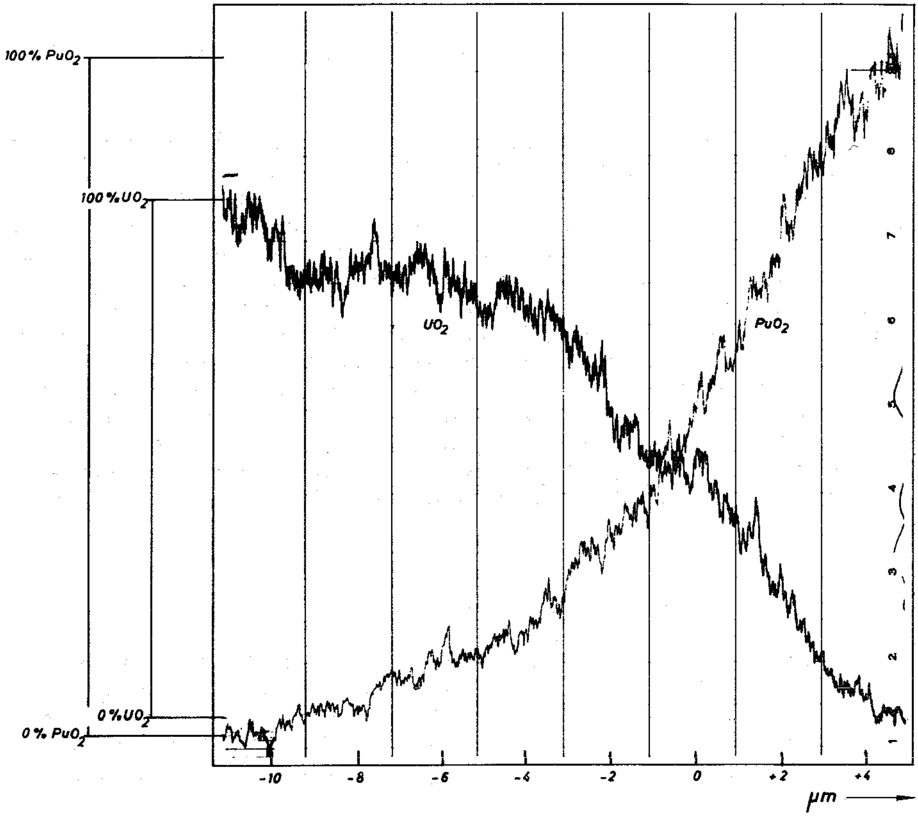


FIG. 5. Microprobe determination of interdiffusion in mixed U, Pu oxides at 1600°C, 32 h

Davies and Novak [9] for the interdiffusion in UO_2-PuO_2 samples at this temperature. Furthermore, these values are comparable with recent determinations of uranium-cation diffusion in UO_2 (UO_2 coated with an $^{233}UO_2$ layer) by Alcock et al. [10]. Alcock found an activation energy for uranium diffusion in UO_2 of 70 kcal/mol compared to activation energies of 67.8 kcal/mol for diffusion in PuO_2 and 64.9 kcal/mol for Pu diffusion in UO_2 from the present studies. For Alcock the temperature dependence of the U diffusion coefficient is expressed by the relation

$$D_U = 4 \times 10^{-7} \exp(-70\,000/RT) \quad (cm^2/sec)$$

whereas the diffusion coefficients of uranium and plutonium in our studies are described by

$$D_U = 9.25 \times 10^{-5} \exp(-67\,800/RT) \quad (cm^2/sec)$$

$$D_{Pu} = 12.4 \times 10^{-5} \exp(-64\,900/RT) \quad (cm^2/sec)$$

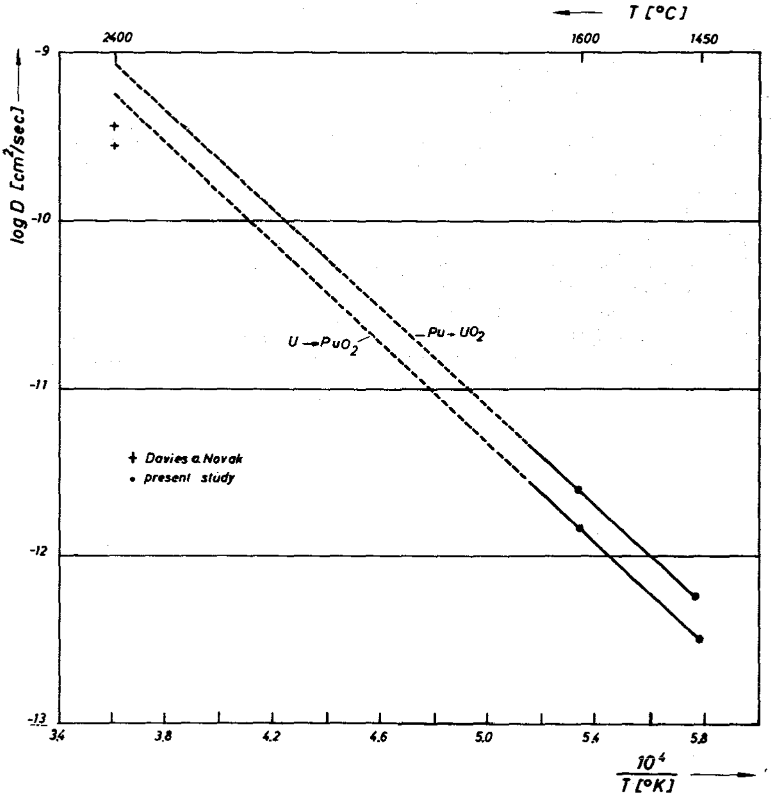


FIG. 6. Interdiffusion in mixed U, Pu oxides during sintering in Ar = 5% H_2

CONCLUSION

The present work demonstrates that the electron microprobe is ideally suited to the study of the distribution of uranium and plutonium in mixed oxides. A precise knowledge of these distributions is a necessary prerequisite to understanding the behaviour and performance of plutonium-bearing fuel elements during irradiation.

ACKNOWLEDGEMENTS

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