Diffusion of Non-Gaseous Fission Products in UO_2 Single Crystals II

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The release of short-lived non-gaseous fission products from UO_2 single crystals was studied in the temperature range of 1400 – 2500 °C by means of post-irradiation annealing. The release of the fission products studied appears to follow the kinetics of a diffusion process. Analysis of the data obtained gives the following diffusion constant,

$$D_{\text{Mo}} = 3.9 \times 10^{-4} \exp(-54{,}000/RT), \quad D_{\text{I}} = 1.5 \times 10^{-3} \exp(-59{,}000/RT),$$
$$D_{\text{Te}} = 6.6 \times 10^{-3} \exp(-70{,}000/RT), \quad D_{\text{La}}\,(\text{tentative}) = 2.2 \times 10^{-6} \exp(-35{,}000/RT)$$

where the dimensions of D and RT are cm²/sec and cal/mol, respectively.

Qualitative [1, 2] and quantitative [3, 4] data on diffusion of non-gaseous fission products in UO_2 have shown that the non-gaseous fission products diffuse with velocities comparable with those of gaseous fission products.

In our previous paper [4] the diffusion of Ce, Ru, Cs, Sr, and Zr-Nb in UO_2 single crystals was studied. In the present paper, further data on the out-diffusion of comparatively short-lived fission products (^{99}Mo, $^{131-2}$I, ^{132}Te, and ^{140}La) from irradiated UO_2 single crystals in the temperature range of 1400 – 2500 °C are reported. We also discuss the evaporation of the fission products from the surface of UO_2.

Experimental

All the experiments were carried out by heating neutron irradiated single crystals (weight 1 – 8 mg) in a coiled tungsten filament in He atmosphere for 20 – 120 min. The fractional release of each fission product was determined from the difference in activity before and after the heating. In addition to the points already mentioned in our previous paper [4] the following points should be added.

1. Purity of He: The oxygen and moisture contents of the He used were checked, since they may influence the diffusion in oxide systems [5]. The O_2 content, analyzed by using the MINOXO indicator (Engelhard Ind., Newark, U.S.A.), was less than 5 ppm. Also, the coiled tungsten heater would have burned when the He had contained more than 0.003% of oxygen. The moisture content was checked by the ordinary dew point method and was less than 3 ppm, the dew point being below – 70 °C. In order to avoid any contamination of the gas during the experiments the heating apparatus was connected to the gas cylinder with tight pipings.

2. O/U ratio of the UO_2 single crystals: The O/U ratio was analyzed polarographically and was found to be 2.0047.

3. Surface to volume ratio of the crystals: The ratio was calculated from the macroscopic dimension of each crystal as reported earlier. However, small changes in weight of the crystal occured when heated to more than 2000 °C. The single crystal took up UO_2 evaporated from that part of the UO_2 boat which reached higher temperatures. For example, a 7.0 mg UO_2 crystal increased by 0.2 mg in weight when heated for 1 hr at 2000 °C. However, this point does not affect our calculation of diffusion constants because the heating time became shorter at higher temperatures.

4. Determination of the amounts of fission products released: UO_2 single crystals were irradiated in the JRR-2 (nvt, 5×10^{16} n/cm²) or in the TTR-1 (nvt, 1.5×10^{15} n/cm²) and were cooled for one to three weeks. Analysis of nuclides was done by γ-spectrometry with a 256 channel pulseheight analyzer for ^{99}Mo (745 kev), ^{131}I (364 kev), ^{132}I (670 kev), ^{132}Te (230 kev), and ^{140}La (490 kev and 1.6 mev). In the case of ^{132}I correction was made for the decay of ^{132}Te during the experiments.

Results and Discussion

If we consider a single crystal as a sphere for the sake of simplicity, the diffusion constant D of a gaseous fission product is easily determined from the measured fractional release F in t, the time of heating, according to the equation [6]

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[2] J. L. Bates, J. A. Christensen, and W. E. Roake, Nucleonics **20**, No. 3, 88 [1962].

[3] F. Schmidt and R. Lindner, Z. Naturforschg. **16 a**, 1096 [1961].

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[5] R. Lindner, Proc. 2nd. Intern. Conf. on the Peaceful Uses of Atomic Energy P/167, Vol. 20, 116 [1958].

[6] H. S. Carslow and J. C. Jaeger, Conduction of Heat in Solid. Univ. Press, Oxford 1947, Chapter 9.

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\{-D\, n^2 \pi^2\, t/a^2\}, \qquad (1)$$

where a is the radius of the equivalent sphere. The actual evaluation of D was done by either plotting [7] F vs. $(D\,t/a^2)^{1/2}$ or by using the following approximation [8] when $D\,t/a^2 \ll 1$:

$$F = 2\sqrt{D\,t/\pi} \cdot (S/V) \qquad (2)$$

where S and V are the surface area and the volume of the crystal, respectively.

For non-gaseous fission products, however, we must also take into account the evaporation condition, since the release is caused by the evaporation of the fission products at the surface. It is reasonable to assume that the amount of a fission product evaporating per unit time from unit surface area of the crsytal is proportional to the concentration at the surface.

Thus $$-D\frac{\partial C}{\partial r} = \alpha\, C \quad \text{at} \quad r = a$$

and the fractional release is given [7] by

$$F = 1 - \sum_{n=1}^{\infty} \frac{6\, L^2 \exp\{-\beta_n^2\, D\, t/a^2\}}{\beta_n^2\{\beta_n^2 + L(L-1)\}} \qquad (3)$$

where $L = \alpha\, a/D$ and $\beta_n \cot \beta_n + L - 1 = 0$.

α may vary with temperature. For $L \gg 1$ eq. (3) reduces to eq. (1).

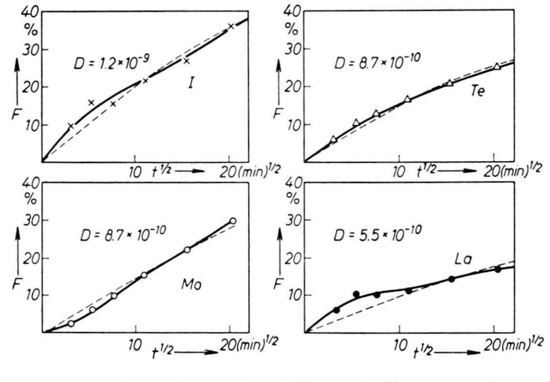

Fig. 1. The variation of F (%) with $t^{1/2}$ at 1900 °C.

Fig. 1 shows the variation of F with $t^{1/2}$ at 1900 °C for each fission product examined. Also shown in the figure with dotted lines are theoretical curves given by eq. (1) for suitably chosen D values. The fact that the two curves are in good coincidence for I, Te, and Mo seems to indicate that the L values are sufficiently large and that eq. (1) represents the fractional release in these cases. On the other hand, in the case of La, even for the best fitted D value there is no good agreement. Therefore, the D values of La should be regarded as only tentative.

It should be pointed out that Fig. 1 does not provide a complete proof of the validity of eq. (1) for the whole temperature range. But the D values obtained can serve as a lower limit of the diffusion coefficients. This was also the case for the diffusion coefficients of Ce, Ru, Cs, Sr, and Zr-Nb in our previous paper [4]. However, considering the size of the single crystals used (radius $\sim 5 \times 10^{-2}$ cm), the L values are actually sufficiently large for most of the fission products in the high temperature range ($\geqq$ 1500 °C). This was found in another investigation, the results of which will soon be published. Therefore, the diffusion coefficients were calculated from eq. (1). They are plotted in Fig. 2 against $1/T$.

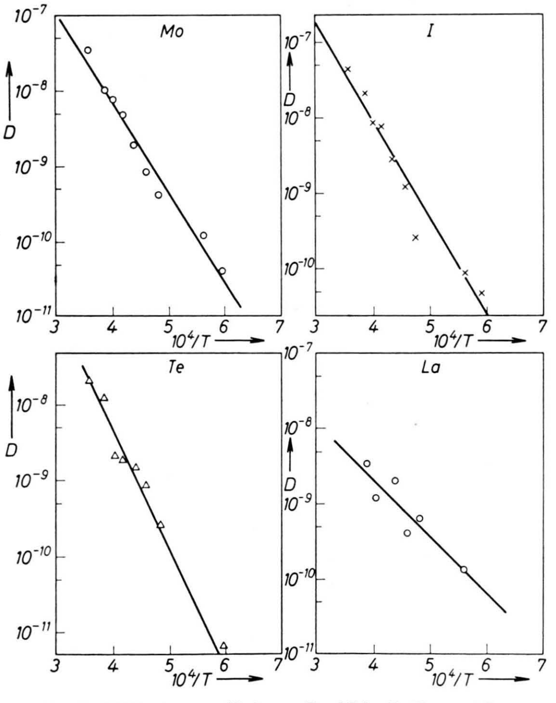

Fig. 2. Diffusion coefficients D of Mo, I, Te, and La.
Mo: $D = 3.9 \times 10^{-4} \exp(-54{,}300/R\,T)$;
I: $D = 1.5 \times 10^{-3} \exp(-59{,}400/R\,T)$;
Te: $D = 6.6 \times 10^{-3} \exp(-70{,}000/R\,T)$;
La: $D = 2.2 \times 10^{-6} \exp(-34{,}600/R\,T)$.

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[7] J. Crank, Mathematics of Diffusion, Univ. Press, Oxford 1956, Chapter VI.

[8] W. Inthoff and K. E. Zimen, Trans. Chalmers Univ. Technol., Gothenburg No. **176** [1956].

As the D values of Te, I, and Mo follow quite well the relation

$$D = D_0 \exp(-Q/R\,T) ,$$

D_0 and Q were determined by the least square method and are listed in Table 1, together with the tentative data for La.

	UO_2 single crystals		UC_2 single crystals [9]	
	D_0	Q	D_0	Q
Mo	3.9×10^{-4}	54		
I	1.5×10^{-3}	59	4.1×10^{-8}	53.3
Te	6.6×10^{-3}	70	1.3×10^{-5}	67.0
La	2.2×10^{-6} *	35 *		
Xe	3.0×10^{-4}	63	4.6×10^{-6}	68.0

* tentative values.

Table 1. Diffusion constants of fission products in UO_2 compared with those of UC_2.
$D\,(\mathrm{cm^2/sec}) = D_0\,(\mathrm{cm^2/sec}) \exp\{-Q\,(\mathrm{kcal/mol})/RT\}$.

Data are available for Te, I, and Xe release from single crystal UC_2 particles[9]. These are also listed in Table 1 along with our data on the release of Xe from UO_2 single crystals[10]. The values, especially of Q, for UO_2 and UC_2 are in rather marked agreement. It is likely that non-gaseous fission products, with the exception of Zr-Nb and Te, diffuse faster than gaseous fission products (Xe), at temperatures below 2200 °C.

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[10] N. Oi and J. Takagi, to be published.

Untersuchung der harten Röntgen-Strahlung am Theta-Pinch*

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Hard X-rays of several 100 keV can be observed during a few halfcycles of a thetapinch discharge before breakdown. No additional preionization was used. This X-ray emission can be explained by bremsstrahlung of freely accelerated electrons colliding with the wall of the tube.

Investigation of the location of X-ray emission shows that the drift motion of the electrons to the wall is influenced by the potential field of the coil. On the other hand no influence of this potential field can be observed in the halfwave before breakdown when a high degree of ionization has been reached.

Thus time dependent local X-ray emission can indicate the prevailing field configuration.

The ratio of X-ray intensities before and behind a Cu absorber is compared with theoretically calculated values. Absorption measurements at the discharge tube wall at the middle and outside of the coil show that a transport mechanism affects the energy distribution of the electrons reaching the wall.

Bei schnellen Kondensatorentladungen (Halbwertsdauer $\tau = 3{,}2\ \mu$s) über eine Theta-Pinchspule, welche ein gasgefülltes Rohr umgibt, können in den Halbwellen vor der Zündung Elektronen bis zu Energien von einigen 100 keV beschleunigt werden. In diesen Halbwellen reicht die Ladungsträgerdichte für eine Zündung noch nicht aus. Ebenso ist die Neutralteilchendichte bei ca. $2 \cdot 10^{-2}$ Torr Füllgasdruck so gering, daß ein Elektron während der Beschleunigungsphase mit nur geringer Wahrscheinlichkeit einen unelastischen Stoß erfährt. Damit wird das Elektron auf einer Bahn beschleunigt[1], die durch das Ein-Teilchen-Modell beschrieben werden kann.

Für eine Beschleunigung zu hoher Energie kommen nur solche Elektronen in Frage, welche schon innerhalb eines kurzen Zeitraums (ca. $1 \cdot 10^{-9}$ s) nach dem Nulldurchgang des ansteigenden Magnet-

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* Dissertationsauszug, Technische Hochschule München 1965.

** Jetzt: FOM Laboratorium voor Massascheiding, Amsterdam, Kruislaan 407.

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