Diffusion of Non-Gaseous Fission Products in UO₂ Single Crystals II

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The release of short-lived non-gaseous fission products from UO₂ 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, 

\[ D_t = 3.9 \times 10^{-4} \exp(-54,000/RT), \]

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 UO₂ 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 UO₂ single crystals was studied. In the present paper, further data on the out-diffusion of comparatively short-lived fission products (²⁹Mo, ¹³¹I, ¹³²Te, and ¹⁴⁰La) from irradiated UO₂ 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 UO₂.

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 O₂ content, analyzed by using the MINOXO indicator (Engelhard Ind., Newark, N.J.), 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 UO₂ 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 the weight of the crystal occurred when heated to more than 2000 °C. The single crystal took up UO₂ evaporated from that part of the UO₂ boat which reached higher temperatures. For example, a 7.0 mg UO₂ 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: UO₂ single crystals were irradiated in the JRR-2 (nvt, 5 × 10¹⁶ n/cm²) or in the TTR-1 (nvt, 1.5 × 10¹⁵ 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 ²⁹Mo (745 keV), ¹³¹I (364 keV), ¹³²I (670 keV), ¹³²Te (230 keV), and ¹⁴⁰La (490 kev and 1.6 mev). In the case of ¹³²I correction was made for the decay of ¹³²Te 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

\[ F = \frac{6D}{r^2} \int_0^t \exp\left(-\frac{D}{r^2} t\right) dt \]

where \( r \) is the radius of the crystal.

\[ D = \frac{2.2 \times 10^{-6}}{m^2/sec} \exp\left(-\frac{35,000}{RT}\right) \]

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

\[
F = 2\sqrt{D t/x} \cdot (S/V) \tag{2}
\]

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 crystal 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 by

\[
F = 1 - \sum_{n=1}^{\infty} 6 L^2 \exp \left\{ -\beta_n^2 D t/a^2 \right\} \tag{3}
\]

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

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

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. 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 \((\geq 1500°C)\). 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: \(D = 3.9 \times 10^{-4} \exp\left( -54,300/R T \right)\);

I: \(D = 1.5 \times 10^{-3} \exp\left( -59,400/R T \right)\);

Te: \(D = 6.6 \times 10^{-3} \exp\left( -70,000/R T \right)\);

La: \(D = 2.2 \times 10^{-6} \exp\left( -34,600/R T \right)\).

\(^7\) Crank, Mathematics of Diffusion, Univ. Press, Oxford 1956, Chapter VI.

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

$$ D = D_0 \exp \left( -\frac{Q}{RT} \right), $$

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

<table>
<thead>
<tr>
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<th>UO$_2$ single crystals</th>
<th>UC$_2$ single crystals $^*$</th>
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<tbody>
<tr>
<td></td>
<td>$D_0$</td>
<td>$Q$</td>
</tr>
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<tr>
<td>Xe</td>
<td>3.0X10$^{-4}$</td>
<td>63</td>
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</table>

* tentative values.

Table 1. Diffusion constants of fission products in UO$_2$ compared with those of UC$_2$.

$D$(cm$^2$/sec) = $D_0$(cm$^2$/sec)$\exp\{-Q$(kcal/mol)/RT$\}$.

Data are available for Te, I, and Xe release from single crystal UC$_2$ particles. These are also listed in Table 1 along with our data on the release of Xe from UO$_2$ single crystals. 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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