Evaporation Behavior of Non-gaseous Fission Products from UO_2

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The evaporation behavior of non-gaseous fission products from UO_2 was studied. The release rate of non-gaseous fission products during the post-irradiation annealing of UO_2 was found to be controlled by the proportionality constant of evaporation, α, as well as the diffusion constant. The values of α for Ru, Ce, La, Mo and Te were determined at temperatures ranging 750 to 1600 °C and the general method of treating non-gaseous fission product release from UO_2 was discussed.

Zumwalt et al.[1] have reported the diffusion constants of I, Te and Ba in UC_2 single crystals, while Oi and the author[2,3] have measured the diffusion constants of various non-gaseous fission products in UO_2 single crystals. In these works, the diffusion was studied by application of the method usually used for the determination of the diffusion of gaseous fission products, Kr and Xe[4,5], where the fractional release F of the fission products from a sphere of radius a is given by

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

D; diffusion constant, t; annealing time.

However[3], when the surface evaporation condition

$$-D \frac{\partial C}{\partial r} = \alpha C \qquad \text{(surface)}$$

α; proportionality constant of evaporation,
is taken into consideration[6,7], the fractional release should be given by the equation

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

$$L = \frac{a\,\alpha}{D}, \quad \beta_n \cot \beta_n + L - 1 = 0 .$$

For the single crystals with equivalent radii of 0.3 – 0.7 mm used in the previous works, equ. (1) was assumed to hold for reasons to be mentioned later on in this paper. The data obtained in this way from equ. (1) are listed in Table 1 for various fission products, among which the values for Ru, Ce, Sr and Zr – Nb result from the previous ones and additional experiments.

Nuclides	D_0 (cm²/sec)	Q (cal/g · atom)
^{106}Ru	5.5×10^{-7}	27,000
^{144}Ce	1.2×10^{-4}	50,000
^{90}Sr	1.0×10^{-6}	27,000
^{95}Zr – ^{95}Nb	2.4×10^{-2}	92,000
^{131,2}I	1.5×10^{-3}	59,000
^{99}Mo	3.9×10^{-4}	54,000
^{132}Te	6.6×10^{-3}	70,000
^{140}La	2.2×10^{-6}	35,000

Table 1. D values obtained by single crystals ($a = 0.3 - 0.7$ mm).

On the other hand, the fractional release of non-gaseous fission products from UO_2 samples consisting of grains with much smaller radii (0.055 μ) proved to be fairly smaller than expected from equ. (1) with the D's of Table 1. This suppressed release arises from the slow evaporation of non-gaseous fission products and is successfully explained by equ. (2) with suitably chosen L values. An attempt is made to clarify the release behavior of non-gaseous fission products by determining evaporation rate coefficient α for Ru, Ce, La, Te and Mo. The treatment will present a general method applicable to systems where non-diffusional transfers of fission products like initial burst[4] and trapping[8] are negligible.

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Experimental

The UO_2 powders obtained from DEGUSSA (Germany) consisted of crystal grains with an average radius 0.055 μ which suffered significant growth when heated over 1000 °C. The grain size at each temperature of annealing was measured by the BET and electron microscopic method. It was confirmed by Oi[9] that the release of Xe from the samples satisfies eq. (1) only if corrections for the increase of a are made.

Each 10 – 20 mg of the UO_2 powder irradiated in TTR-1 ($n\,v\,t$, 1.5×10^{15} n/cm^2) or in JRR-2 ($n\,v\,t$. 5×10^{16} n/cm^2) and cooled for 1 – 8 weeks was heated in a platinum boat by a tungsten filament. The heating continued for 10 – 60 min under a constant flow of He (~ 1 m/min at the sample position) at 750 °C to 1600 °C. γ-ray spectra were taken for each sample before and after the heating and the fractional release was calculated from the difference of the activities for each fission product examined.

Results and Discussions

(1) Equation (2) implies that the fractional release depends not only upon the diffusion constant D but upon the parameter L which is also a function of the evaporation rate coefficient α. F increases with L and in the limit of $L \to \infty$, equ. (2) reduces to equ. (1), which means that the evaporation is so rapid that the release rate is determined by diffusion alone. Solutions of equation (2) for some L values are tabulated in the literature[10].

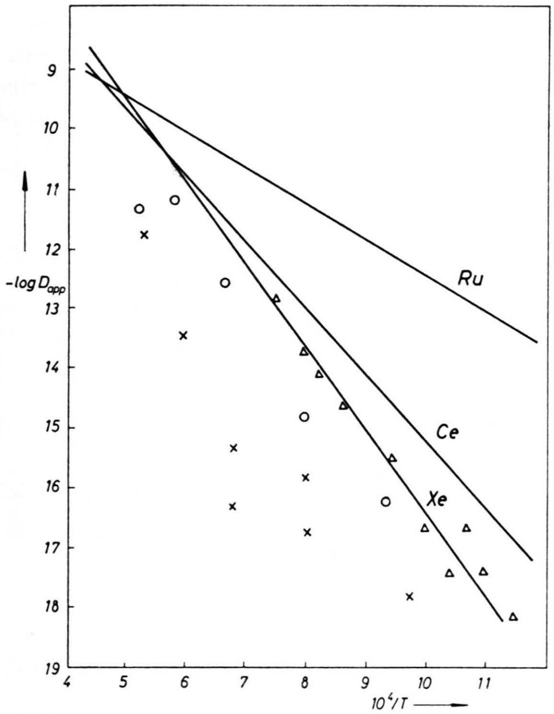

Fig. 1. D values calculated from Table 1 (solid lines) and apparent D values obtained by application of eq. (1) on fine UO_2 powders (△ - - - - Xe, ○ . . . Ru, × . . . Ce).

For small a and therefore small L the results obtained by application of equ. (2) differ much from those obtained from equ. (1). An example is illustrated in Fig. 1 for Ru and Ce. The phenomena can not be ascribed to structural differences between the two kinds of specimen, since the release of Xe follows equ. (1) in both cases.

With the observed F values and the D values of Table 1 the values of α were evaluated for each fission product and at each temperature investigated. For this purpose F vs L $(0.1 \leqq L \leqq 100)$ was plotted for experimentally given $\sqrt{D\,t/a^2}$ values. This was performed by computing the summation of equ. (2) up to the term $n = 2$, and by solving

$$\beta_n \cot \beta_n + L - 1 = 0$$

graphically. The errors of this method of estimation are quite small as compared with the experimental scatters.

In most cases, L was found to lie below 0.1. In these cases, the α was calculated independently of D by the following approximation

$$\beta_1 = \sqrt{3\,L}\,, \qquad F = 1 - \exp\left(-\frac{3\,\alpha\,t}{a}\right) \qquad (3)$$

Fig. 2 shows Arrhenius plots of α's for the five fission products examined. Generally, α may be written in the form $\alpha = \alpha_0 \exp(-E_\alpha/R\,T)$, where E_α is the activation energy of evaporation. The observed values of E_α are listed in Table 2 along with the melting points and boiling points of the metals. Although little significance is attributed to the absolute values of α, as they may change with experimental conditions, e. g. sweep gas flow rate[11], α can serve as a measure of the relative evaporation behavior of various fission products from UO_2 (Table 3). Furthermore, E_α will be of help in identifying the evaporating species: observed small values might suggest the formation of some volatile compound. Detailed investigations on the in-pile evaporation

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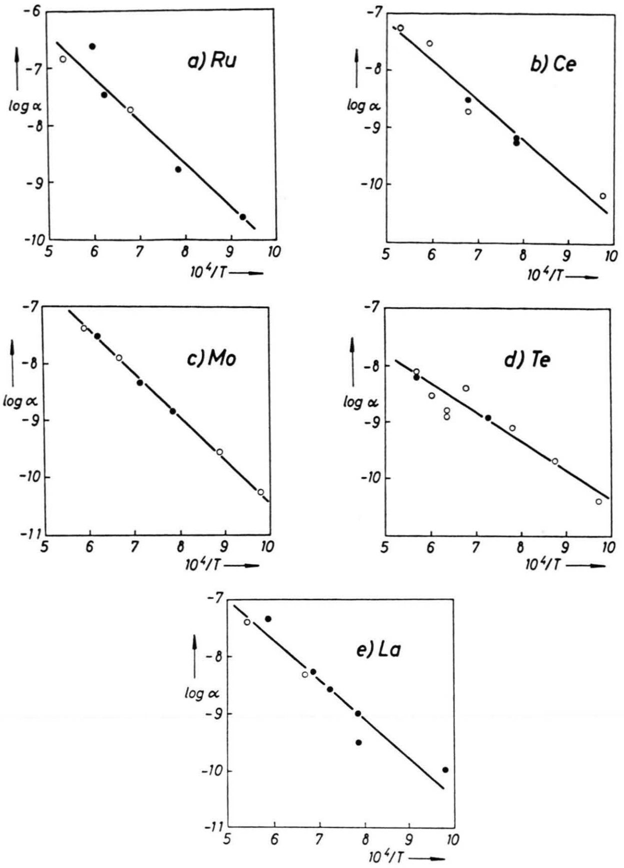

Fig. 2. ARRHENIUS plots of α (cm/sec) $\left[\begin{array}{l}\bigcirc \ldots L \geqq 0.1\\ \bullet \ldots L < 0.1\end{array}\right]$

Elements	E_α (Cal/g · atom)	Melting points (°C)	Boiling points (°C)
Ru	34	2,500	4,100
Mo	37	2,620	4,800
Te	22	452	1,390
Ce	30	804	1,400
La	30	920	4,500

Table 2. Activation energy of evaporation.

behavior of fission products at much higher temperatures have been reported by the ORNL group [12, 13].

In publications [14, 15] concerning the release of fission products into reactor coolants from defected fuel elements, it was observed that the release rates of fission products other than the rare gases are much lower than predicted from the diffusional behaviour, while Kr and Xe release was found to follow the diffusional mechanism [16]. Table 3 seems to explain the fact fairly well, although, of course, the whole of these in-pile behaviours are too complicated to be interpreted by single mechanism.

(2) In the aforementioned treatment the diffusion constants previously obtained by the use of single crystals were regarded as good approximate values, since $L = \infty$ was believed to hold for most of the fission products examined, the reason being as follows.

(i) The variation of F with $\sqrt{t}$ follows equ. (1) except in case of La, where the agreement of measurement with equ. (2) is not so good. The results were discussed previously [3].

(ii) In evaluating α values in Fig. 2, the α's were determined by using D values for L values above 0.1. The α values plotted as hollow circles agree well with the points for $L < 0.1$ which were calculated directly from equ. (3) without use of D (solid circles). This agreement establishes the self-consistency of the present treatment.

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Elements	Ru	Ce	Mo	Te	La	Xe
α (cm/sec)	1.6×10^{-8}	4.0×10^{-9}	1.0×10^{-8}	1.7×10^{-9}	7.2×10^{-9}	—
D (cm²/sec)	5.3×10^{-11}	3.6×10^{-12}	3.7×10^{-12}	3.1×10^{-13}	1.5×10^{-11}	1.4×10^{-12}
L $(= a\,\alpha/D)$	0.03	0.11	0.27	0.55	0.48	∞
F for present experimental conditions (%)	25	6.7	14	2.9	12	72
Relative release	1	0.27	0.56	0.12	0.48	2.9

Table 3. Relative release at 1200 °C predicted from α values for $a = 1.0 \times 10^{-4}$ cm and $t = 600$ sec.

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