Xe Diffusion in UO_2 Single Crystals

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The release of Xe-133 from UO_2 single crystals and UO_2 fine particles was investigated in He atmosphere in the temperature range of $600-2400$ °C. The D value obtained was

$$D\ (\text{cm}^2/\text{sec}) = 3.0\times10^{-3}\ (\text{cm}^2/\text{sec})\ \exp\{-63{,}000\ (\text{cal/mol})/R\,T\}\,.$$

Much work has been carried out on Xe diffusion in UO_2 (l. c.[1]), but the diffusion constants reported have a scatter of more than three orders of magnitude, well beyond the limit of experimental errors. The scattering of data may principally arise from the use of UO_2 pellets instead of single crystals.

A few published data on single crystals also seem to scatter. In the present work, the diffusion of Xe-133 in UO_2 single crystals and UO_2 fine particles was investigated in He atmosphere in the temperature range $600-2400$ °C.

Experimental

The apparatus used was much the same as that used for non-gaseous fission products diffusion[2, 3] and therefore will be described here only summarily.

Three kinds of samples were used; Sample-A, UO_2 single crystals ($1-7$ mg) prepared by molten salt electrolysis, Sample-B, very fine UO_2 particles (average diameter 0.11 μ) which could be regarded as single crystals according to X-ray and the electron microscopic analysis, obtained from DEGUSSA (Germany), and Sample-C, UO_2 particles prepared by annealing the Sample-B at 1500 °C for two hours in He atmosphere (diameter 8 μ). These specimens were irradiated in the JRR-2 ($n\,v\,t\sim5\times10^{16}$ n/cm²) or the TTR-1 ($n\,v\,t\sim7\times10^{14}$ n/cm²) and were then cooled for $5-15$ days. A coiled tungsten filament (outside diameter of the coil 7 mm, nine turns, diameter of the filament 1 mm) supported by two stainless steel rods sealed into a glass bulb (diameter 20 cm), was used as a heating apparatus. A single crystal (Sample-A) or $5-10$ mg of powder in a small Pt boat (Sample B or C) was placed on a UO_2 slab which was put inside the filament and was subsequently heated for 20 min to 3 hrs with a current of $20-50$ A in He atmosphere. The temperature was calibrated by the melting of pure metals such as Cu, Au, Ni, and Cr. The maximum temperature which could be attained with this apparatus was limited by the melting of the UO_2 boat at 2750 °C. Measurements up to 2400 °C were carried out fairly easily.

He gas was swept through the bulb and was passed to a liquid nitrogen cooled charcoal trap where released Xe-133 was collected. The total Xe gas in each specimen was analyzed by dissolving it in $Na_2S_2O_7$ melt and collecting the Xe released in the He sweep by means of a cold trap. The Xe activities of both traps were counted by a scintillation counter. The diffusion constant D was calculated from the fractional release F in t sec according to the equation[4]

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

where a is the radius of the equivalent sphere. The actual evaluation of D is done either by using the graphical plot[5] of F vs. $(D\,t/a^2)^{1/2}$ or by the approximation[6] (when $D\,t/a^2 \ll 1$)

$$F = 2\sqrt{\frac{D\,t}{\pi}}\cdot\frac{S}{V}$$

where S/V is the surface to volume ratio of the sample. In case of Sample-A, S/V was evaluated from the weight of each sample by assuming a cube for the shape of the crystal. In cases of Sample-B and C, it was determined by the BET gas adsorption method as well as from the electron microscopic photographs. Because of the growth of particle sizes occuring in the case of fine particles, it was necessary to correct S/V at each annealing temperature. For this purpose, the change of particle radius with annealing temperatur was examined. The result is shown in Fig. 1. The growth of particle radius was not appreciably influenced by extended annealing times.

Results

1. $t^{1/2}$ vs F Relationship

Fig. 2 shows the $t^{1/2}$ vs F relationship measured at 1500, 1800, and 2000 °C for UO_2 single crystals (Sample-A). No initial burst was observed.

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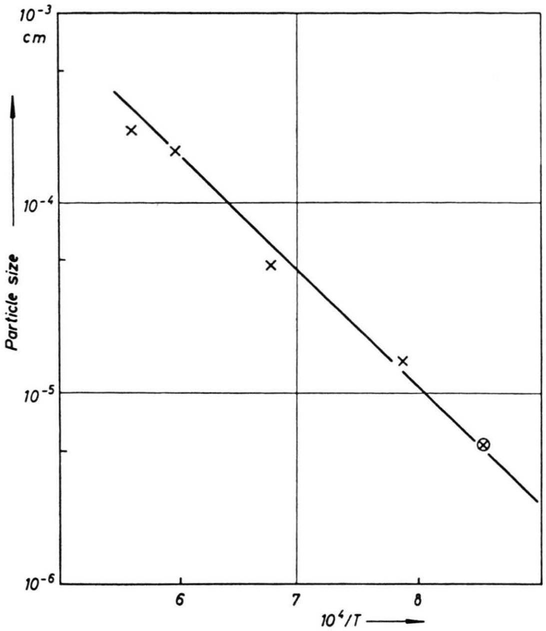

Fig. 1. Grain growth with annealing temperature. He atmosphere, Annealing time 30 min. — × from electron microscopic photographs, o from BET gas adsorption method.

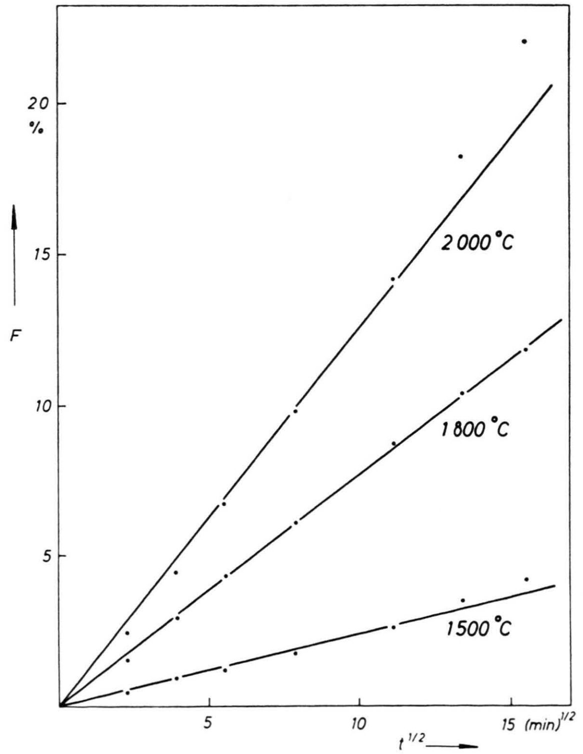

Fig. 2. The variation of $F(\%)$ with $t^{1/2}$ at 1500°, 1800°, and 2000 °C.

2. *D* Values

The annealing experiments were performed at 1300 – 2400 °C for Sample-A, 600 – 1150 °C for Sample-B and 1000 – 1400 °C for Sample-C. These temperature ranges were selected in order to minimize the errors which arise from too small and also near complete fractional releases. The D values are plotted in Fig. 3 against the reciprocal of absolute temperature, where for Sample-B correction of the particle growth was made from Fig. 1 for the calculation of the D values at higher temperatures.

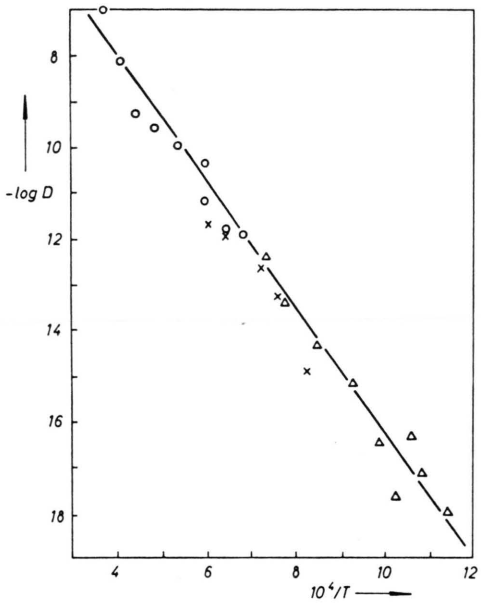

Fig. 3. Diffusion constants of Xe-133. ○ single crystals, △ UO_2 fine particles not annealed, × annealed UO_2 particles.

It is noteworthy that these twenty-three D values for the three quite different kinds of specimens fall on a straight line covering more than eleven orders of magnitude in the diffusion constant. By means of the least square method the D values are calculated and expressed by

$$D = 3.0 \times 10^{-3} \exp(-63{,}000/RT)$$

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

Discussion

Release of fission gases from UO_2, especially above 1000 °C, has been believed to follow essentially the kinetics of solid diffusion processes, although the results of some in-pile experiments at relatively low temperature (400 – 1300 °C) can well be explained by fission recoil and trapping mechanisms [7] rather than by volume diffusion.

Some influencing factors on the release of Xe from UO_2 single crystals has been summarized by FELIX et al. [8]; evaporation of UO_2 at high temperatures, irradiation dose effect, initial burst and incomplete gas release. These factors were fully considered in our experiment. Evaporation of UO_2 which tends to give high D values especially above 1600 °C in vacuum, is almost negligible in He (<2000 °C) and it was further reduced by the short annealing time at high temperatures (>2000 °C). This is one of the reasons why we performed the experiments in He atmosphere. The influence of irradiation doses which is responsible for the trapping of gas atoms in the lattice, may be disregarded above 1200 °C [9]. For lower temperature experiments (600 – 1400 °C) however, slightly irradiated powders ($n\,v\,t < 10^{15}$ n/cm²) were used.

Initial burst and other abnormal releases which have often been found [7, 10] especially in very small F value ranges seem to originate from the surface condition of the sample. In our experiments, annealing conditions were selected so as to give sufficient Xe release to fully cover the tiny abnormal release from the surface. As is shown in Fig. 2, the F vs $t^{1/2}$ relationship demonstrates a straight line without initial burst. Therefore, in this experiment, the diffusion can be regarded as ideal.

Our value for the activation energy 63 kcal/mol can be favorably compared with the data for single crystals of the Mol (70 ± 5 kcal/mol) and the BMI (70 kcal/mol) which are listed in the paper by FELIX et al. [8] but not with the data of BARNES et al. [10] (30 kcal/mol).

Although the experiments were carried out in He atmosphere, instead of in vacuum, it is believed that this makes no marked difference, as was pointed out by other workers [11].

ZENER [12] suggested that the activation entropy of diffusion in metals should be small and positive and that large negative values indicate the availability of short-circuiting paths for the diffusing species. If this theory can be applied to UO_2, the entropy of activation (ΔS) may be estimated from the D_0 by the relation

$$D_0 = \gamma\, a^2\, \nu \exp(\Delta S/R)$$

where γ is unity for f.c.c. crystal and a is the lattice parameter. The atomic frequency ν was evaluated to be 2.6×10^{12} sec^{-1} according to the atomic diffusion model proposed by WERT and ZENER [13], rather than to estimate it from the tentative DEBYE temperature of UO_2 (l. c. [14]) as was done by LUSTMAN [15].

$$\nu = (E/2\, m\, \lambda^2)^{1/2},$$

E: Activation energy,
λ: distance between the interstitial positions.

From the D_0 value 3.0×10^{-3} and the activation energy of 63 kcal/mol, the small negative value -1.9 eu was obtained. This value, although still negative, is fairly larger than that expected from most of the D_0 values hitherto reported.

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