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November 1966

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ABSTRACT

The lattice diffusion coefficient of  $Xe^{133}$  in cast uranium monocarbide was measured by postirradiation anneal experiments in the temperature range 1000°C to 2000°C. The experimental results were analyzed by a small-time solution of Fick's law in which the effect of depletion of the surface layer due to recoil was incorporated in the initial distribution. The diffusion coefficient of specimens consisting of large grains (700 to 1000 microns) was best approximated by

$$D = (1.17 \pm 0.16)10^{-6} \exp \left[ - \frac{54900 \pm 1200}{RT} \right]$$

in the range 1000°C to 2000°C. Specimens with small grains (20 to 150 microns) exhibited the same diffusion coefficient as the large grain samples above 1500°C. Below 1500°C diffusivities in small-grained specimens varied widely, indicating dependence on grain size and hence, the existence of appreciable grain-boundary diffusion.

## INTRODUCTION

One important criterion of a new high-temperature reactor fuel, such as uranium carbide, is its fission product retention characteristics at elevated temperatures. The release of the noble gases by diffusion is of particular interest in this regard.

Previous experiments on the diffusion of xenon in uranium monocarbide have been limited to small particles and relatively low temperatures. Lindner and Matzke (1) used specimens obtained by crushing arc-cast UC (20-250 microns) and studied release over the temperature range 800 to 1300°C. Auskern and Osawa (2) employed very fine powders (0.27 m<sup>2</sup>/gm) and covered the temperature range from 1000 to 1400°C. The discrepancies between the diffusion coefficients reported in these two studies are greater than three orders of magnitude. Such differences may be due to one or more of the following reasons:

- (1) The history and method of preparation of the samples are important variables, since diffusional processes are quite sensitive to impurities and imperfection in the crystal structure;
- (2) The surface area measured by gas adsorption techniques may not represent the surface available for diffusional release (1);
- (3) In the case of the large fractional releases characteristic of small particles, the apparent diffusion coefficients are strongly dependent upon the grain size distribution (3).

The postirradiation anneal experiments reported here attempted to circumvent some of these difficulties by employing large samples (cast right circular cylinders, 0.5 × 0.5 cm) which were examined metallographically for grain size and microstructure prior to irradiation.

The data analysis was based upon the assumption that lattice diffusion was the controlling mechanism, and that the surface area available for gas release was equivalent to the geometrical area of the cylinder. Because of the small surface-to-volume ratio of the large specimens, release occurred primarily from the region close to the surface. Since this region is precisely the one most affected by depletion due to fission fragment recoil, the usual solution to the Fick's-law diffusion equation (4) was re-examined in order to account for the initial non-uniformity in xenon concentration.

#### Experimental Procedure

The cast specimens were obtained from the Battelle Memorial Institute and exhibited typical hyperstoichiometric uranium monocarbide structure.

The carbon contents ranged from 4.97 to 5.15 w/o, and the grain sizes from 20 to 150 microns. The grain size was relatively uniform in each specimen, as shown in Figs. 1-3. Larger grain sizes (up to 1000 microns) were obtained by annealing the specimens at 2000°C before irradiation. Figure 4 is typical of the increase in grain size resulting from this treatment.

The specimens were initially prepared, at the Battelle Institute, by carbon arc melting in an inert atmosphere and then drop casting in 1/4 inch diameter graphite molds. The castings were radiographed before and after machining to final size, then sealed in glass tubes containing Drierite for shipment. The material was stored in vacuum desiccators and was exposed to air only during the few minutes required for experimental handling.

Specimens were transferred from the desiccator to pyrex test tubes, which were evacuated, sealed, and irradiated in the Livermore reactor for 2-10 minutes at a flux of  $\sim 5 \times 10^{12}$  n/cm<sup>2</sup>-sec and at a temperature of approximately 20°C. The irradiated samples were cooled for at least 3 days before the anneal to permit all precursors to decay to Xe<sup>133</sup>.

A sketch of the annealing apparatus is shown in Fig. 5, and the induction chamber in Fig. 6. The sealed pyrex tube was broken, the specimen transferred to a tungsten cup, and the top of the cup covered with a tungsten disc. The loaded cup was hung by three wires in the induction chamber. The entire apparatus was then evacuated and the sample held at the desired temperature for approximately 12 hours. The sample temperature was obtained from optical-pyrometer measurements, with suitable corrections for emissivity and transmission.

The fission products released from the sample were passed through a silver trap to remove iodine and then to a liquid-nitrogen charcoal trap to collect the noble gases. The rise in the 81 keV photopeak with time was measured by a system consisting of a NaI crystal, photomultiplier tube, preamplifier, and pulse-height analyzer. In order to determine the fractional release during the anneal, the total Xe<sup>133</sup> in the specimen was measured by later melting the entire sample and recording the total Xe<sup>133</sup> activity collected on the trap.

Additional details concerning the conduct of the experiment are given in reference (5).



### Data Analysis

The specimens used in the study were right circular cylinders 0.5 cm in diameter and 0.5 cm in height. The  $\text{Xe}^{133}$  produced by neutron irradiation is distributed uniformly throughout the specimen except for a partially depleted layer one recoil range thick next to the surface. The diffusion coefficient was assumed independent of position and direction of transfer, and the surface area available for release was identical to the geometrical surface area of the specimen. The effects of grain boundary diffusion and increased surface area due to roughness were not considered in the analysis.

To illustrate the method of solution, consider an infinite cylinder in which the recoil range is much less than the radius of the cylinder. The concentration of the diffusing species is governed by Fick's law:

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \quad (1)$$

where  $D$  is the diffusion coefficient, the boundary conditions are:

$$C(a, t) = 0, \quad t \geq 0 \quad (2a)$$

$$\left( \frac{\partial C}{\partial r} \right)_{r=0} = 0, \quad t \geq 0 \quad (2b)$$

The initial concentration distribution within the recoil range  $\mu$  of the surface is approximated by that for a plane surface: (2)

$$C(r, 0) = \begin{cases} C_0, & \text{for } 0 \leq r < (a-\mu) \\ \frac{C_0}{2\mu} (a + \mu - r), & \text{for } (a-\mu) \leq r \leq a \end{cases} \quad (2c)$$

The cumulative fractional release,  $f$ , is defined as:

$$f = \frac{\int_0^a r[C(r,0) - C(r,t)]dr}{\int_0^a rC(r,0)dr} \quad (3)$$

Similar relations can be written for the semi-infinite slab. The solutions for these two geometries for short times are identical, and are given by: (5)

$$f = 2\left(\frac{S}{V}\right) \sqrt{\frac{Dt}{\pi}} \left\{ \frac{1}{2} + \frac{\sqrt{\pi Dt}}{\mu} \left[ \frac{1}{4} - i^2 \operatorname{erfc} \left( \frac{\mu}{2\sqrt{Dt}} \right) \right] \right\} \quad (4)$$

$i^2 \operatorname{erfc}$  denotes an integral error function and is tabulated in Reference (6).

The characteristic dimension,  $a$ , has been replaced by the surface-to-volume ratio,  $S/V$  (for the sphere, infinitely long cylinder and semi-infinite slab,  $S/V$  is  $3/a$ ,  $2/a$ , and  $1/a$ , respectively, where  $a$  is the radius of the sphere or cylinder, or the half thickness of the slab). Equation (4) is also applicable to the finite cylinders used as specimens in the study. As  $\mu$  approaches zero (no recoil), Eq. (4) reduces to the usual expression by which postirradiation anneal experiments have been analyzed (4, 7) (i.e., the bracketed term approaches unity).

The diffusion coefficient cannot be obtained by the simple expedient of measuring the slope of a plot of  $f$  versus  $\sqrt{t}$ . The evaluation of  $D$  proceeded as follows: Eq. (4) is differentiated with respect to  $\sqrt{t}$ , and the result written as

$$D = \left[ \frac{\sqrt{\pi} \left( \frac{df}{d\sqrt{t}} \right)}{2(s/V)} \right]^2 \left[ \frac{2}{1 + \frac{\sqrt{\pi}}{2} \frac{\text{erf}\theta}{\theta}} \right]^2 \quad (5)$$

$$\text{where } \theta = \frac{\mu}{2\sqrt{Dt}} \quad (6)$$

The term  $df/d\sqrt{t}$  was taken from the plot of fractional release versus the square root of anneal time, in the region of the plot which showed the linearity characteristic of a diffusional process. The first bracketed term in Eq. (5) represents the diffusion coefficient in the absence of recoil. The second bracketed term is a correction factor to the diffusion coefficient due to recoil, and is plotted in Fig. 7. The diffusion coefficient was computed by an approximate trial-and-error solution of Eq. (5). The time  $t$  appearing in the correction factor was taken to be the middle of the linear portion of the  $f$  vs  $\sqrt{t}$  plot (usually at  $\sqrt{t} \approx 150 \text{ sec}^{1/2}$ ), and the recoil range  $\mu$  taken as 5 microns. A first estimate of  $D$  was obtained from the non-recoil model [i.e., the first bracketed term in Eq. (5)], and this was used to compute the correction factor of the second bracketed term and consequently, a new value of  $D$ . The process was repeated until convergence.

The recoil effect was most significant for the low temperature anneals; for  $D \approx 10^{-14} \text{ cm}^2/\text{sec}$ , the correction factor resulted in a diffusion coefficient four times larger than that calculated by the non-recoil model. For  $D \approx 10^{-12}$ , the recoil correction was of the order of 10-20%.

Equations (4) and (5) are valid when terms of the order of  $[2(s/V)\sqrt{Dt}]^2$  can be neglected, which is equivalent to fractional release of  $\leq 0.3$ . (8) Since  $f$  was  $\leq 0.01$  in all of the experiments, the use of a short-time form of the solution is considered adequate.

The recoil correction fraction represented by the bracketed term of Eq. (4) was compared to the approximate numerical correction factor developed by Inthoff and Zimen (9). Their correction factors are smaller than those of Eq. (4) by a factor of  $\sqrt{\pi/2}$ .

#### Abnormalities in the Release Rates

Most postirradiation anneal studies have reported large initial releases of gas followed by a slower release which was presumed to represent a true diffusional process (4, 10). This rapid initial release was observed in this work for temperatures above 1400°C. Experiments in the range 1000°-1200°C, however, appeared quite normal in the early stage of the anneal; after 3 to 4 hours, the release rates became much larger than that expected from the diffusion coefficients calculated for the seemingly normal short-time release data. [It is possible that the same phenomenon was responsible for the abnormally large release rates in both the low and high temperature anneals; if so, the phenomenon causing the non-diffusional component of the gas release must be even more strongly temperature dependent than the diffusion coefficient.] At low temperatures this abnormally high release rate did not appear until 3 to 4 hours after the anneal began, whereas at high temperatures it was either not present or had occurred during the first hour in the characteristic initial burst of xenon. There are a number of possible causes of this behavior:

- (1) A 12 hour anneal at 1600°C showed that acicular  $UC_2$ , present before the anneal, had disappeared by the end of the experiment. Figure 8 shows the uranium-carbon phase diagram and the range of carbon contents in the specimens. It is possible that this mixture

of acicular  $UC_2$  and UC may have transformed either into UC and  $U_2C_3$  or into cubic UC, accelerating the release rates in the process.

(2) In their study of xenon diffusion from  $UC_2$ , Zumwalt, et al (10) attributed the initial burst release to the release of xenon attached to defect sites on the surface and within the crystal. The diffusion coefficients as calculated herein are not characteristic of this mechanism.

(3) Since the primary source of the released xenon was the region very close to the surface, any chemical contamination or porosity just several microns thick should strongly affect the release characteristics of the sample. In all experiments, care was taken not to expose the sample to the atmosphere for a period of more than a few minutes. One specimen, however, was purposely exposed to the atmosphere for eight days prior to anneal; the diffusion coefficient for this sample was found to be 1500 times greater than expected. X-ray diffraction examination of the surface of this sample, however, revealed only UC, and the increased diffusion coefficient might have been due to a large increase in the microscopic surface area.

(4) The initial burst release could result from an initially transient diffusion process. The concentration of gas available for release by this process must decrease rapidly with time, even during the periods of small fractional release characteristic of these experiments.

While the ultimate source of the enhanced release rates remains a matter of speculation, the portion of the fractional release versus time plot which exhibited the smallest slope was in most cases substantial and well defined; the diffusion coefficients were computed from the data in these regions of the release curves.

## Results

The model used in the analysis of the data assumed that the entire sample behaved as a single crystal as far as the diffusion process was concerned. This implies that: (a) there are no internal surfaces (cracks, pores), and (b) grain boundary diffusion is negligible compared to lattice diffusion.

Of the twelve specimens which were subjected to metallographic examination, only one showed visual signs of porosity: during the subsequent postirradiation anneal, the diffusion coefficient of this specimen was 1000 times greater than expected.

Typical fractional-release data are shown in Fig. 9, and the temperature dependence of the diffusion coefficients is shown in Fig. 10. Data for the sample of unusual porosity and for the sample exposed for a long period to the atmosphere prior to post-irradiation anneal are not included. The solid circles represent specimens in which grain growth was accomplished by annealing for 12 hours at 2000°C before irradiation. These specimens developed grains as large as 700-1000 microns, which meant that the entire cross section of the 0.5 cm diameter cylinder consisted of ~5 grains. The open circles represent specimens with grain size from 20 to 150 microns. The diffusion coefficient for these two sets of grain size fall in the same line above 1400-1500°C. Below this temperature, only the large grain specimens continue according to the same line. The small grain specimens deviate substantially from the high temperature trend. Such behavior strongly suggests that grain boundary diffusion can be important at temperatures below 1400-1500°C, whereas lattice diffusion is the predominant release mechanism at higher temperatures.

The straight line of Fig. 10 is of the form

$$D = D_0 e^{-E/RT} \quad (7)$$

where  $D_0 = (1.17 \pm 0.16) \times 10^{-6} \text{ cm}^2/\text{sec}$

$$E = (54.9 \pm 1.2) \text{ kcal/mole}$$

The indicated errors, as determined from a least-square analysis of the data in Fig. 10 are greater than the estimated precision of measurements. Because the presence of the non-diffusional release mechanism distorted the release rate curves (cf. Fig. 9), definitive verification of the recoil effect predicted by Eq. (4) was not possible. The approximate method for correcting the apparent diffusion coefficients for recoil was based upon comparing the derivative of Eq. (4) with regard to  $\sqrt{t}$  with the slope which appeared to represent the diffusional portion of a plot of fractional release versus the square root of anneal time. Substantiation of the recoil model would require that the computed diffusivities, when inserted into Eq. (4), reproduce the time variation of the fractional release. This will be possible only when the non-diffusional release can be experimentally eliminated.

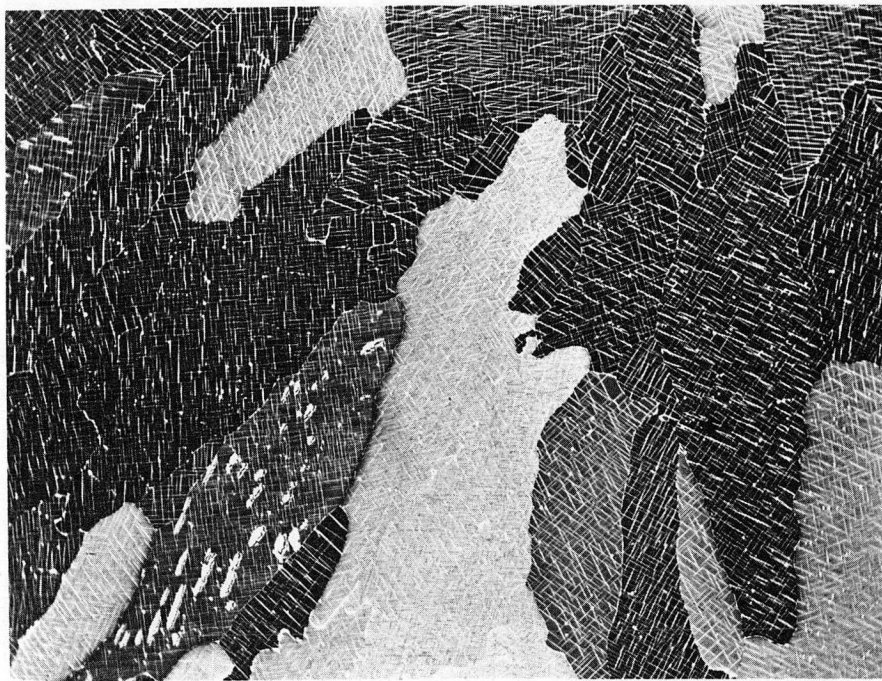
NOMENCLATURE

- a radius of cylinder, radius of sphere, or half width of slab, cm.
- C concentration of  $Xe^{133}$  in specimen,  $cm^{-3}$ .
- $C_0$  initial concentration of  $Xe^{133}$  in specimen (inner portion),  $cm^{-3}$ .
- D diffusion coefficient,  $Xe^{133}$  in UC,  $cm^2/sec$ .
- $D_0$  pre-exponential factor in Eq. (7),  $cm^2/sec$ .
- E activation energy for diffusion.
- f fraction of  $Xe^{133}$  released in time t.
- r radial distance from center line of cylinder, cm.
- S/V surface-to-volume ratio of specimen,  $cm^{-1}$ .
- t time, sec.
- T temperature, °K.
- $\mu$  recoil range of  $Xe^{133}$  in UC, cm.
- $\theta$  defined by Eq. (6).



REFERENCES

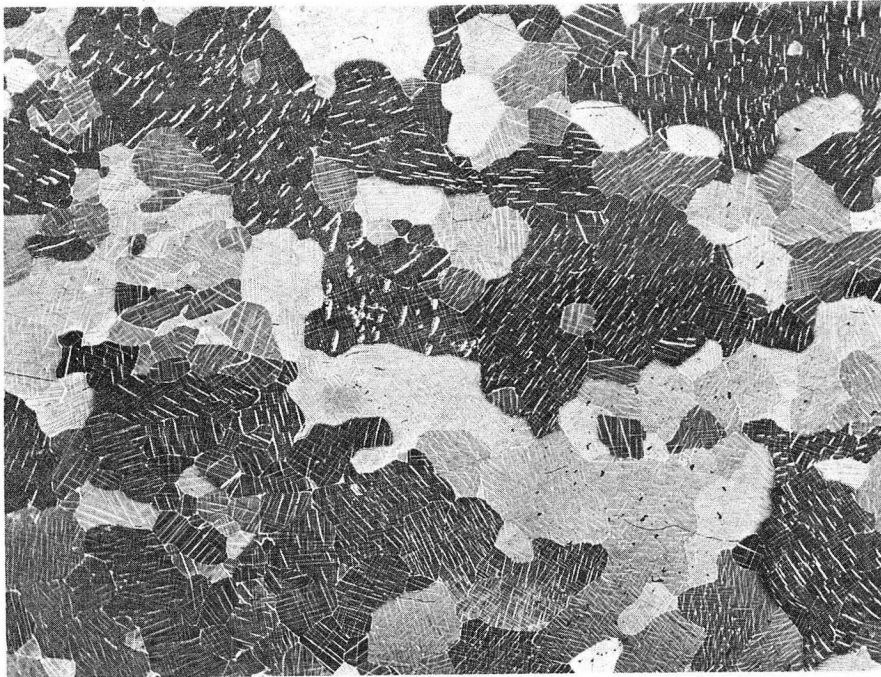
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0.2 mm

ZN-3584

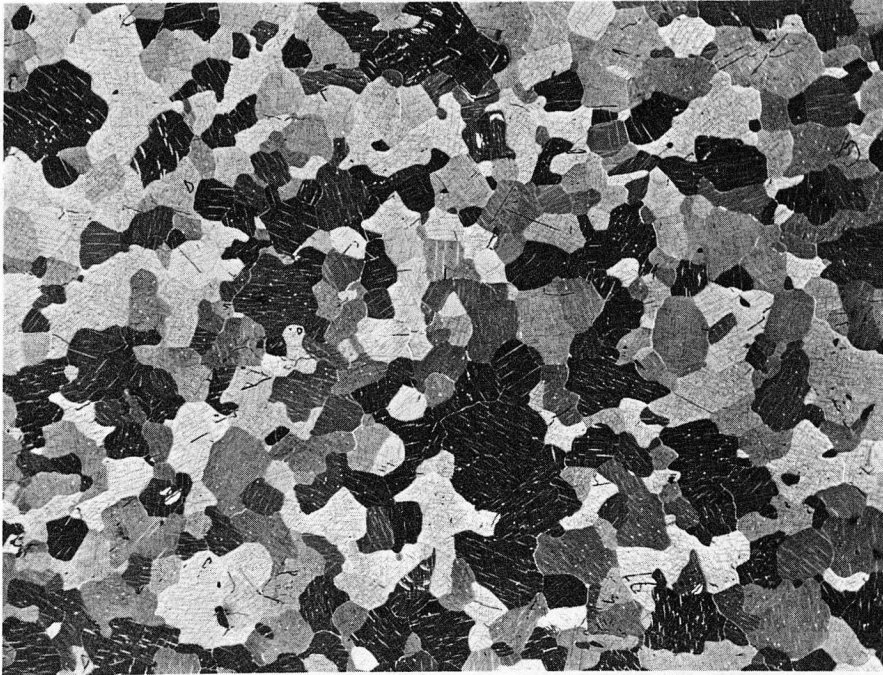
Fig. 1 Microstructure of Casting 12, as cast. 5.07 w/o carbon.  
(Courtesy Battelle Memorial Institute)



0.2 mm

ZN-3585

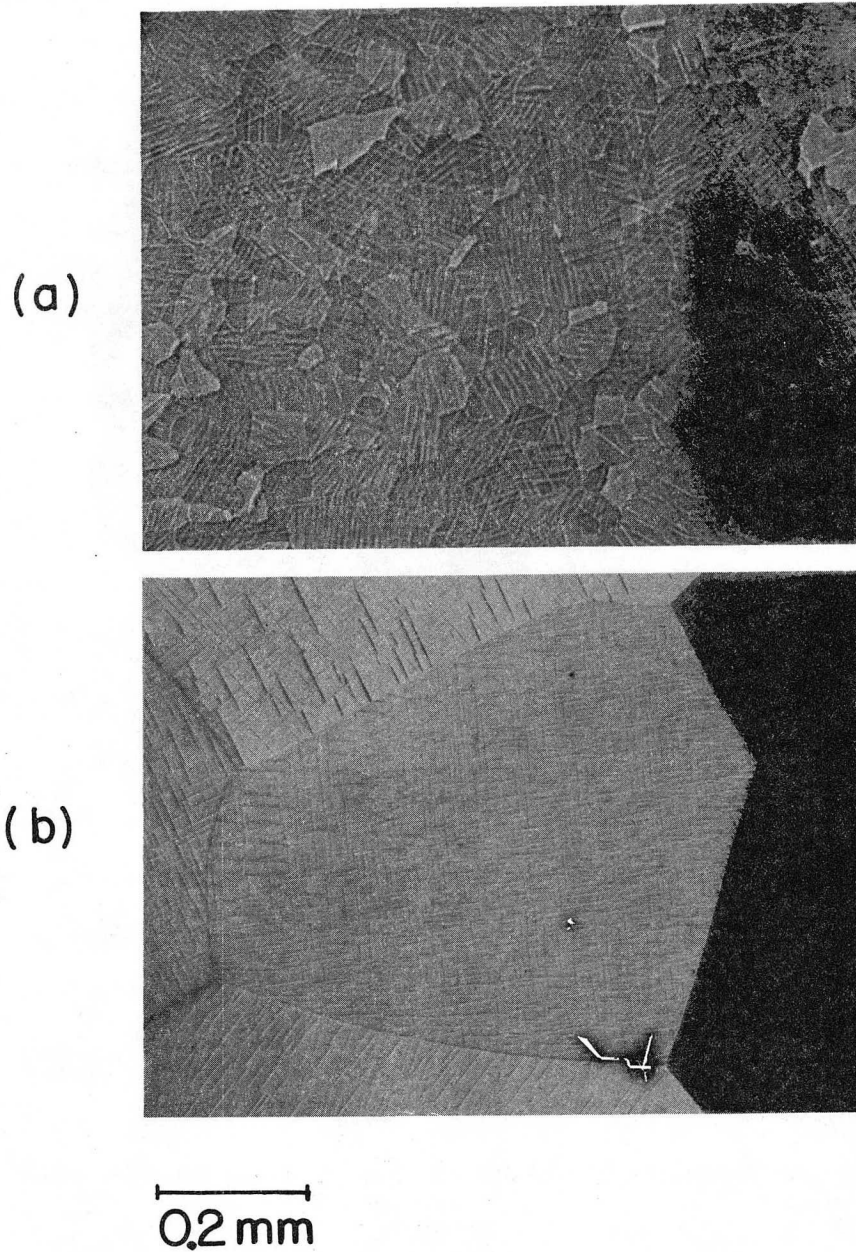
Fig. 2 Microstructure of Casting 6, as cast. 5.09 w/o carbon.  
(Courtesy Battelle Memorial Institute)



0.2 mm

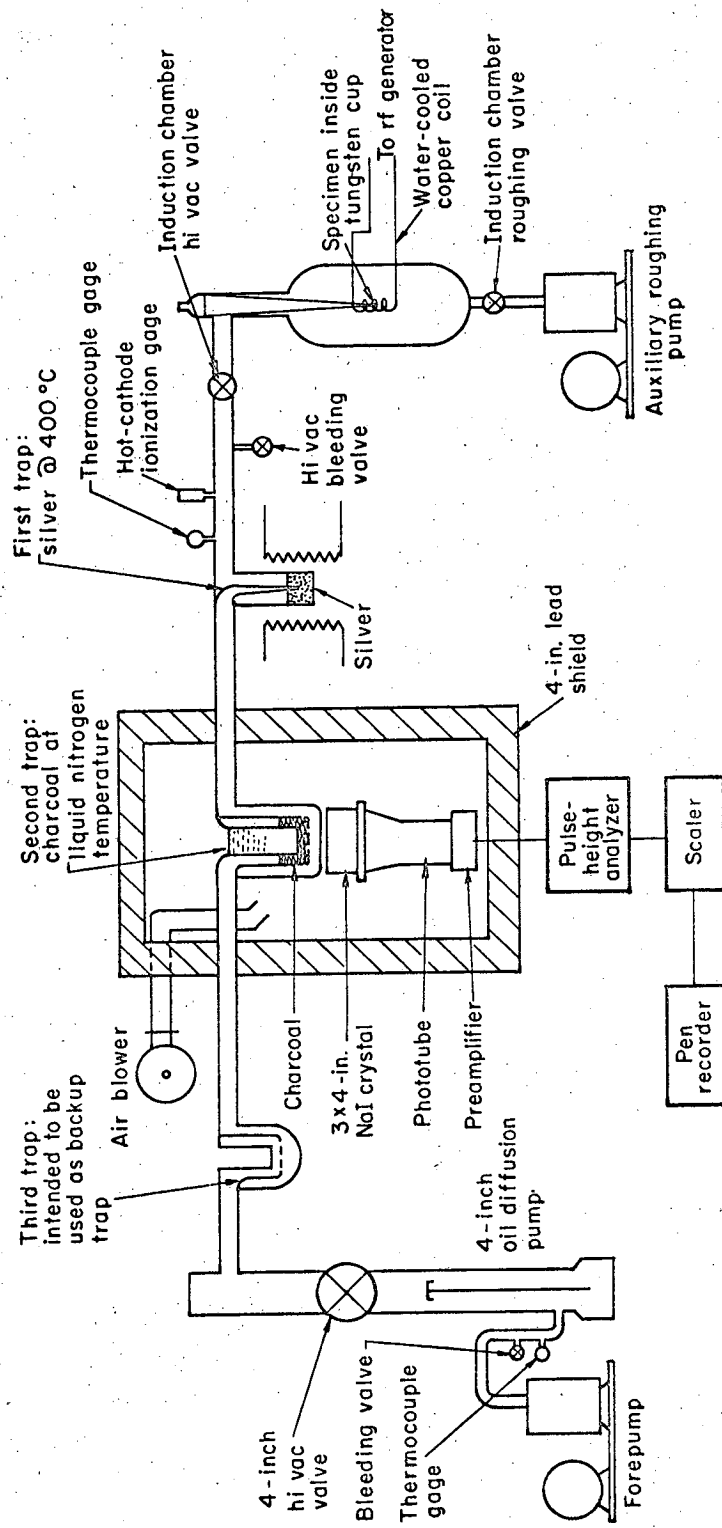
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Fig. 3 Microstructure of Casting 25, as cast. 5.06 w/o carbon.  
(Courtesy Battelle Memorial Institute)



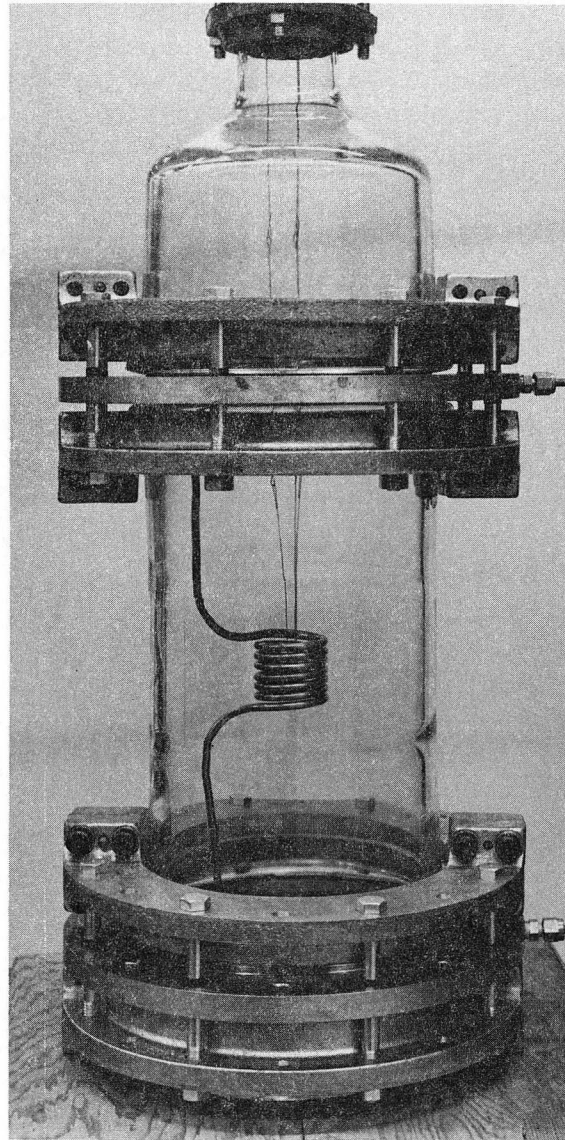
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Fig. 4 Microstructure of Specimen 1601: (a) as cast; (b) after 11 hr. anneal at 2000° C., 5.07 w/o carbon.



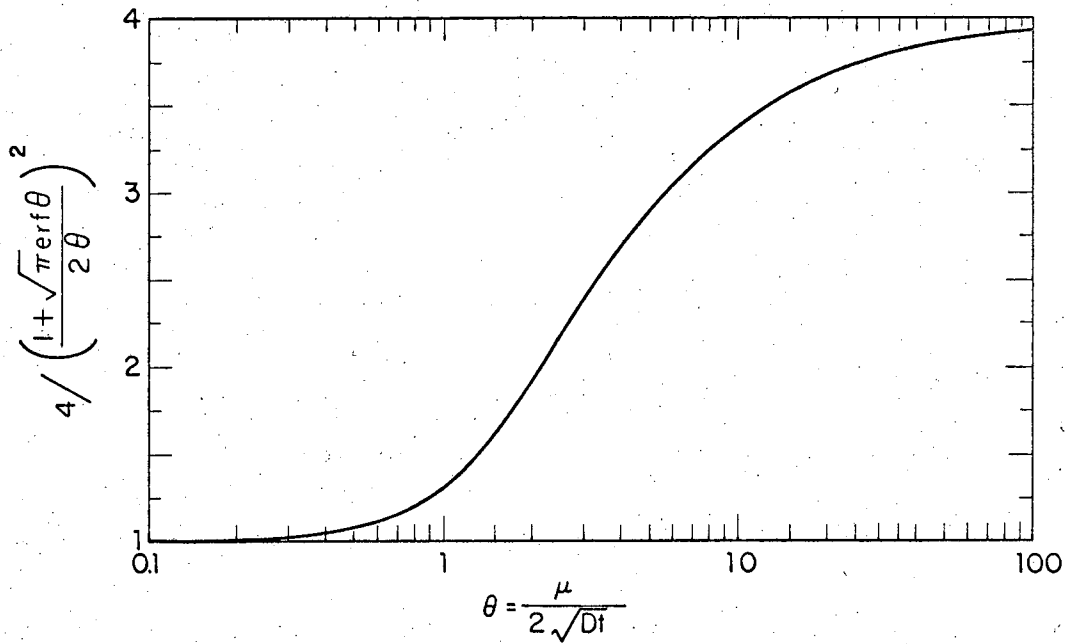
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Fig. 5 Apparatus for postirradiation anneal experiments



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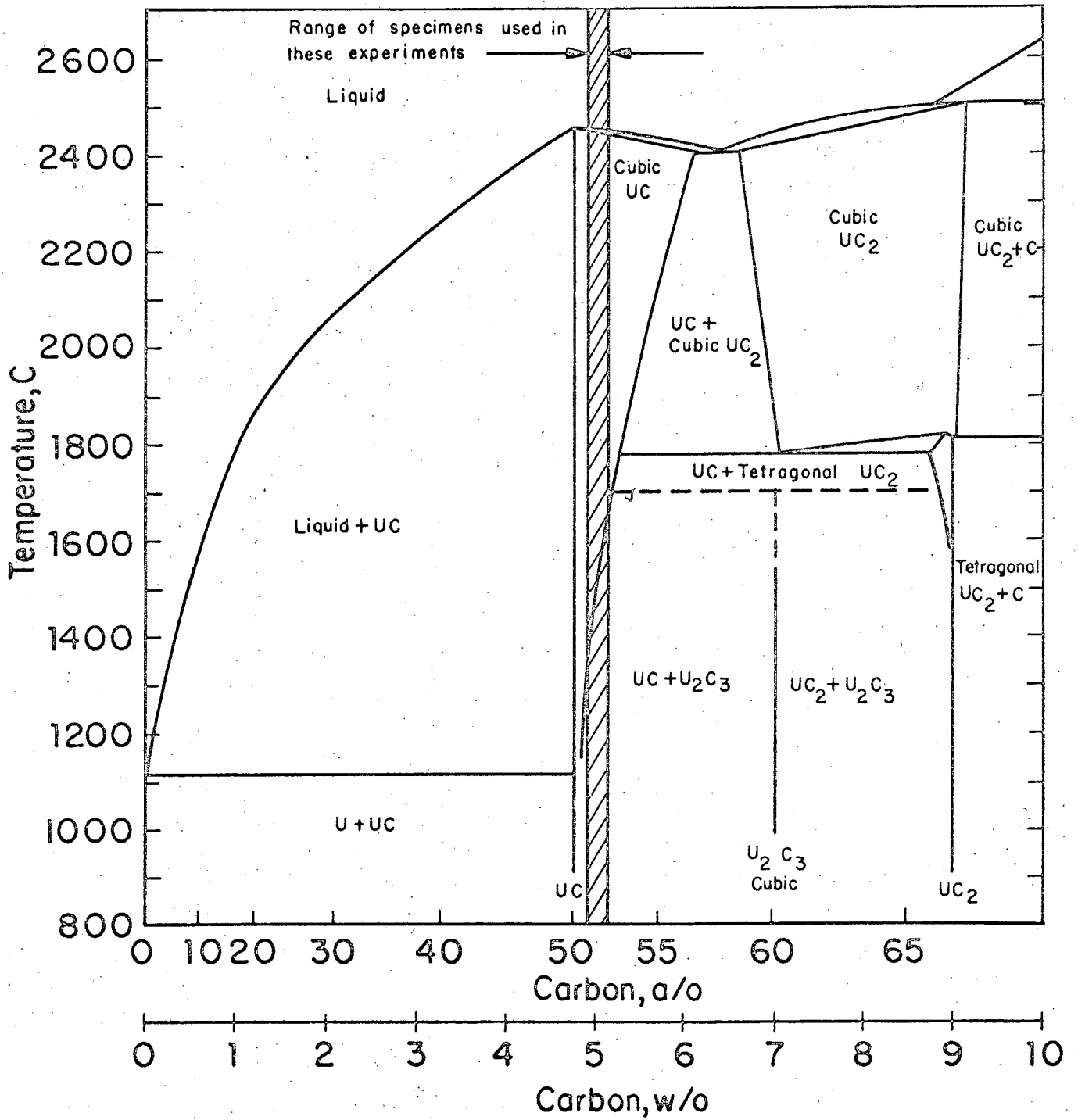
Fig. 6 The induction chamber.



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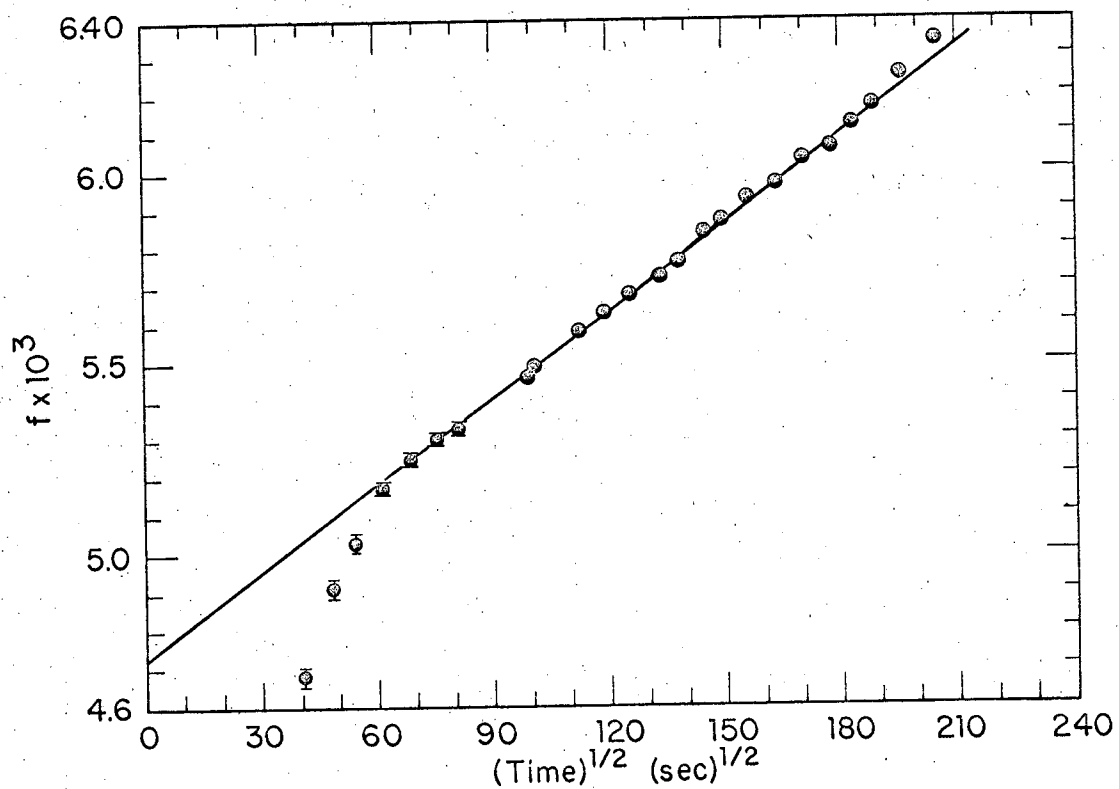
Fig. 7. The recoil correction factor for the diffusion coefficient





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Fig. 8 Uranium-carbon phase diagram (Reference 11)



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Fig. 9 Fractional release vs time at 1600°C.  
Solid line indicates calculated release  
for  $D = 6.7 \times 10^{-13} \text{ cm}^2/\text{sec}$ .

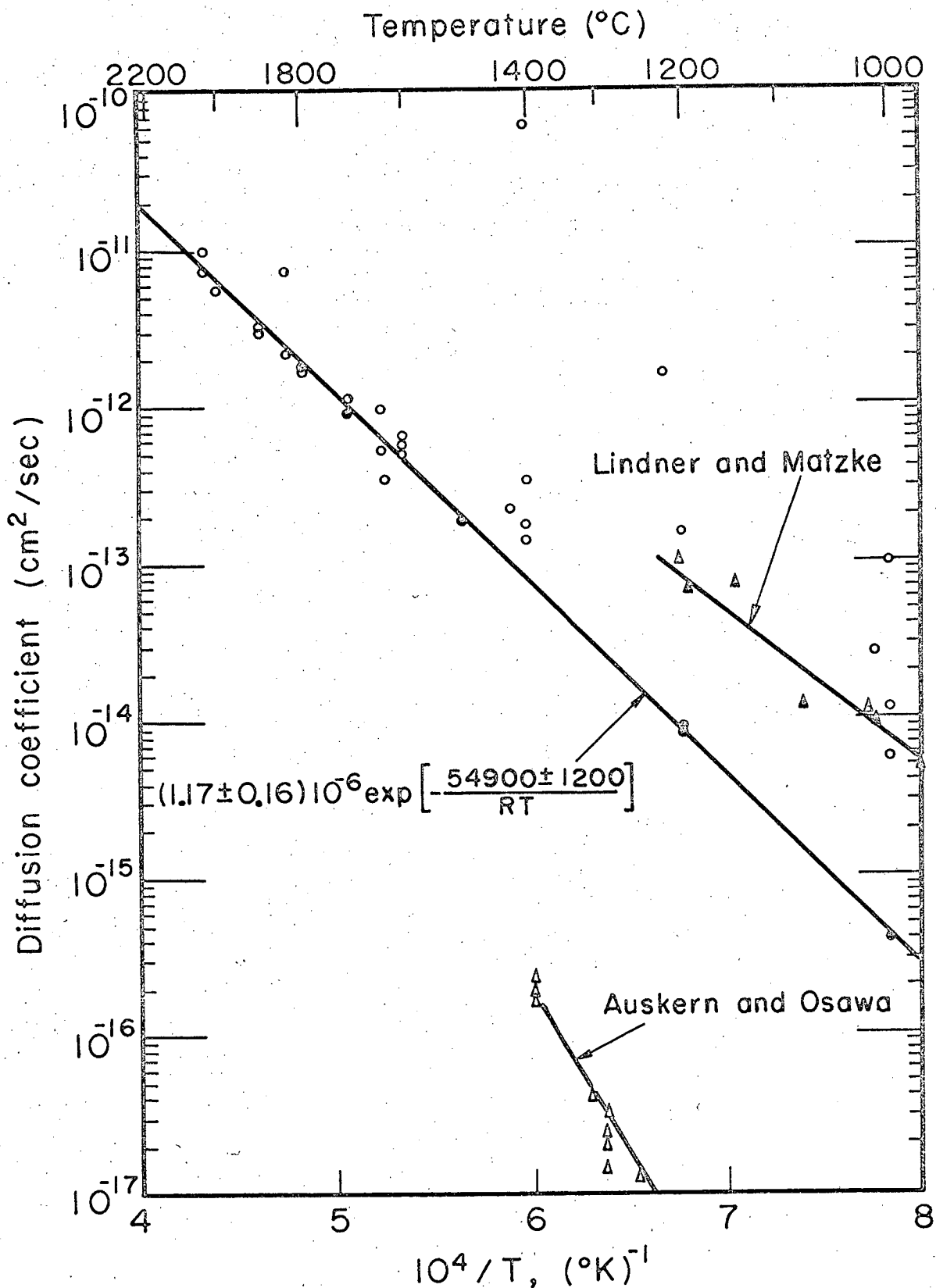


Fig. 10 Diffusion coefficient of Xe<sup>133</sup> in UC:  $\odot$  grain size 700-1000 microns;  $\circ$  grain size 20-150 microns;  $\Delta$  data of Lindner and Matske (1), anneal time 50-100 hr.;  $\triangle$  data of Auskern and Osawa (2), no anneal time specified.

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