The Behavior of Fission Products Captured in Graphite Powder by Nuclear Recoil. V. Effect of Fission Fragment Damage on the Diffusion of the Fission Product Xenon

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The radiation damage to graphite caused by neutron irradiation is of great importance in reactor technology, and many studies have been made in this field[1-4]. However, in the case of the dispersed type of fuel, when the fissionable material is dispersed throughout a matrix of graphite powder, the damage from fission fragments is more severe than the neutron damage[5-8].

The present authors have been studying[9-12] the behavior of fission products captured in several kinds of graphite powder by fission recoil.

For the present work, diffusion experiments on Xe-133 and Xe-135 captured in graphite powder were carried out over an extensive range of fission product concentrations. It has become clear through this work that with natural graphite the diffusion behavior of xenon in graphite is far more strongly affected by fission fragment damage than by neutron damage to the graphite crystal, and that the behavior changed markedly with an increase in the fission product concentration. However, in the case of artificial graphite, the effects of both fission fragment damage and neutron damage were insignificant over the range of fission product concentrations covered in this experiment.

Experimental

Preparation and Irradiation of Samples.—The graphite samples examined in this experiment were of two kinds, natural graphite (NG-1) and artificial graphite (AG), as described in our previous report[12]. Mixed with this graphite was natural uranium in the form of dioxide powder with a particle size of less than 1 μ, which ensured that most of the fission products would recoil out of the uranium dioxide particles into the surrounding graphite. The relation of the fission product capturing factor of the graphite to the uranium dioxide ratio of the mixture were discussed in detail in a previous report[5].

The mixing ratios adopted for the samples in the present experiments were 33 : 1 and 1 : 1 by weight, at which ratios the capturing factors were 0.95 and 0.70 respectively.

The prepared mixtures were sealed in quartz ampules in a vacuum and were irradiated in the JRR-1[*1], the JRR-2[*2] and the research reactor of the Brookhaven National Laboratory. Data concerning the preparation and irradiation of the samples are given in Table I. In this table the fission product concentration was calculated according to the equation given in the footnote below[*3].

Since the radioactivity of samples numbered 13, 14, 15 and 16 was too strong for them to be handled immediately upon initial irradiation, these samples were cooled for four months. After this time, they were reirradiated with thermal neutrons to a ϕt ratio of 8 to produce the fission-recoiled Xe-133 in the samples.

Samples No. 17 and No. 18, after four months' cooling, were treated with nitric acid[*4] to remove the uranium dioxide; then the remaining graphite powder was washed with water and acetone, and dried. The powder was then heated for 2 hr. in an argon flow at 1000 and 1440°C respectively. After the heat treatment, the graphite powder was again mixed with uranium dioxide powder to a

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1) W. K. Woods, L. P. Bupp and J. F. Flecher, Proceedings of the First International Conferences on Peaceful Uses of Atomic Energy, Geneva (United Nations, New York, 1956), Vol. 7, p. 455.

2) G. H. Kinchin, ibid., Vol. 7, p. 472.

3) G. R. Henning and J. E. Hove, ibid., Vol. 7, p. 666.

4) W. Bollman, *J. Appl. Phys.*, 32, 869 (1961).

5) E. Nishibori, R. Ueda, S. Yajima, S. Ichiba, Y. Kamemoto and K. Shiba, *Plansee Berichite*, to be published.

6) L. D. Loch and J. A. Slyh, CF-53-3-276(Del.), Radiation damage Conference, Part I, p. 93, Dec. 20, 1954.

7) R. H. Kernoban, ibid., p. 98.

8) R. J. Harrison, ibid., p. 113.

9) T. Nakai, S. Yajima, K. Shiba, J. Osugi and D. Shinoda, This Bulletin, 33, 494 (1960).

10) T. Nakai, S. Yajima, K. Shiba, J. Osugi and D. Shinoda, ibid., 33, 497 (1960).

11) S. Yajima, S. Ichiba, Y. Kamemoto and K. Shiba, ibid., 34, 493 (1961).

12) S. Yajima, S. Ichiba, Y. Kamemoto and K. Shiba, ibid., 34, 697 (1961).

[*1] Japan Research Reactor-1, water boiler type, operated at 50 kW thermal out-put.

[*2] Japan Research Reactor-2, CP-5 type, operated at 1000 kW thermal out-put.

[*3] The number of fission product atoms captured in a unit volume of graphite was calculated according to the following equation:

$$\text{Number of f. p. atoms/cm}^3\text{ of graphite} = 2\cdot{}^{235}\mathrm{U}\cdot\sigma\cdot\phi\cdot t\cdot\alpha\cdot d$$

where,

^{235}U : Number of U-235 atoms
: Fission cross-section of U-235
ϕ : Neutron flux
t : Irradiation time
α : Capturing factor of fission products in graphite
d : Density of graphite

[*4] The fission products captured in graphite did not leach out of the graphite to any significant extent by this nitric acid treatment[9].

weight ratio of 33 : 1 and reirradiated with thermal neutrons to a ϕt ratio of 8, to produce the fission-recoiled Xe-133 in the samples.

Samples No. 19 and No. 20 were irradiated at 500°C and, after four months' cooling, were reirradiated with thermal neutrons to a ϕt ratio of 2, to produce the fission-recoiled Xe-133 in the samples.

The difference between the effects on the diffusion of xenon in the graphite of neutron damage and of fission fragment damage was examined with sample No. 21. In this sample natural graphite powder alone was first irradiated with neutron to a ϕt ratio of 58 in JRR-2; then, after this irradiation, the powder was mixed with uranium dioxide powder to a weight ratio 33 : 1, and reirradiated with neutrons to a ϕt ratio of 1 to produce the fission-recoiled Xe-133 in the sample.

Obtaining the Heating Curve.—To obtain the heating curves, Xe-133 was used as the tracer for most experiments, but in some cases of low fission product concentration, Xe-135 was used as the tracer. The optimum cooling times for the experiments, after irradiation or reirradiation, were 1 day for Xe-135 and 7 days for Xe-133. After cooling, the samples were dissolved in nitric acid to remove the uranium dioxide, and the remaining graphite powder was washed with water and acetone and then dried.

The apparatus used for the diffusion experiment was the same as that described in a previous report. A prepared graphite sample was placed in an alundum boat and inserted into an alundum tube, forming the core of an electric furnace with a platinum heater. The temperature was raised at the rate of 5°C/min. The radioactive xenon released from the graphite crystal was carried off with purified argon*5 and trapped in an activated charcoal trap cooled with dry ice. To remove the undesirable radioactive iodine released from the graphite with the radioactive xenon, a trap of glass wool with a silver nitrate deposit was inserted in front of the charcoal trap. The charcoal trap was changed every five minutes until the temperature reached 1500°C. Then the graphite sample was fired with oxygen mixed with argon (volume ratio 1 : 1) at 1200°C, and the residual xenon which had not diffused out of the graphite during heating was caught in the charcoal trap. The excess oxygen and carbon dioxide were removed with a mixture of pyrogallol and potassium hydroxide solutions, and then the water vapor was trapped with a phosphorus pentoxide drying tube.

The Xe-133 and Xe-135 collected in the charcoal traps were placed in a sodium iodide well (2 inches in diameter by 1.75 inches high) attached to a Baird Atomic γ-ray spectrometer to obtain their spectra.

When Xe-133 was used as the tracer, the spectra obtained were radioactively pure, but with Xe-135, traces of the Xe-133 spectrum were discernible along with the Xe-135 spectrum. The portion of

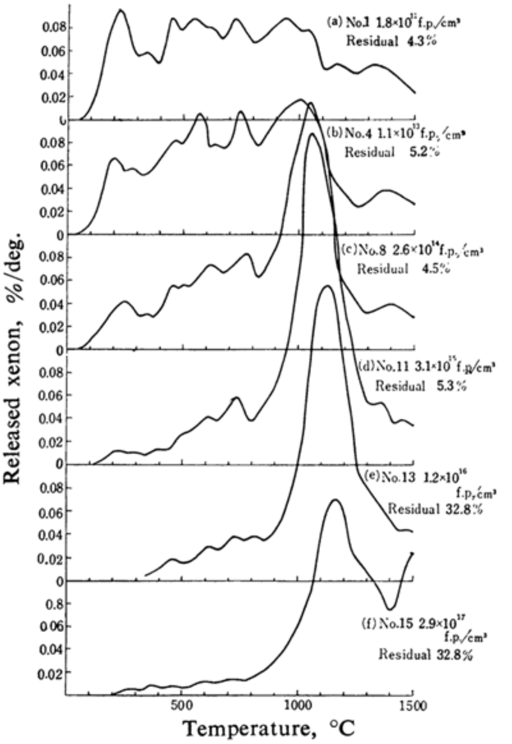

Fig. 1. Heating curves (5°C/min.) of natural graphite (NG-1).

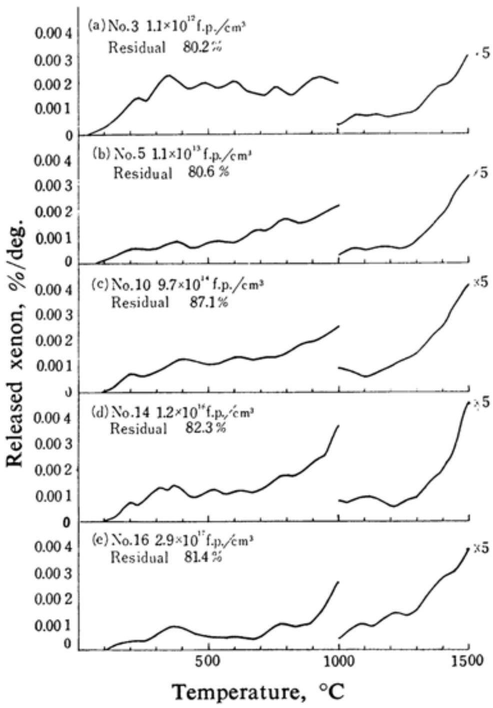

Fig. 2. Heating curves (5°C/min.) of artificial graphite (AG).

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*5 The argon used was 99.99% pure and was further passed through a copper gauze bed heated to 400°C, a phosphorus pentoxide trap, and a sponge titanium bed heated to 800°C to remove the small amounts of oxygen, water vapor and other impurities.

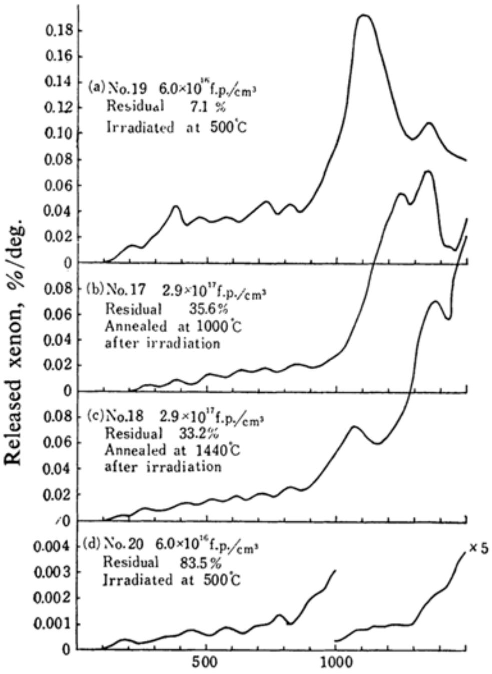

Fig. 3. Heating curves (5°C/min.) of heat-treated graphite sample.

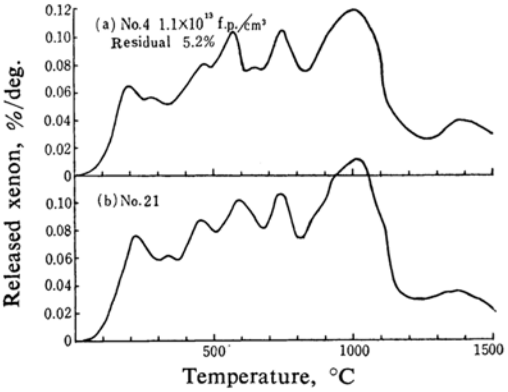

Fig. 4. Heating curve (5°C/min.) of preliminarily neutron-irradiated graphite sample.

Xe-133 was, therefore, subtracted from the obtained total spectrum area. The portion of Xe-135 was, furthermore, calibrated by means of its decay curve, because the Xe-135 nuclide is short-lived.

The fraction of the total activity formed by the activity of each charcoal trap was divided by the temperature rise in the 5 min. interval during which the trap was in use. The plots of this value against the temperature (heating curve) are shown in Figs. 1, 2, 3 and 4.

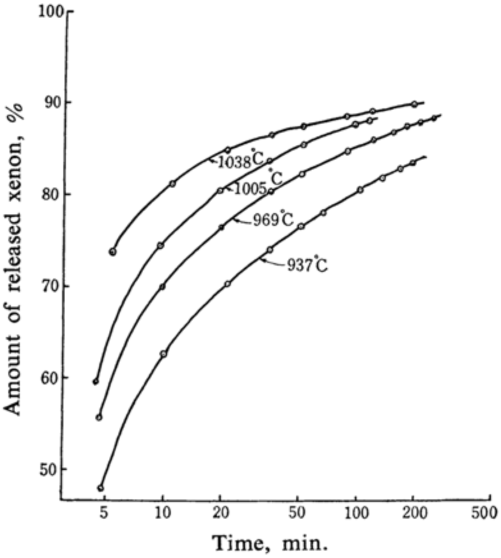

Fig. 5. Isothermal curves in the range 937∼1038°C.

Determination of Activation Energy.—As is shown in Fig. 1, the heating curves of natural graphite change markedly with the fission product concentration. The activation energy for the diffusion of xenon in natural graphite at a temperature corresponding to the peak seen in Fig. 1 (about 1000°C) was measured by Dienes' method[13]. The furnace was maintained at a fixed temperature, and the graphite sample inserted into the heating tube as rapidly as possible. The released xenon was trapped in a charcoal trap, which was replaced by a new one at the optimum time interval of about 3 hr. The radioactivity of the charcoal traps was plotted against the time (isothermal curve) (Fig. 5). The samples were prepared by the same irradiation treatment as No. 4 in Table I. These samples were preheated to 700°C for 30 min. to eliminate the spectra from xenon released in the range below 700°C and thereby to bring out the isothermal curves of diffusion at about 1000°C. Thus, the ordinate in Fig. 5 does not represent the fraction of released xenon referred to the total activity but the fraction referred to the residual after the preheat treatment. The isothermal curves were obtained for 937, 969, 1005 and 1038°C respectively. The relation between the annealing time (plotted logarithmically) and the temperature (reciprocal of the absolute temperature) is given in Fig. 6. The activation energy can be obtained from the slopes of the $1/T$ plot according to the following equation, derived by Dienes et al.:

$$t \times e^{-E/RT} = C$$

where,

t = diffusion time required to obtain a certain diffusion fraction of the isothermal curve
E = activation energy, cal./mol.
$\boldsymbol{R}$ = gas const., 1.978 cal./deg.
T = temperature, °K
C = constant

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[13] G. J. Dienes and W. E. Parkins, "An Improved Method for Determining Activation Energies of Relaxation Processes", NAA-SR-60.

TABLE I. DESCRIPTION OF SAMPLES

Sample No.	Kind of[*1] graphite	UO_2 mixed with 1 g. graphite mg.	Thermal neutron[*2] dose, n/cm^2	ϕt ratio[*3]		Irrad. temp., °C	Fission product concn.
				Initial irrad.	Reirrad.		
1	NG-1	30	1.5×10^{14}	1/60		40	1.8×10^{11}
2	NG-1	30	9.0×10^{14}	1/10		40	1.1×10^{12}
3	AG	30	9.0×10^{14}	1/10		40	1.1×10^{12}
4	NG-1	30	9.0×10^{15}	1		40	1.4×10^{13}
5	AG	30	9.0×10^{15}	1		40	1.4×10^{13}
6	NG-1	30	5.4×10^{16}	6		125	6.4×10^{13}
7	AG	30	5.4×10^{16}	6		125	6.4×10^{13}
8	NG-1	30	2.2×10^{17}	24		125	2.6×10^{14}
9	NG-1	30	8.2×10^{17}	91		125	9.7×10^{14}
10	AG	30	8.2×10^{17}	91		125	9.7×10^{14}
11	NG-1	30	2.6×10^{18}	288		125	3.1×10^{15}
12	AG	30	2.6×10^{18}	288		125	3.1×10^{15}
13	NG-1	30	9.9×10^{18}	1092	8	125	1.2×10^{16}
14	AG	30	9.9×10^{18}	1092	8	125	1.2×10^{16}
15	NG-1	1000	9.9×10^{18}	1092	8	125	2.9×10^{17}
16	AG	1000	9.9×10^{18}	1092	8	125	2.9×10^{17}
17	NG-1	1000	9.9×10^{18}	1092	8	125	2.9×10^{17}
18	NG-1	1000	9.9×10^{18}	1092	8	125	2.9×10^{17}
19	NG-1	1000	2.4×10^{18}	482	4	500	6.0×10^{16}
20	AG	1000	2.4×10^{18}	482	4	500	6.0×10^{16}
21	NG-1	30	5.0×10^{17}	58	1	40	1.1×10^{13}

[*1] NG-1 and AG respectively represent natural and artificial graphite powders of certain specifications.

[*2] In every case the doses of fast neutrons were 1/10 of those of thermal neutrons. The thermal neutron dose was measured with cobalt monitoring wire and fast neutron dose with nickel monitoring wire.

[*3] The flux time was compared with that of sample No. 4, taken as standard.

4 The Xe nuclide used as a tracer on diffusion experiment was Xe-135 for samples of Nos. 1—3 and Xe-133 for samples of Nos. 4—21, respectively.

5 The samples of Nos. 1—4 were irradiated in JRR-1, the samples of Nos. 5—20 were irradiated in Graphite Research Reactor of the Brookhaven National Laboratory and the sample of No. 21 was irradiated in JRR-2.

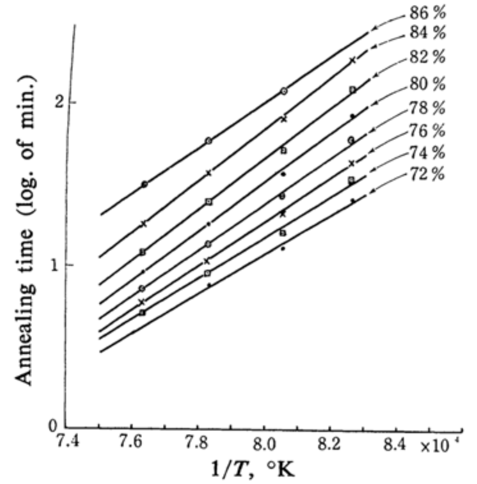

Fig. 6. Annealing time versus $1/T$ in the range 937～1038°C.

The activation energies thus obtained are shown in Table II.

TABLE II. ACTIVATION ENERGIES IN THE RANGE 937～1038°C

Fraction	Slope $\times10^3$ deg.	Activation energy kcal./mol.
0.72	1.24	56.6
0.74	1.26	57.8
0.76	1.40	63.9
0.78	1.43	65.3
0.80	1.53	70.1
0.82	1.59	72.7
0.84	1.60	73.2
0.86	1.40	64.7
	Mean value	65.5

Results

The heating curves of natural graphite sample (Nos. 1, 4, 8, 11, 13 and 15) are shown in Fig. 1, and those of artificial graphite samples (Nos. 3, 5, 10, 14 and 16), in Fig. 2. The curves of natural and artificial graphite samples irradiated under heat (Nos. 17 and 18) and natural and artificial graphite samples annealed after irradiation (Nos. 19 and 20) are shown in Fig. 3. Figure 4 represents the neutron-irradiated natural graphite sample (No. 21).

The following remarks may be made on the basis of the above figures.

1) Sample No. 15 was irradiated with the same doses as No. 13, but the fission product concentration of No. 15 was 24 times larger than that of No. 13, and their heating curves (e) and (f) in Fig. 1 were found to differ considerably from each other.

The graphite portion of sample No. 21 was preliminarily irradiated with a dosage 58 times larger than that of No. 4, but the fission product concentrations in both samples stayed almost identical in shape (Fig. 4). From this, it can be said that the effect of neutron irradiation on the heating curve spectra is very much smaller than the irradiation of fission fragments, at least in the range of the dosage in question.

2) The heating curves of natural graphite represent a continuous spectrum, possessing several peaks.

3) The positions of these peaks do not change appreciably with the fission product concentration.

4) To determine the influence of the fission products concentration on the temperatures at which radiation damage is mainly brought about, three temperature ranges, A (0～850°C), B (850～1350°C) and C (above 1350°C), were arbitrarily established. The fraction of the total xenon released in each temperature range was plotted against the fission product concentration (Fig. 7). In this figure, the fraction. of xenon released in range A is seen to begin decreasing at about 10^{13} f. p./cm^3 graphite, but the fraction of range B goes on increasing with the fission product concentration to reach its maximum at about 10^{15}～10^{16} f. p./cm^3 graphite. The fraction of C stays unchanged up to 10^{15} f. p./cm^3 graphite; from there on, it increases rapidly. This would appear to indicate that with the increasing fission product concentration, the imperfections of graphite crystal corresponding to range A are taken over by imperfections corresponding to range B and, further, to range C.

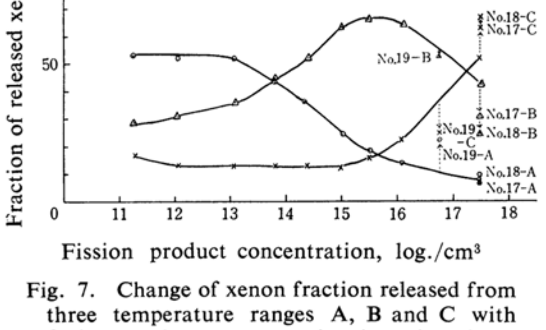

Fig. 7. Change of xenon fraction released from three temperature ranges A, B and C with fission product concentration in unit volume of graphite.

⊙ Natural graphite, range A (0～850°C)
△ Natural graphite, range B (850～1350°C)
× Natural graphite, range C (>1350°C)
⊡ Artificial graphite, range C (>1350°C)

5) Returning to Fig. 1, the position of the peak near 1000°C (in range B) shifts toward higher temperatures with the increase in fission product concentration; that is, the position of the peak is 1010°C in curve (b) and shifts with the increasing fission product concentration to reach 1170°C in curve (f). This temperature shift might be explained as a lag of the release rate of xenon against the rising temperature, taking account of the fact that the chance of xenon being captured before diffusing out of the graphite increases with the number of imperfections, which influences the position of the peak, which in turn would depend on the fission product concentration. Another explanation is that the trapping power of the imperfections corresponding to this peak increases gradually with the fission product concentration; that is, the depth of imperfection becomes deeper with the increasing fission product concentration. This temperature shift is not observed in other peaks found in the lower temperature range.

6) As in the case of natural graphite, the heating curves of artificial graphite (Fig. 2) were translated into a curve relating the portion of the released xenon to the fission product concentration (uppermost curve in Fig. 7). This curve represents the fraction of xenon released in range C and indicates that the fraction of C retains a constant value of over 90% and is thus predominant over those of both A and B, which are so small as to be within the range of experimental error. In conclusion, it is obvious that, in the range of fission product concentration examined in this experiment, xenon trapped in natural graphite can more easily diffuse out than that trapped in artificial graphite.

7) The curves of heat-treated samples, Nos. 17, 18 and 19 (Fig. 3), were also analyzed; they are plotted in Fig. 7. It is seen that the fraction of xenon release in temperature range C is greater for samples 17 and 18 than that of the corresponding non-treated sample, No. 15. From this it may be said that heat treatment at 1000 or 1440°C after irradiation will heal radiation damage corresponding to ranges

A and B, but not to that of range C. It may also be seen that the fission fragment damage due to reirradiation is very small compared with the residual from range C caused by initial irradiation.

In the same figure, the plot for sample No. 19 lies above the curve for non heat-treated samples in the case of the fraction for range A. This means that heat treatment of the sample at 500°C during irradiation will impede damage in range C. It may be concluded that heat treatment after irradiation is not effective in removing damage corresponding to higher temperatures, but, on the other hand, that heat treatment during irradiation will considerably reduce this damage. This phenomenon is in accord with the release curve of stored energy in artificial graphite irradiated with fast neutrons of the order of 10^{20} nvt. (see remark 8 below). The heating curve of sample No. 20 in Fig. 3 does not differ from that of the samples unheated during irradiation in Fig. 2.

8) The release of stored energy in artificial graphite irradiated with fast neutrons of the order of 10^{20} nvt. has already been extensively studied(1,4). The release curve of stored energy (an example was given in Fig. 8) has peaks at points apparently in good correspondence with the xenon release curve of natural graphite. This correspondence might be explained by considering that they both represent the progress of annealing or recovery from strain caused in the graphite crystal by neutrons or by fission fragments, manifesting itself on the one hand in a release of stored energy and, on the other hand, in a release of xenon from the crystal. It should be noted that, while the stored energy release curve represents by the temperature scale, the absolute quantity as well as the depth of damage, the xenon heating curve represents only the depth of damage by the same scale.

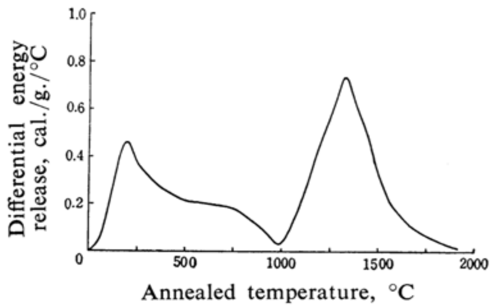

Fig. 8. Differential stored energy release (after Woods et al.(1)).

Xenon atoms trapped in imperfections of graphite crystal are released from the imperfections by heating at a given temperature, when some of them will diffuse out from the graphite particles[*6] and others will be trapped again in other imperfections of a higher trapping power. The probability of either happening will be determined by the chemical and physical state of the diffusing atom, the depth of the trapping power of the imperfection, and the number of imperfections per unit volume.

The release curve of stored energy in artificial graphite irradiated with neutrons indicates that the imperfections corresponding to temperature range C are insignificantly few in number (Fig. 8), but the heating curves of artificial graphite (Fig. 2) indicate the fraction of the range C to far surpass those of ranges A and B. This brings out the significance of the studies that should be undertaken on the capturing process of xenon in artificial graphite.

9) The activation energy of xenon diffusion in natural graphite at the peak of about 1000°C in the heating curves is 65.5 kcal./mol. According to Suzuki's study(15), the imperfections existing in ranges A and B may be presumed to be interstitial cluster and mono-vacancy respectively.

The diffusion experiments of highly irradiated samples (Nos. 6—20) were carried out at the Brookhaven National Laboratory. S. Yajima and K. Iwamoto, those of the present authors who went to the Laboratory to undertake the experiment, are particularly indebted to Dr. F. T. Miles, Dr. D. H. Gurinsky Dr. E. Fujita and Mr. H. Munkelwitz for invaluable help and suggestions during their work at Brookhaven.

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[*6] Suzuki et al.(14) reported that the xenon atoms which exist between the layers of graphite crystal diffuse very easily and that the calculated activation energy of this diffusion is about 0.03 eV.

14) T. Iwata, E. Fujita and H. Suzuki, *J. Phys. Soc. Japan*, **16**, 197 (1961).

15) H. Suzuki, private communication.