Activation Energy for Annealing Single Interstitials in Neutron-Irradiated Graphite and the Absolute Rate of Formation of Displaced Atoms*

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The activation energy for the process of annealing single interstitials in neutron-irradiated graphite and the absolute rate of formation of displaced atoms have been determined experimentally from both the dimensional expansions and c-axis expansions of graphite irradiated at temperatures between 77°K and 490°K. The activation energy obtained is 0.068 to 0.074 eV and lies between the value of 0.1 eV estimated by Dienes and the value of 0.016 eV calculated by Iwata, Fujita, and Suzuki for the migration energy of a single interstitial.

The absolute rate of formation of displaced atoms corresponds to the rate of displacement when no annealing occurs during the irradiation process. The value obtained (5×10^{-3}% displaced atoms/MWD), is 2.5 times the rate of displacement at 30°C and is in excellent agreement with theoretical estimates.

The dimensional changes occurring during the first irradiation of graphite are the result of the three processes:

(1) ϕ (fast neutron) $+C^0 \rightarrow C_1+$vacancy,

(2) $C_1+C_1 \rightarrow C_2$,

(3) C_1+trap $\rightarrow C_1T$.

Reaction (1) corresponds to the displacement of a single interstitial by collision of a fast (high-energy) neutron and the graphite lattice. This reaction is temperature independent. Reaction (2) represents the collision of two interstitials to form a stable C_2 complex. The dimensional changes (rate of growth) occurring in graphite are due to the constant (zero-order) rate of formation of C_2. Some of the single interstitials anneal (without causing dimensional changes) by being trapped at pores, edge atoms, etc. Reaction (3) describes this process. The rate-determining step for both reaction (2) and reaction (3) is the rate of migration of the single interstitial.

INTRODUCTION

THE activation energy for the process of annealing single interstitials in irradiated graphite has been a subject of controversy for many years.[1–3] In some of the literature dealing with the annealing of irradiated graphite, the stored energy released at 200°C has been attributed to the annealing of single interstitials. The large increase in annealing rate with temperature indicates the stored energy release at 200°C has a high activation energy making it difficult to reconcile the experiments with the low values for the activation energy estimated theoretically. Hennig and Hove[1] have interpreted paramagnetic resonance data obtained from irradiated graphite by assuming that the single interstitial acquires an unpaired electron. The release of stored energy at 200°C was assumed to be due to combination of two similarly charged interstitials to form a neutral C_2 complex. Although this picture accounts for several properties of irradiated graphite, the agreement between paramagnetic resonance annealing and the 200°C stored energy annealing in damaged graphite is not good. After an irradiation of 1100 MW days per adjacent ton of uranium (MWD), the data show that no spin centers anneal[1] at 200°C while 30% of the total stored energy can be removed. Recently Muller[4] has extended some of the spin resonance measurements and has shown that the resonance effects are caused by mobile charge carriers and not by paramagnetic carbon centers.

It is shown that appreciable concentrations of mobile single interstitials do not exist in neutron-irradiated graphite.

It is also shown that the activation energy for the radiation annealing of single interstitials can be measured experimentally and is 1/2 of the migration energy of a single interstitial.

EXPERIMENTAL

Growth measurements were made with a Sheffield Optical Comparator on 160 4-in. graphite cylinders (3/4-in. diam) and about 80 2-in. samples. The precision of the readings was 0.0005% on the 4-in. samples and 0.001% on the 2-in. samples. After the samples are machined and marked, the average deviation of 36 measurements for a typical growth change is found to be about 0.2% of the total change with maximum deviations of about 1%.

The growth rate was determined from 10 sets of measurements made on each sample over a total irradiation interval (in the Brookhaven Graphite Research Reactor) of 1000 MWD. (In the BGRR, 1 MWD $=7\times10^{16}$ *nvt* for neutrons above 0.6 MeV.)

Rate of Annealing

When neutrons of high energy collide with lattice atoms, the rate of displacement of the atoms is flux-intensity dependent but should not be dependent on the sample temperature because of the high energies involved.[3] A displaced atom (interstitial) of high energy will undergo many collisions rapidly, until its energy is reduced to values corresponding to the lattice tem-

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[1] G. R. Hennig and J. E. Hove, in *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, United Nations, 1955* (United Nations, New York, 1956), Vol. 7, p. 666, Paper No. 751.

[2] W. K. Woods, L. P. Bupp, and J. F. Fletcher, reference 3, p. 455, Paper No. 746.

[3] G. J. Dienes, J. Appl. Phys. **23**, 1194 (1952); G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957).

[4] K. A. Muller, Phys. Rev. **123**, 1550 (1961).

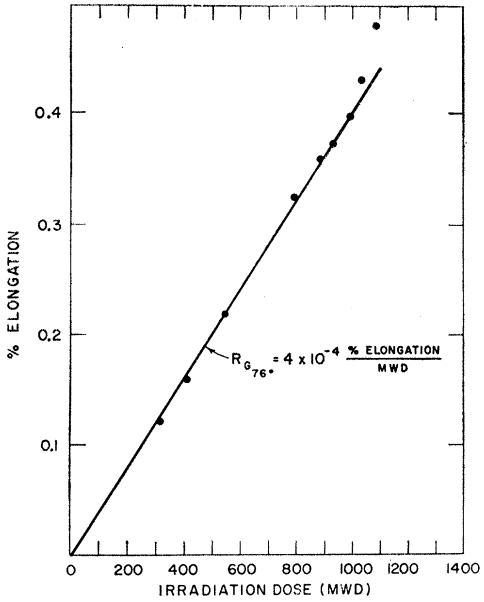

FIG. 1. Dimensional change of graphite at 76°C vs irradiation interval.

perature. During this process some interstitials remain in stable configurations and some anneal out immediately. The number of interstitials that do not anneal cause an increase in the dimensions of the sample. A good deal of evidence[2,3] indicates that the dimensional increases are directly proportional to the concentration of these interstitials. Thus, the difference between the absolute rate of formation of displaced atoms and the rate of dimensional change at any temperature is a measure of the rate of annealing of interstitials at that temperature. The rate of annealing at temperature T $[R_a(T)]$ is then given by

$$R_a(T)=\bar{K}-R_g(T), \tag{1}$$

where $R_g(T)$ is the rate of growth at temperature T, and $\bar{K}$ can be considered as the maximum or absolute rate of growth for the particular type of graphite. [It should be noted that $\bar{K}$ is expressed in the same units as R_g (change per MWD), and is therefore normalized for flux intensity.]

The rates of growth of various graphites are well known at 30°C but almost no data exist between 30 and 150°C. Figure 1 shows a typical curve of growth vs irradiation time at 76°C. Figure 2 is a plot of the slopes of the lines obtained from curves similar to Fig. 1 for different irradiation temperatures. The data do not appear to fall on a smooth curve, the rates of growth change by about 25–30% from 20 to 80°C, while they change by about a factor of 8 from 80 to 220°C.

Activation Energy for Annealing

In order to obtain the activation energy for the annealing process, a value of $\bar{K}$ must be selected to give a straight line on an Arrhenius plot. (This treatment assumes that the rate of annealing is an exponential function of temperature.) No straight line is obtained until the value selected for $\bar{K}$ exceeds 2.2 times the growth rate at 30°C. For increasing values of $\bar{K}$ above $2.2R_g(30°C)$, a series of straight lines are obtained with activation energies that decrease as $\bar{K}$ is increased. A reasonably precise value of $\bar{K}$ can be selected if the data are required to account for the rate of growth at 77°K. Keating's[5] work shows that the growth rate at room temperature is 1/2 of the growth rate at 77°K.

To account for a rate of growth at 303°K which is 50% of the growth rate at 77°K, the value of $\bar{K}$ is found to be 2.5 times the rate of growth at 30°C. The corresponding activation energy is then 0.034 eV. The rate of annealing at some temperature T, can now be given

$$R_a(T)=2.5R_g(30°C)-R_g(T), \tag{2}$$

where R_g is in % expansion per MWD.

An Arrhenius plot of R_a vs $1/T$ for $\bar{K}=2.5R_g(30°C)$ is shown in Fig. 3 along with a similar plot obtained from Hanford data.[6,7] (In Figs. 3–4 the ordinate functions have been multiplied by a factor of 2 so that the data could be plotted on 1-cycle semilog paper.) Although the rate of growth of the Hanford graphite is different from the Brookhaven graphite, the curves are in good agreement, in both cases indicating that the maximum rate of growth for a graphite is about 2.5 times its rate of growth at 30°C.

The same activation energy and absolute rate of formation of displaced atoms obtained from the temperature dependence of the growth rates can also be obtained from the temperature dependence of the rate of c-axis expansion (R_c). Earlier work done at this laboratory[8] indicated that the c-axis expansion was linear with irradiation interval to at least 500 MWD.

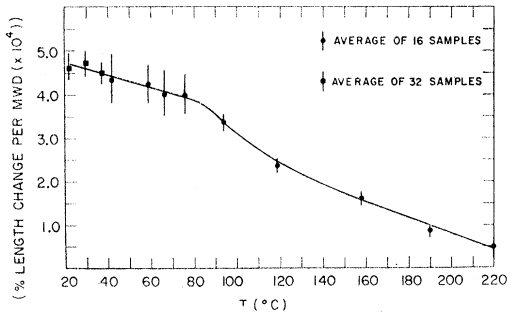

FIG. 2. Rates of growth vs irradiation temperature.

[5] D. T. Keating, Phys. Rev. **98**, 1859 (1955).
[6] R. E. Nightingale, J. M. Davidson, and W. A. Snyder, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy* (United Nations, Geneva, 1958), Vol. 7, p. 295.
[7] J. M. Davidson, E. M. Woodruff, and H. H. Yoshikawa, General Electric Hanford Atomic Products Operation Report HW57900 Rev., 1959.
[8] D. H. Gurinsky, G. J. Dienes, and W. L. Kosiba, Brookhaven National Laboratory Report BNL-255.

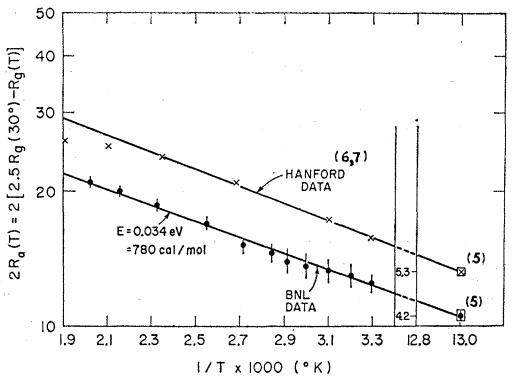

FIG. 3. Rate of annealing single interstitials vs temperature.

We have found, in agreement with this work, that although the rate of c-axis expansion is about 10 times the rate of dimensional expansion, the temperature dependence of both properties are the same. Figure 4 shows the rate-of-annealing function $[\bar{K}_c - R_c(T)]$ vs the reciprocal of the irradiation temperature. The function was calculated in the same manner as was Eq. (2). The rate of c-axis expansion at 77°K is twice the rate of expansion at room temperature.[5] The absolute rate of c-axis expansion ($\bar{K}_c$) necessary to obtain the linear Arrhenius plot is again shown to be 2.5 times the rate at 30°C. The activation energy obtained from the c-axis data (0.037 eV) is in excellent agreement with the activation energy (0.034 eV) obtained from the dimensional expansion data. (Table I lists the data used to plot Fig. 4.)

Dienes[3] has shown that the rate of production of displaced atoms at 30°C is about $2\times10^{-3}\%$/MWD. The absolute rate ($\bar{K}$) is then equal to $5\times10^{-3}\%$ displaced atoms per MWD.

Radiation Growth Mechanism

The radiation growth mechanism which yields kinetic equations in agreement with the experimental Eq. (1), is

$$\phi(\text{fast neutron}) + C^0(\text{graphite}) \rightarrow C_1 + \text{vacancy}, \quad \bar{K} \tag{3}$$

$$C_1 + C_1 \rightarrow C_2, \quad k_2 \tag{4}$$

$$C_1 + \text{trap} \rightarrow C_1T. \quad k_3 \tag{5}$$

Reaction (3) represents the temperature-independent absolute rate of formation of displaced atoms (single interstitials). The rate of growth (R_g) is due to the formation of C_2 or

$$R_g = dC_2/dt. \tag{6}$$

The rate of annealing of single interstitials during the irradiation is given by reaction (5), where T represents various types of trapping sites with no energy barriers. The concentrations of these traps are assumed to be fixed. The activation energy for reactions (4) and (5) are therefore the migration energy of the single interstitial.

At steady state the single interstitial concentration does not change and

$$dC_1/dt = \bar{K} - k_2C_1^2 - k_3C_1 = 0. \tag{7}$$

The rate of growth (R_g) is then

$$dC_2/dt = k_2C_1^2. \tag{8}$$

Solving for C_1 and substituting in Eq. (8), one obtains

$$dC_2/dt = (1/4k_2)[2k_3^2 + 4k_2\bar{K} - 2k_3(k_3^2 + 4k_2\bar{K})^{1/2}]. \tag{9}$$

It can be shown that $4k_2\bar{K} > k_3^2$ over 80% of the total annealing range (irradiation temperatures from 77 to about 420°K) and the ratio $4k_2\bar{K}/k_3^2$ is independent of the steady-state concentration (C_1). For example, for $\bar{K} = 5\times10^{-3}\%$ displaced atoms/MWD and $R_g = 3\times10^{-3}\%$ displaced atoms/MWD,

$$dC_2/dt = 3\times10^{-3}\% = k_2C_1^2. \tag{10}$$

If $C_1 = 10^{-5}\%$, then $k_2 = 3\times10^7$. Substituting for the above values in Eq. (7), one finds

$$k_3C_1 = 2\times10^{-3}\%, \quad \text{or} \quad k_3 = 2\times10^2. \tag{11}$$

The ratio $4k_2\bar{K}/k_3^2 = 4\times3\times10^7\times5\times10^{-3}/(2\times10^2)^2 = 15$. Similarly, if $C_1 = 10^{-8}\%$, then

$$k_2 = 3\times10^{13}, \quad k_3 = 2\times10^5,$$

and

$$4k_2\bar{K}/k_3^2 = 4\times3\times10^{13}\times5\times10^{-3}/(2\times10^5)^2 = 15. \tag{12}$$

Neglecting the second-order k_3 terms, Eq. (9) then reduces to

$$dC_2/dt = (1/4k_2)[4k_2\bar{K} - 2k_3(4k_2\bar{K})^{1/2}], \tag{13}$$

or

$$dC_2/dt = \bar{K} - (\bar{K}/k_2)^{1/2}k_3. \tag{14}$$

The rate constants can then be expressed as exponentials:

$$k_2 = k_0e^{-E/RT}, \tag{15}$$

$$k_3 = k_0'e^{-E/RT} \tag{16}$$

(where E is the migration energy of the single interstitial). The temperature dependence of the rate of growth obtained by substitution of Eqs. (15) and (16)

TABLE I. c-axis expansion data for $\bar{K}_c = 2.5R_c(30°C)$.

R_c (% c-axis expansion per 1000 MWD)	Irradiation temp. (°C)	$\bar{K}_c - R_c$
10.2[a]	−196	2.6
5.1	30	7.7
4.4	55	8.4
3.3	85	9.5
2.4	118	10.4
1.3	180	11.5

[a] See reference 5.

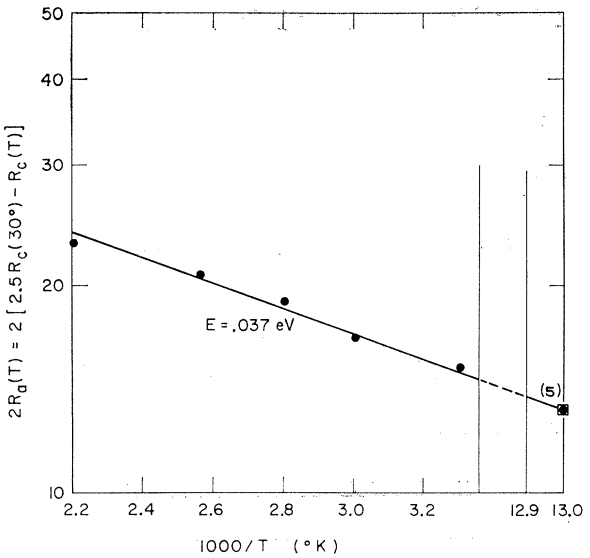

FIG. 4. Rate of annealing single interstitials from c axis expansions.

into Eq. (14) is

$$dC_2/dt=\bar{K}-(\bar{K}/k_0)^{1/2}k_0'e^{(-E+E/2)/RT}, \quad (17)$$

or

$$R_g=\bar{K}-k_4e^{(-E/2)/RT}. \quad (18)$$

From Eq. (1) the rate of annealing (R_a) is therefore

$$R_a=k_4e^{(-E/2)/RT}=\bar{K}-R_g, \quad (19)$$

where (from Fig. 3) $E/2=0.034$ eV and $E=0.068$ eV.

In the above model, the formation of C_2 is necessary to fit the derived kinetic equations with the experimental results. Similar mechanisms in which the dimensional changes are assumed to be due to a particular type of trapped single interstitial, do not yield a temperature dependence for the rate of growth.

If the mechanism is

$$\phi+C^0\rightarrow C_1+\text{vacancy}, \quad \bar{K} \quad (20)$$

$$C_1\rightarrow C_1^* \quad \text{(dimensional increase)}, \quad k_2 \quad (21)$$

$$C_1+T\rightarrow C_1T \quad \text{(no dimensional change)}, \quad k_3 \quad (22)$$

the steady-state equation is first order with C_1, or

$$dC_1/dt=\bar{K}-k_2C_1-k_3C_1=\bar{K}-k_1C_1. \quad (23)$$

The rate of growth is, therefore,

$$dC_1^*/dt=k_2C_1. \quad (24)$$

C_1 will build up exponentially to the steady-state concentration $\bar{K}/(k_2+k_3)$, and Eq. (24) becomes

$$dC_1^*/dt=\bar{K}k_2/(k_2+k_3). \quad (25)$$

Since reactions (21) and (22) should have the same activation energy, the rate of growth will have no temperature dependence and is given by

$$dC_1^*/dt=(\bar{K}k_0e^{-E/RT})/[(k_0+k_0')e^{-E/RT}]=\bar{K}k_0/(k_0+k_0'). \quad (26)$$

Mechanisms involving the formation of a complex C_n (where $n>2$) result in higher order differential equations. Steady-state assumptions cannot be justified if additional reactions such as

$$C_2+C_1\rightarrow C_3, \quad (27)$$

are used. The resulting differential equations cannot be solved in closed form and do not appear to reduce to equations similar to Eq. (18).

CONCLUSIONS

Dimensional and c-axis expansions resulting from the neutron irradiation of graphite can be used to obtain both the migration energy of the single interstitial and the absolute rate of formation of displaced atoms. The values obtained appear to be in excellent agreement with the estimates of Seitz, Dienes,[3] and Iwata *et al.*[9] The results show that single interstitials exist in steady-state concentrations only during the irradiation. The linear rate of growth of graphite during irradiation appears to be due to the production of only one interstitial species, the C_2 complex.

The annealing described in this work corresponds to annealing during the irradiation. In future papers, it will be shown that thermal annealing involves clustering and reclustering reactions. Additional experimental techniques will again show that the linear rate of growth of graphite is the result of the formation of only one species and that the traps described here do not appear to be vacancies. Some evidence will be presented indicating why C_3 does not form from C_2+C_1 during irradiation.

ACKNOWLEDGMENTS

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[9] T. Iwata, F. E. Fujita, and H. Suzuki, J. Phys. Soc. Japan **16**, 197 (1961).