

THE APPLICATION OF CHEMICAL RATE THEORY TO FAST NEUTRON IRRADIATION DAMAGE IN GRAPHITE
 II. The effect of thermal annealing and thermal equilibrium defect concentrations

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1. Introduction

A simple chemical rate theory of fast neutron irradiation damage in graphite has been presented⁽¹⁾ and shown to give reasonable accord with experiment.⁽²⁾ It was noted in the presentation of the theory that it possessed a number of deficiencies including

- (1) The neglect of the effect of vacancy mobility parallel to the hexagonal axis.
- (2) The neglect of thermal annealing of non-saturable sinks and point defects by the equilibrium defect concentration.

The purpose of this paper is to consider the modifications necessary in the theory to accommodate these processes.

2. Theory

The simple chemical rate theory of irradiation damage in graphite assumes that it is sufficiently accurate to distribute the sources and sinks for the point defects homogeneously throughout the solid. The particular sinks for point defects (other than the mutual annihilation of interstitial atoms and vacancies) which are assumed to be present in the solid at constant concentration are:

- (a) For interstitial atoms, the interstitial loop with density $N_i \text{ cm}^{-3}$.
- (b) For vacancies, the vacancy line, density $N_L \text{ cm}^{-3}$, and the crystal boundaries defining the crystal-lite size L_a parallel to the basal plane.

The uniform interstitial and vacancy concentrations denoted by x_i and C_v are obtained as solutions of the equations:-

$$G_i - K_i^2 D_i x_i - Z v_i R x_i C_v = 0 \quad (1)$$

$$G_i \left[1 - 2x' \frac{N_L}{N_o} \right] - K_v^2 D_v C_v - Z v_i R x_i C_v = 0$$

(valid for temperatures where thermal defect concentrations are not significant). Where G_i is the atomic displacement rate in atoms/atom/sec, in a neutron flux ϕ (measured in Equivalent DIDO nickel units), R is the repulsive barrier to interstitial - vacancy recombinations, Z is the number of neighbours from a vacancy from which recombination occurs, and x' is the number of sites adjacent to the end of a vacancy line, D_i and D_v are the diffusion coefficients for interstitials and vacancies respectively, parallel to the basal planes. K_i^2 and K_v^2 are the terms defined in (I) related to the mean free paths for interstitials and vacancies respectively, given in terms of the defects by

$$K_i^2 = 2\pi r Z_i N_i \quad (2)$$

$$K_v^2 = \frac{4Z_v}{dL_a} + \frac{8N_L}{N_o a^2}$$

where r is the interstitial loop radius, d the inter-layer spacing, a the basal jump distance and Z_i , Z_v are small numbers allowing for the effects of stress fields.⁽¹⁾

The motion of vacancies parallel to the hexagonal axis enables them to annihilate interstitial atoms in the loops. This process has been analysed by Reynolds and Thrower⁽²⁾ and Baker and Kelly.⁽³⁾ The rate of change of the radius of a single loop r in a crystal with uniform vacancy concentration C_v due to movement parallel to the hexagonal axis is

$$\frac{dr}{dt} = xy/\alpha v_c \left\{ \exp \left[\frac{-F_c \alpha - E_{fv} - E_{mc}}{kT} \right] - C_v \exp \left[\frac{-E_{mc}}{kT} \right] \right\} \quad (3)$$

where x is the fraction of edge sites on the loop which can absorb vacancies, y is the co-ordination number of an edge atom (6 or 7), α is the area/atom in the loop, v_c is the atomic vibration frequency parallel to the hexagonal axis, E_{fv} is the formation energy of a vacancy, E_{mc} is the activation energy for vacancy movement parallel to the c-axis, k is Boltzmann's constant and T is the absolute temperature.

The parameter F_c is defined by

$$F_c = - \frac{1}{2\pi r} \left(\frac{dE}{dr} \right) \quad (4)$$

where E is the energy of the dislocation loop. The term $\exp(-E_{fv}/kT)$ is small up to a temperature 2500°K while for loops of reasonable size $\exp(-F_c \alpha/kT)$ is less than unity, when (3) may be approximated by

$$\frac{dr}{dt} = -xy/\alpha v_c \exp(-E_{mc}/kT) C_v \quad (5)$$

Inclusion of the interstitial loops as sinks for vacancies in the second of Eqn (2) modifies it to

$$K_v^2 = 4Z/dL_a + 8N_L/N_o a^2 + \frac{2\pi x y v_c}{D_o \alpha} \exp \left[- \frac{(E_{mc} - E_{ma})}{kT} \right] \quad (6)$$

where $D_v = D_o \exp(-E_{ma}/kT)$

without modifying the equation for K_i^2 .

The growth rate of a graphite crystal parallel to the c-axis, $X_c^{-1}(dX_c/dv)$ in the usual notation⁽¹⁾ is

$$\frac{1}{X_c} \frac{dX_c}{dv} = \frac{D_i K_i^2 x_i}{\phi^2} - \frac{2\pi r}{\alpha \phi} \left(\frac{N_L}{N_o} \right) \left(\frac{dr}{dt} \right) \quad (7)$$

$$\text{Defining as before, (1), } \eta = 4Z_i G_i / D_i D_v K_i^2 K_v^2 \quad (8)$$

$$\text{and } \mu = - \frac{N_L Z_i}{N_o} \frac{1}{2} \eta \quad (9)$$

then the solution of Eqn (1) is, as before:

$$\left. \begin{aligned} x_i &= \frac{D_v K_v^2}{2v_i R Z} \left\{ \left[(1 + \mu)^2 + \eta \right]^{1/2} - [1 + \mu] \right\} \\ C_v &= \frac{D_i K_i^2}{2v_i R Z} \left\{ \left[(1 + \mu)^2 + \eta \right]^{1/2} - [1 - \mu] \right\} \end{aligned} \right\} \quad (10)$$

Substitution of Eqn (10) in (7) and re-arranging leads to, finally:

$$\frac{1}{X_c} \cdot \frac{dX_c}{dv} = \frac{2G_i}{\phi} \frac{1}{\eta} \left\{ \left[(1 + \mu)^2 + \eta \right]^{\frac{1}{2}} - [1 + \mu] \right\} - \frac{x y v_c (K_1^2/K_v^2)}{Z_1 N_o D_o v \sqrt{\alpha}} \exp \left[- \frac{(E_{mc} - E_{ma})}{kT} \right] \left\{ \left[(1 + \mu)^2 + \eta \right]^{\frac{1}{2}} - [1 - \mu] \right\} \quad (11)$$

In irradiations at very high temperatures, it is possible in principle for the interstitial loops to emit interstitial atoms and the collapsed vacancy lines to emit vacancies. There may also be equilibrium concentrations of interstitial atoms x_o and vacancies C_o . In this case Eqn (1) is replaced by:

$$\left[G_o + \frac{N_l}{N_o} \cdot \frac{2\pi r}{\alpha} \left(\frac{dr}{dt} \right)_i \right] - D_i K_1^2 x_i - v_i R Z (C_v + C_o) (x_i + x_o) = 0 \quad (12)$$

$$\left[G_o \left(1 - \frac{2N_l}{N_o} x' \right) + \frac{N_l}{aN_o} \left(\frac{d\bar{L}}{dt} \right) \right] - D_v K_v^2 C_v - v_i R Z (C_v + C_o) (x_i + x_o) = 0$$

where \bar{L} is the average length of the N_l vacancy lines, $(dr/dt)_i$ is the rate of change of loop radius dose to interstitial emission.

The pair of Eqns (12) can be solved, but the complexities of the solution obscure the behaviour and many of the numerical parameters are not known. Consider the most likely case, that $x_o \ll x_i$, $(dr/dt)_i = 0$, and eventually $C_o \gg C_v$, then Eqn (12) can be written:

$$G_o - D_i K_1^2 x_i - v_i R x_i C_o = 0 \quad (13)$$

$$G_v - D_v K_v^2 C_v - v_i R x_i C_o = 0$$

with the solutions

$$x_i = \frac{G_o}{D_i K_1^2 + v_i R C_o} \quad (14)$$

and

$$C_v = \frac{G_v}{D_v K_v^2} + v_i \frac{R C_o}{D_v K_v^2} \left[\frac{G_o}{D_i K_1^2 + v_i R C_o} \right] \quad (15)$$

The crystal growth rate parallel to the hexagonal axis is

$$\frac{1}{X_c} \cdot \frac{dX_c}{dv} = \frac{D_i K_1^2 x_i}{\phi} - \frac{2\pi r}{\phi v} \left(\frac{N_l}{N_o} \right) \left(\frac{dr}{dt} \right) \quad (16)$$

where the last term is due to the annealing of the interstitial loops by the equilibrium vacancy concentration.

Substituting for K_1^2 and x_i in the first term gives

$$\frac{1}{X_c} \cdot \frac{dX_c}{dv} = G_o \frac{2\pi r Z_u N_l}{\phi} D_{oi} \exp \left[- \frac{E_{mi}}{kT} \right] x \left\{ \frac{1}{D_{o1} \exp \left(- \frac{E_{mi}}{kT} \right) 2\pi r Z_1 N_l + v_{o1} \exp \left(- \frac{E_{mi}}{kT} \right) R C_o} \right\} - \frac{2\pi r}{\phi v} \left(\frac{N_l}{N_o} \right) \cdot \left(\frac{dr}{dt} \right) = \frac{G_o}{\phi} \left[\frac{1}{1 + (v_{oi} R C_o / 2\pi r Z_1 N_l D_{o1})} \right] - \frac{2\pi r}{\phi} \left(\frac{N_l}{N_o} \right) \left(\frac{dr}{dt} \right) \quad (17)$$

where D_{o1} and v_{o1} are respectively the pre-exponential factors of interstitial diffusion and the interstitial jump frequency parallel to the layer planes:

$$\text{Now } C_o = A_v \exp (- E_{fv}/kT) \quad (18)$$

where A_v is the pre-exponential factor, (4) and to a good approximation

$$\frac{dr}{dt} = x y / \alpha v_c \exp (- E_{mc}/kT) \cdot A_v \exp (- E_{fv}/kT) \quad (19)$$

On substitution into (17) this gives finally:

$$\frac{1}{X_c} \cdot \frac{dX_c}{dv} = \frac{G_o}{\phi} \left[\frac{1}{1 + (v_{oi} R A_v \exp \{- E_{fv}/kT\} / 2\pi r Z_1 N_l D_{o1})} \right] - \frac{2\pi r x y}{\phi \sqrt{\alpha}} v_c A_v \exp \left[- \frac{(E_{fv} + E_{mc})}{kT} \right] \left(\frac{N_l}{N_o} \right) \quad (20)$$

The effect of the vacancy concentration in the first term becomes important when

$$A_v \exp (- E_{fv}/kT) \gg \frac{2\pi r Z_1 N_l D_{o1}}{v_{oi} R} \quad (21)$$

and then the first term diminishes rapidly.

3. Discussion

The second term in Eqn (11) was evaluated for parameters appropriate to reactor graphite, $E_{mg} = 5.5$ eV and $E_{ma} = 3.6$ eV. Over the range 1200-1700 K it was negligible. Basically for crystallite sizes $L_a \sim 3000 \text{ \AA}$ all vacancies are disappearing at crystal boundaries before a significant concentration can jump parallel to the hexagonal axis. This could be reversed for very large L_a values.

Eqn (20) is very transparent, the second term is found to be very small, while the first term shows the damage to be temperature independent until the term in the square brackets reduces below unity. Evaluating the bracketed term indicates that this does not occur until $\sim 4000^\circ\text{C}$ for the case $C_v \ll C_o$.

It would be interesting to observe the results of irradiation of pyrographites at very high temperatures.

4. References

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