CHAPTER 4

STORED ENERGY AND THE THERMO-PHYSICAL PROPERTIES OF GRAPHITE

The lowest energy configuration of an assembly of carbon atoms is the perfect graphite crystal. The introduction of crystal lattice defects increases the energy of the crystal above that of the parent crystal. If the thermal vibrations introduced by heating the crystal permit rearrangement of these defects to states of lower energy then the change in energy is released as heat. This energy is known as Wigner energy, after the well-known physicist who first suggested that it might occur in neutron irradiated material. The phenomenon was already known to occur in self-bombarded (n,α) minerals and to metallurgists because of its occurrence in cold-worked metals. The first recorded, although not recognised, observation was made by Berzelius in gadinolite in 1815. In graphite, diamond and silicon carbide irradiated with fast neutrons at ambient temperature very large amounts of energy can be stored as lattice defects. Values of up to 2700 $J.g^{-1}$ have been observed in graphite which if released as heat under adiabatic conditions would raise its temperature by ~ 1500 °C, an obviously undesirable occurrence!

Stored energy in graphite has two important practical effects. Firstly, following irradiations at temperatures below ~150 °C, it is possible to reach a state in which a small temperature rise can be followed by a much larger rise due to the stored energy. Graphite irradiated at ~30 °C for instance and then heated to 70 °C can rise rapidly in temperature to ~400 °C, which is approximately that required for thermal oxidation. Secondly, in the case of graphite irradiated at higher temperatures, the presence of stored energy reduces the heat capacity and hence affects the progress of any transient temperature condition. In other words the presence of stored energy can be responsible for, or seriously modify, reactor accidents.

Measurements of the stored energy content of graphite are generally made by one of two methods, although others are possible:

(i) The total stored energy can be determined as the difference in the heat of combustion of irradiated and unirradiated graphite. The standard method of measurement of the heat of combustion uses high accuracy bomb calorimetry. The heat of combustion of pure unirradiated graphite is 3.26×10^4 $J.g^{-1}$ while measurement accuracy is ±4 $J.g^{-1}$. Fig 4.1 shows values of total stored energy determined this way as a function of dose for various irradiation temperatures. The energy content cannot increase indefinitely with dose and there is a large effect of irradiation temperature, the rate of energy storage decreasing with increasing temperature.

(ii) In the second method the temperature of the sample is raised in a controlled way and the energy release rate measured. This method generally requires two experiments on the same sample to determine the proportion of energy supplied by stored energy. Two well-known variants are:

(a) To place the sample in isothermal, high heat capacity surroundings and observe the sample temperature-time relation in two successive runs. This is particularly useful when the sample has a very high release rate at low temperatures.

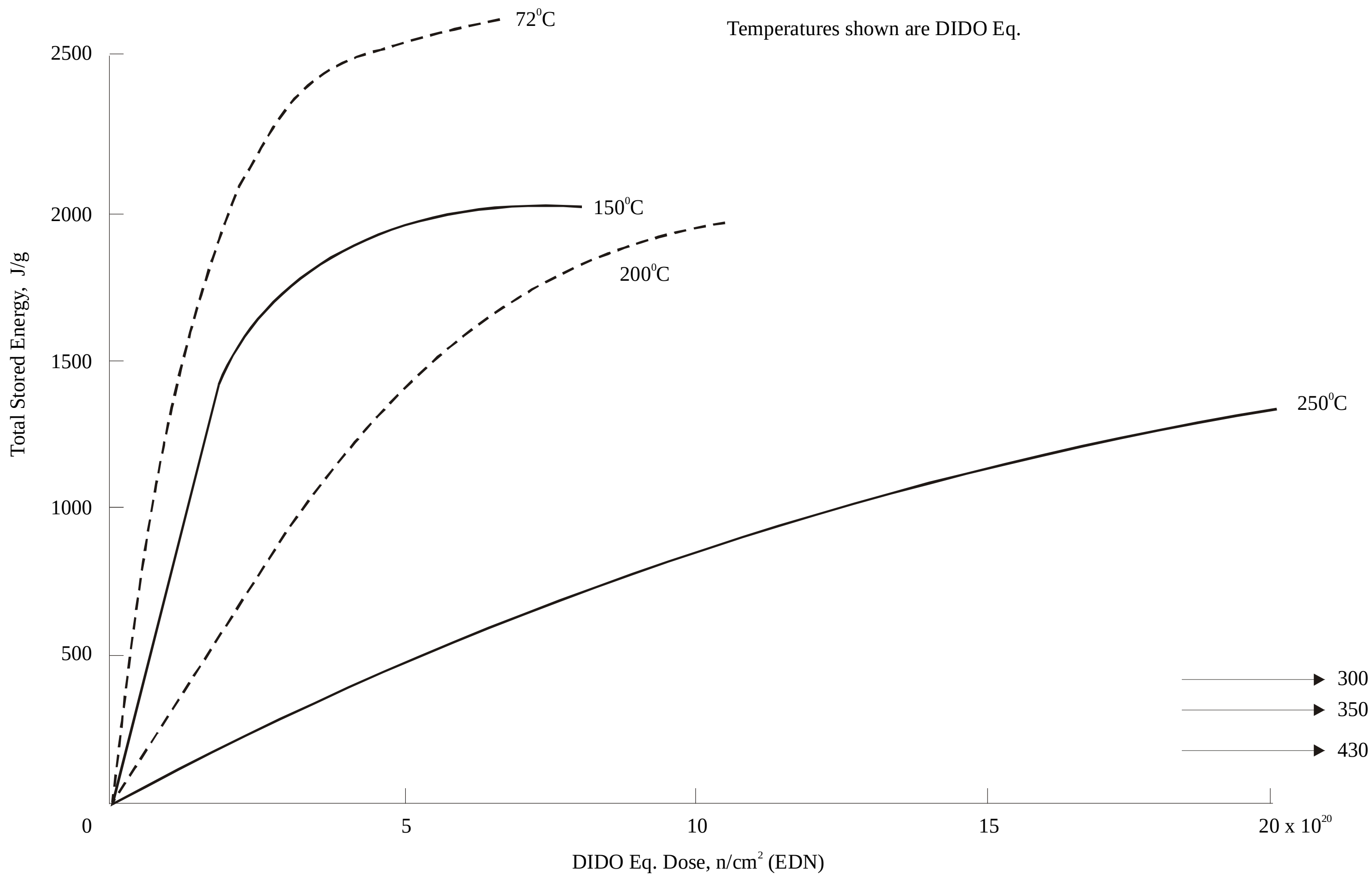

Figure 4.11 Accumulation of total stored energy in graphite at various irradiation temperatures

(b) To supply heat to the sample at the rate required to raise its temperature at a constant rate (linear rise method). The difference in energy supply between two experiments gives the energy release rate.

The energy release rate is usually expressed in terms of unit temperature rise

$$\frac{dS}{dT} = \frac{1}{a}\frac{dS}{dt} \tag{4.1}$$

where S is the stored energy per unit mass, a is the rate of temperature rise, t is the time and T the temperature. Details of the measurement methods are given by Simmons (1965).

The methods described in (ii) have most practical use in that the objective of the measurements is generally the prediction of the temperature progression of a sample subjected to an arbitrary heat source. The measurements of energy release in the case of constant temperature or constant rate of rise of temperature may be used to study the kinetics of energy release. Fig 4.2 shows measurements reported by Bridge, Kelly and Gray (1962) on the rate of energy release per unit temperature rise on samples irradiated to various doses at an irradiation temperature of 30 °C in a water cooled test hole in one of the US Production reactors, but measured in the United Kingdom. These measurements show a well-defined peak at about 200 °C which increases with dose to a maximum value and then diminishes. The energy release rate at higher temperatures increases continuously, but at a decreasing rate until the energy release rate becomes fairly constant. The release rate becomes measurable at a temperature about 80 °C above the irradiation temperature for measurements made at ~2 °C.min^{-1}. As the irradiation temperature is increased the stored energy peak at ~200 °C disappears and the relatively constant level of stored energy release builds up more slowly. Fig 4.3 compares the energy release rates for a dose of 5 x 10^{20} n.cm^{-2} (EDN) following irradiation at 150, 200 and 250 °C. Fig 4.4 shows measurements of energy release rate following irradiations at 350 and 390 °C. The temperature at which the release becomes detectable increases with the irradiation temperature, the gap between the irradiation temperature and temperature of detection decreasing with increasing displacement rate and increasing with rate of temperature rise (Bridge and Mottershead, 1966).

Kelly *et al* (1979) have analysed the published data on the rate of release of stored energy up to 600 °C for irradiation temperatures greater than 140 °C and concluded that there is an irradiation temperature dependent saturation of the rate of release of stored energy. The predicted saturation levels agree well with later data obtained from operating reactors when the appropriate dose and temperature corrections are made, thus verifying the equivalent dose and temperature corrections (see Chapter 1). Bell *et al* (1962) showed that for the same range of irradiation conditions the constant energy release rates were related empirically to the total stored energy in Pile Grade A graphite by

$$\frac{dS}{dT} = \frac{S}{T^*} \tag{4.2}$$

where T^* = 1670 K, independent of irradiation temperature. Analysis of the power reactor data gives T^* = 1910 K which, within errors, is the same.

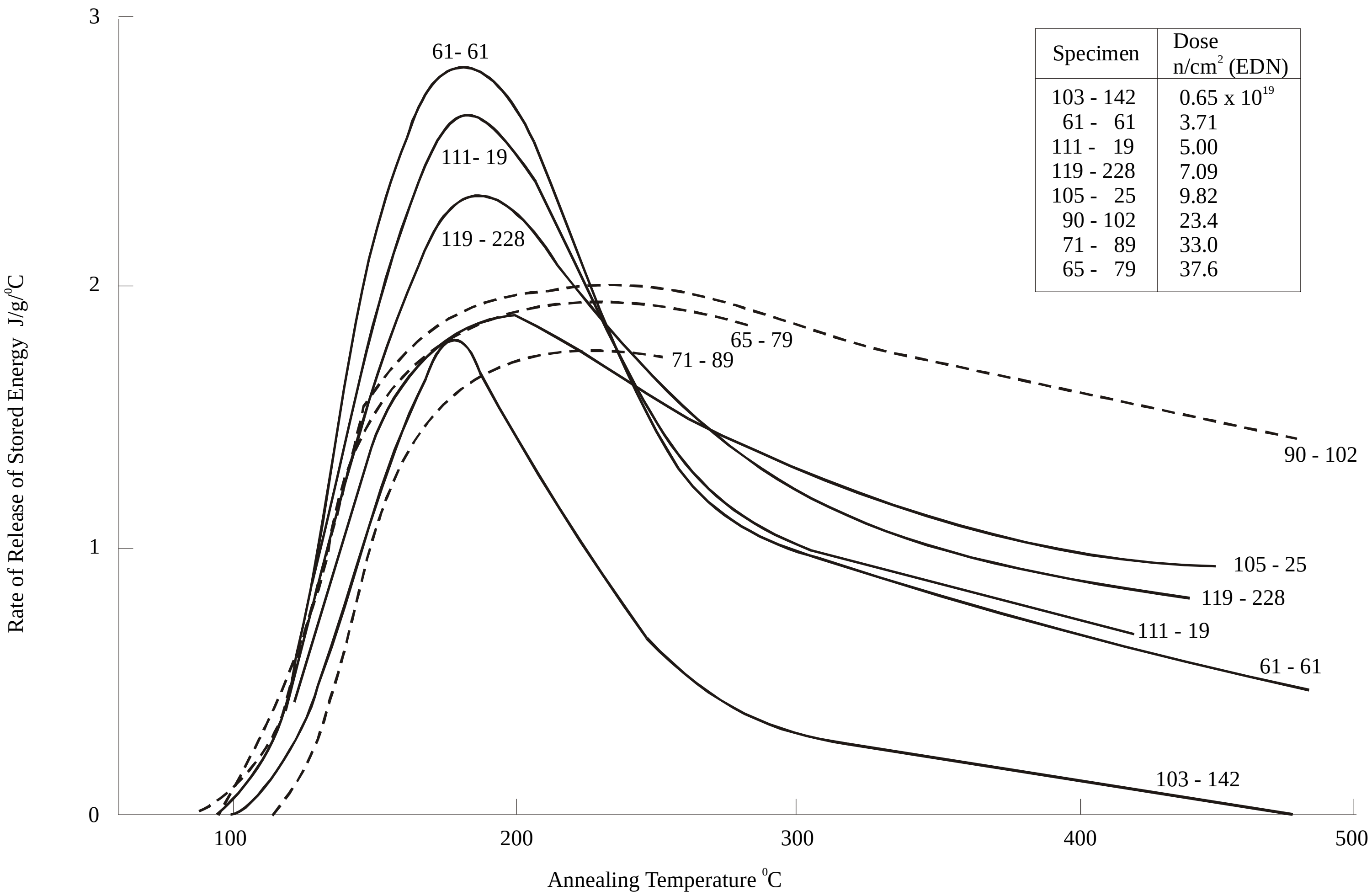

Figure 4.2 Rate of release of stored energy for Hanford cooled test hole graphite irradiated at 30^{o}C

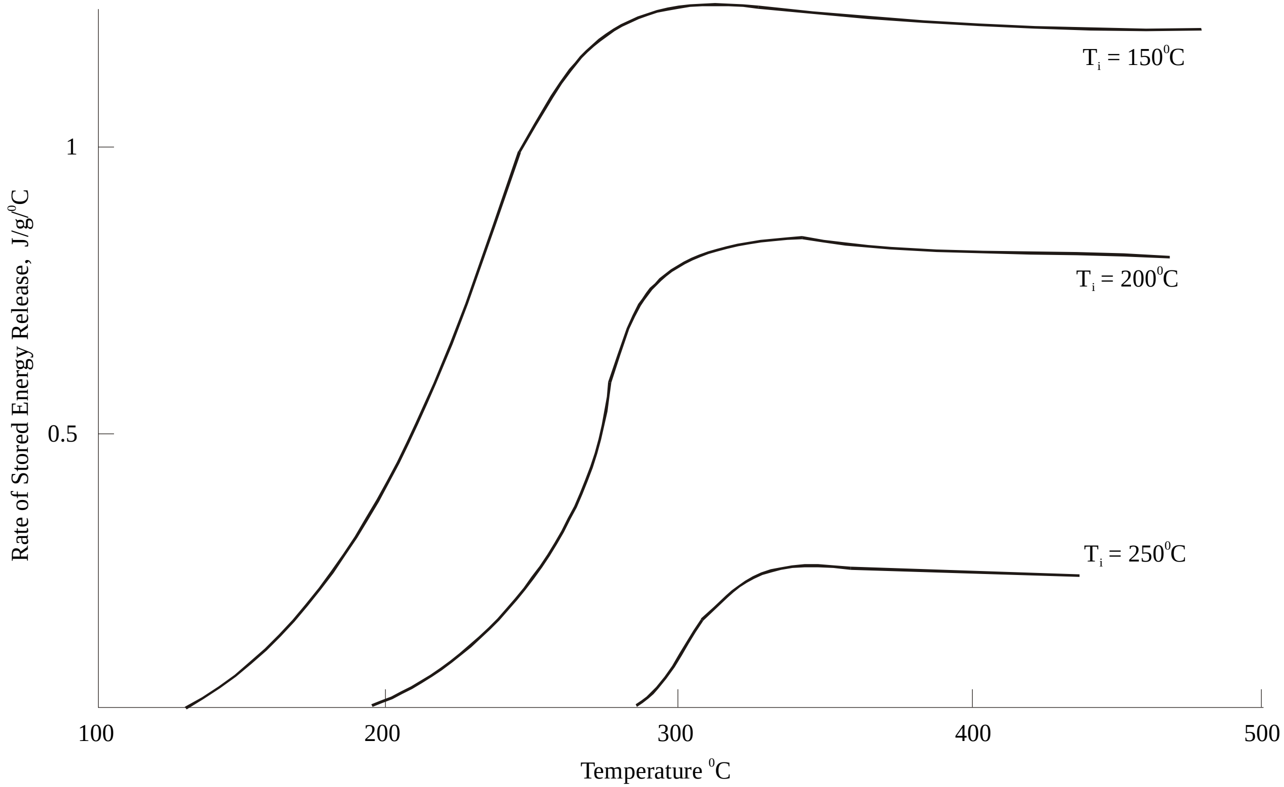

Figure 4.3 Stored energy release curves at dose of $5x10^{20}$ n/cm^2(EDN) for irradiation temperatures of 150°C-250°C

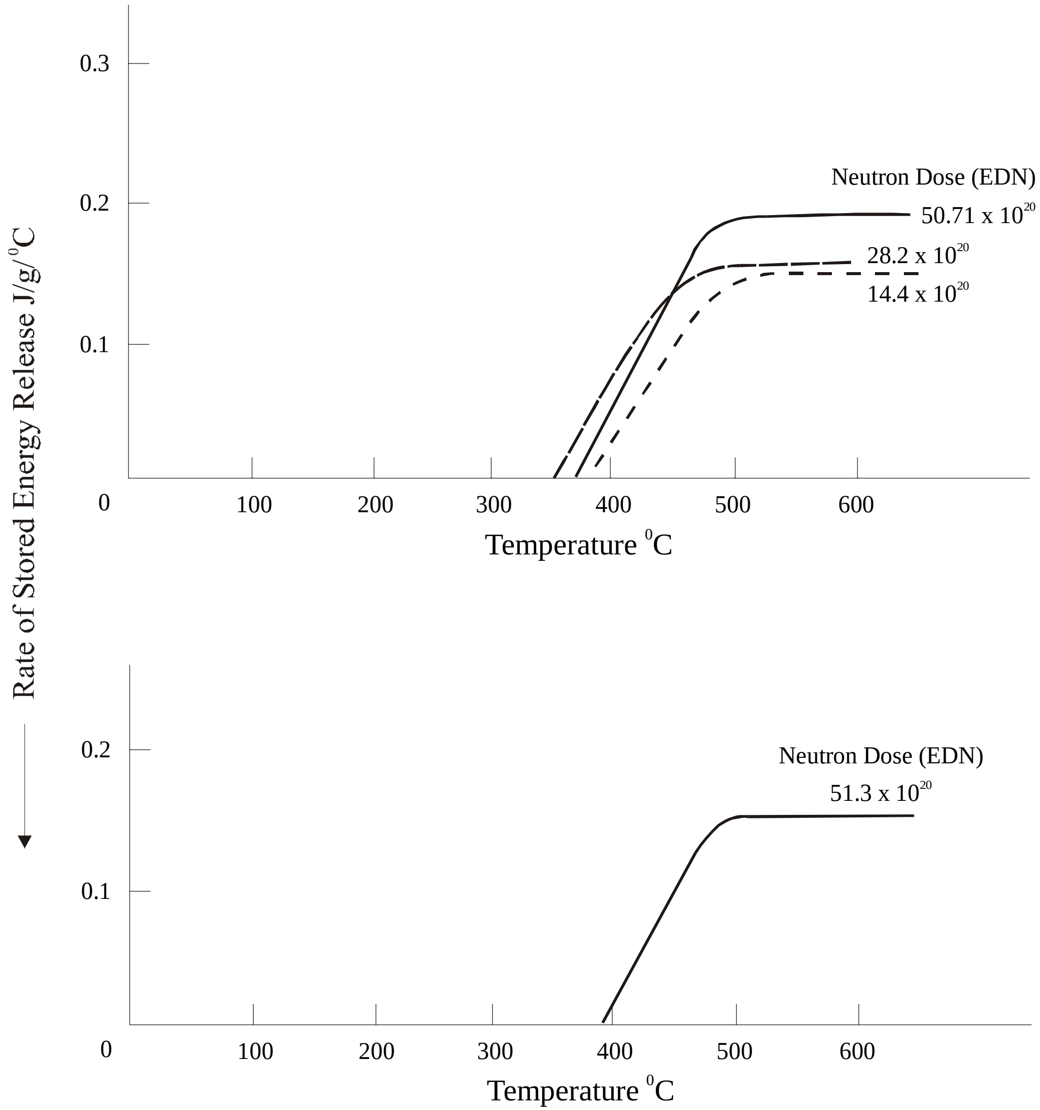

Figure 4.4 Stored energy release curves for irradiation temperatures of 350 and 390°C

At first sight equation (4.2) implies a constant rate of energy release over a wide temperature range, however it is possible to measure *dS/dT* using incremental thermal annealing followed by bomb calorimetry (Bell and Greenough, 1959; Davidson, 1959). Measurements of this type indicated a stored energy release peak at high temperatures, 1000-1500 °C. Rappeneau, Taupin and Grehier (1966) verified the existence of this peak using direct measurements in an all-graphite calorimeter.

Monitoring of the stored energy in power reactor graphite moderators is routine practice where the operating temperature is low, because of the effects it has on the thermal capacity of the moderator in accident situations. The saturation levels of stored energy for irradiations above ~300 °C is too small to be of practical importance.

Stored energy measurements have been made following irradiation with neutrons at temperatures below ambient. Bochirol and Bonjour (1968) made measurements on neutron irradiated graphite exposed at 77 K and 27 K. Three graphites were examined: a stress-annealed very perfect pyrolytic graphite, an annealed pyrolytic graphite and a conventional reactor graphite. The stored energy varied between the materials, the least perfect showing a release extending over a wider temperature range, with less detailed structure.

The stored energy release rates per unit temperature rise show peaks at 75, 110 and 135 K (corresponding to activation energies of 0.09, 0.13 and 0.17 eV). Assuming that the defects are in the form of interstitial-vacancy pairs (Frenkel defects) produced at a rate predicted by the Thompson-Wright model gave a value of 7.1 eV for the Frenkel defect pair. Comparison of stored energies at 77 K in two different neutron spectra showed that the relative damage rates were accurately predicted by the displacement models. The accumulation of stored energy release up to a temperature of 570 K is given by

$$S_{77}^{570} = 1259\left[1 - e^{-0.0889\gamma}\right] \quad \text{J.g}^{-1} \tag{4.3}$$

where γ is the neutron dose with energy > 1 MeV. No difference was observed between reactor and pyrolytic graphite. The non-linear accumulation of stored energy is explained by the overlap of the displacement groups described by Simmons (1965) which thus must have a mean diameter of 17 x 10^{-8} cm.

Austerman (1956) has reported stored energy release spectra in neutron irradiated samples exposed at 120 K.

Stored energy exhibits the phenomenon known as irradiation annealing. If an irradiated sample is exposed to a temperature significantly higher than the original irradiation temperature then the stored energy will decrease as a result of thermal rearrangement of the lattice defects (annealing). However, if the same sample is exposed to the same higher temperature in a neutron flux, the stored energy decreases to a greater extent and for a longer period than in the purely thermal case. This phenomenon was first described by Nightingale (1959), who measured, among other properties, the total stored energy changes of graphite irradiated at ambient and annealed at 375 °C. The effect of irradiation annealing on the stored energy release rate in samples irradiated at a temperature of 130 °C was examined by Bridge, Kelly and Gray (1962) and in more detail, including other properties at 150 °C, by Gray *et al* (1969). This work showed that while thermal annealing raised the temperature at which energy release began, the irradiation annealing lowered the level of the energy release rate over the whole range of temperatures.

It was expected that irradiation annealing might be of practical use in the first generation of graphite moderated power reactors but has not, to the author's knowledge, ever been used. Special cooling circuits were installed in the early UK Magnox reactors to permit raising the moderator temperature uniformly and hence induce irradiation annealing.

Theory of the Release of Stored Energy in Graphite

There has not been any detailed attempt to give a theory of the release of stored energy in terms of the defect concentrations, although correlation of total stored energy with simple models has been achieved. The importance of stored energy release in a variety of reactor accidents has led to detailed empirical methods of treatment of the release applicable to arbitrary temperature-time relationships.

The simplest way of considering the effects of an energy release per unit temperature rise dS/dT as a function of temperature is to note first that this quantity is very insensitive to the conditions of measurement, that is the rate of temperature rise. This permits the definition of an effective specific heat for an irradiated graphite sample:

$$C_p' = C_p - \frac{dS}{dT} \tag{4.4}$$

Fig 4.5 shows the normal specific heat of graphite, C_p.

The conditions necessary for equation (4.4) to be valid were derived by Simmons (1965). If equation (4.4) is negative over a temperature range the effective specific heat is negative and the sample is self-heating, and the possibility of large, virtually adiabatic, temperature rises exists. This condition has only been observed for graphite irradiated at temperatures below 150 °C, where the sharp peak in the energy release rate at 200 °C is observed.

Theoretically it is necessary to specify the state of the graphite and then express the rate of energy release in terms of the state of the graphite. It is usual, because the processes are controlled by thermal activation, to introduce the effect of temperature through a Boltzmann factor $exp[-E/kT]$ where E is an activation energy and k is the Boltzmann constant.

Simmons (1965) has proposed a very general expression for the energy release rate with respect to time:

$$\frac{dS}{dt} = f(S) e^{-\frac{E}{kT}} \tag{4.5}$$

where S is the energy released or remaining. Equation (4.5) may be used in a variety of forms. A considerable number of calculations have been made assuming a constant activation energy E_0 (Cottrell *et al*, 1958) to illustrate the effects of the parameters on the stored energy release. In this case equation (4.5) can be written

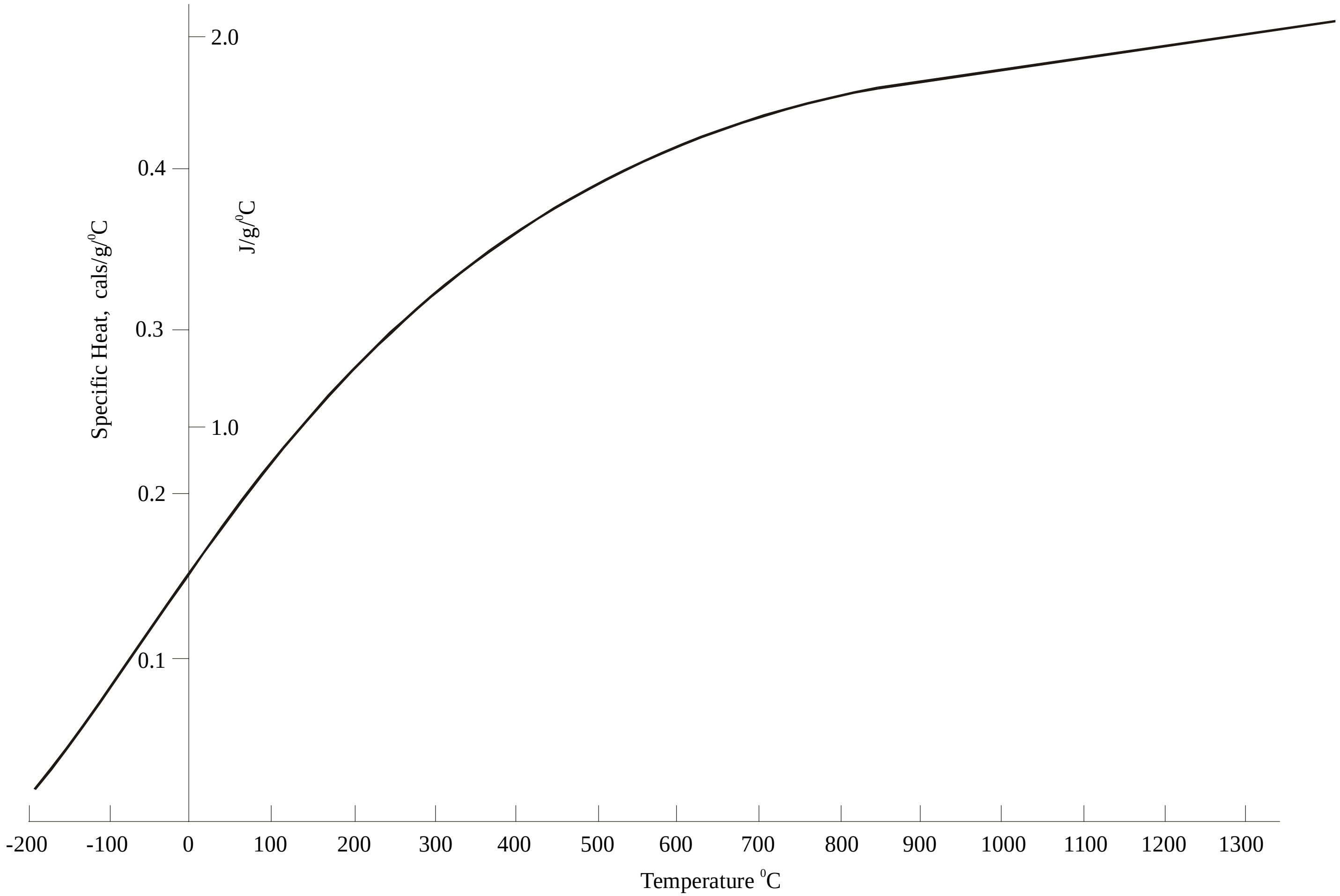

Figure 4.5 Specific heat of graphite

$$\int_{S_0}^{S} \frac{dS}{f(S)} = \int_0^t e^{-\frac{E_0}{kT}} dt \tag{4.6}$$

or

$$F(S) = \tau$$

where τ is a temperature reduced time.

The value of E_0 can be obtained experimentally from annealing experiments in which the rate of change *dP/dt* of a property *P* is measured for the same value of *P* at two different constant temperatures. Then

$$E_0 = \frac{kT_1T_2}{(T_1 - T_2)} \ln\left\{ \frac{\left(\frac{dP}{dt}\right)_1}{\left(\frac{dP}{dt}\right)_2} \right\} \tag{4.7}$$

The constancy or otherwise of E_0 is readily checked by determining it for different values of *P*. If E_0 is known to be constant, the value can be obtained by measuring a property $P(t)$ as a function of time at two different temperatures. If the value of *P* at a time t_1, temperature T_1 is the same as at a time t_n at temperature T_n, the value of τ must be the same, ie:

$$\tau = t_1 e^{-\frac{E_0}{kT_1}} = t_n e^{-\frac{E_0}{kT_n}} \tag{4.8}$$

and thence

$$E_0 = \frac{kT_1T_n}{(T_1 - T_n)} \ln\left(\frac{t_n}{t_1}\right) \tag{4.9}$$

Alternatively, the property *P* can be measured as a function of time at a constant rate of temperature rise *a*, but using different rates *a* and a'. In this case the integral in equation (4.6) is

$$\int_0^t e^{-\frac{E_0}{kat'}} dt' = \frac{E_0}{ka} \int_0^{x'} e^{-\frac{1}{x}} dx \tag{4.10}$$

with

$$x = \frac{kat'}{E_0}$$

The integral is given by

$$\int_o^x e^{-\frac{1}{y}}dy = x^2 e^{-\frac{1}{x}}\left[1 - 2!\,x + 3!\,x^2 - 4!\,x^3 ....\right] \qquad (4.11)$$

For most purposes

$$\tau = \frac{kT^2}{E_0 a} e^{-\frac{E_0}{kT}} \qquad (4.12)$$

is an adequate approximation.

A significant amount of work was carried out in the USA using the relationship

$$\frac{dS}{dt} = -AS^{\gamma} e^{-\frac{E_0}{kT}} \qquad (4.13)$$

with γ, the “order of reaction”, in the range 6 - 8, which produces a sharply peaked curve of *dS/dT* as a function of temperature. Numerous relationships can be obtained between defined parameters such as S_m, the stored energy remaining, and the maximum release rate (which occurs at temperature T_m):

$$\left|\frac{dS}{dT}\right|_{\max} = \frac{S_m E_0}{kT_m^2 \gamma} \qquad (4.14)$$

A single activation energy model is unlikely to be correct, given the very wide range of measurement temperatures at which energy release is observed when the temperature is raised at a constant rate. A simple model in which the activation energy varies was devised by Vand (1943) and further developed by Primak (1955, 1956, 1960). In the simplest form, due to Vand, it is assumed that the energy release process for each group of defects obeys first order kinetics. Thus for a group with activation energy *E* at constant temperature *T*

$$\frac{dS}{dt}(E,t) = -\nu S(E,t) e^{-\frac{E}{kT}} \qquad (4.15)$$

where ν is a constant frequency factor. In an isothermal anneal equation (4.15) integrates to

$$S(E,t) = S_0(E) e^{-\nu t \exp\left(-\frac{E}{kT}\right)} \qquad (4.16)$$

The function *exp[-νt exp(-E/kT)]* varies very rapidly with *E* for fixed time *t*, from 0 at *E* = -∞ to 1 at *E* = +∞, with an inflection point located at

$$E_0 = kT \ln(\nu t) \qquad (4.17)$$

with a value 0.368. The variation with *E* is so rapid that to a good approximation the function can be replaced by a step function of unit height located at E_0. Equation (4.16) can be integrated over activation energy to give the total energy remaining from an initial spectrum $S_0(E)$.

$$S(t) = \int_0^{\infty} S_0(E) e^{-\nu t \exp\left(-\frac{E}{kT}\right)} dE \tag{4.18}$$

which, using the step function, can be approximated by

$$S(t) = \int_{E_0}^{\infty} S_0(E) dE \tag{4.19}$$

which gives on differentiation with respect to time

$$\frac{dS}{dt} = -S_0(E_0)\frac{dE_0}{dt} = -\frac{S_0(E_0)kT}{t} \tag{4.20}$$

E_0 can be regarded as the principal activation energy operating after time t at temperature T K. If the process were a true single activation energy process, then the activation energy would be blurred by this treatment from a sharp line to a spectrum covering a range ~ $2kT$ on either side of E_0.

If the temperature of the sample is raised at a constant rate a it is possible to make a similar approximation, but now the principal activation energy is given by

$$\left(\frac{E_0}{kT}\right) + \ln\left(\frac{E_0}{kT}\right) = \ln(\nu t) \tag{4.21}$$

where $T = at$. Equation (4.21) may be solved to give E_0 as a function of temperature for a given a, provided that ν is known. Nightingale (1959) analysed the thermal annealing of lattice parameter changes and showed that a value of $\nu = 7.5 \times 10^{13}\ s^{-1}$ was suitable to produce "matching" of changes in isothermal annealing at different temperatures and this value has been used by subsequent authors (Bridge, Kelly and Gray, 1962).

Using this value of ν, Bridge and Mottershead (1966) found, to a good approximation

$$E_0 = (33.7 - 1.83 \log_{10} a) T \times 10^{-4} - 0.037 \text{ eV} \tag{4.22}$$

with a in °C.min^{-1}, valid in the range $0.1 < a < 2 \times 10^3$ °C.min^{-1}. As before, the measured rate of energy release per unit time

$$\frac{dS}{dt} = -S_0(E_0)\frac{dE_0}{dt} \tag{4.23}$$

$$\frac{dE_0}{dt} = ka\left(\frac{E_0}{kT}\right)\frac{\left[\frac{E_0}{kT}+2\right]}{\left[\frac{E_0}{kT}+1\right]} \tag{4.24}$$

$$= kaU \qquad \text{say}$$

where U is practically constant for a given value of a, that is $E_0 \propto T$. The activation energy spectrum for a sample can be obtained from the rate of energy release per unit temperature rise as

$$S_0(E_0) = -\frac{\left(\frac{dS}{dT}\right)_a}{kU} \tag{4.25}$$

For an arbitrary temperature history using the same methods, E_0 is obtained from

$$\nu\int_O^t e^{-\frac{E}{kT(t')}}dt' = 1 \tag{4.26}$$

Use of this method is not difficult with modern computers. It should be noted that given S versus T and E_0 versus T the function $E_0(S)$ is readily obtained which may be used in equation (4.5). Preston (1991) has made measurements on a number of samples obtained from the moderator of the BEPO reactor at Harwell and has demonstrated reasonable agreement between equation (4.22) and measured activation energies as a function of temperature. Given $E_0(S)$ of course $F(S)$ can be obtained. The Vand model has been applied to isothermal annealing by Bridge, Kelly and Gray (1962) and shown to give quite good agreement with the amount of energy released. The predicted shape of the energy release curve is not as well reproduced, but is probably adequate for calculations. Fig 4.6 illustrates the predictions and compares them against measurements.

It is possible to devise an alternative treatment of stored energy based on a distribution of frequency factors ν (Lomer, 1959). In this treatment each group of processes is described by

$$\frac{dS(\nu,t)}{dt} = -\nu S(\nu,t)e^{-\frac{E_0}{kT}} \tag{4.27}$$

the activation energy being a fixed value E_0. If $S(\nu,t)d\nu$ is the stored energy released with frequency factor in the range ν to ν + dν then the stored energy at time t is

$$S(t) = \int_o^\infty S(\nu,t)d\nu \tag{4.28}$$

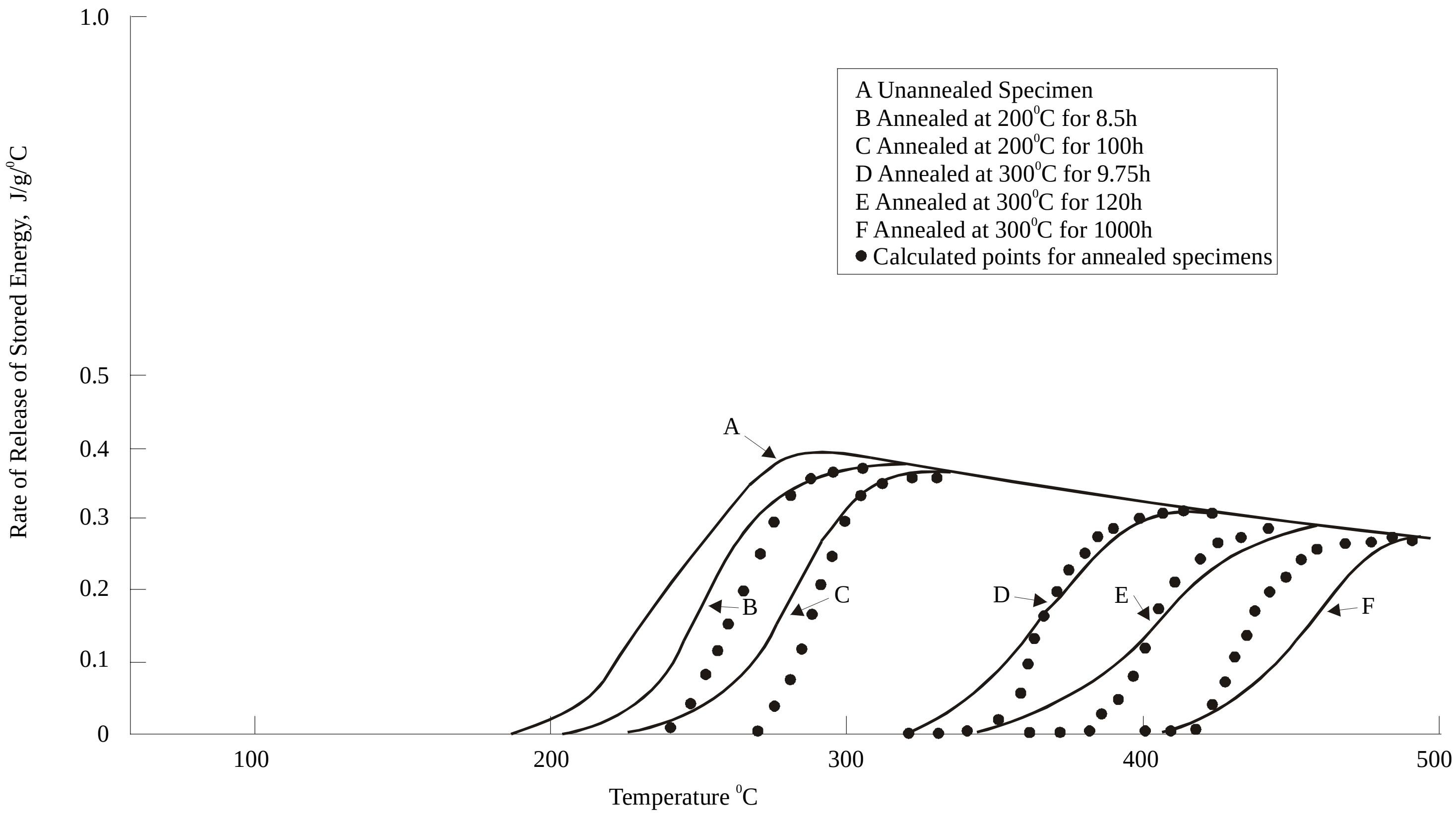

Figure 4.6 The effect of annealing at 200 and 300°C for various times on the linear rise curve of graphite irradiated at 155°C to a dose of 2.35 x 10^{20} n/cm^2

which may be written

$$S(t) = \int_0^{\infty} S(\nu,0)e^{-\nu\tau}d\nu \tag{4.29}$$

where the reduced time τ is

$$e^{-\frac{E_0}{kT}}dt$$

and $S(\nu,0)$ is the initial stored energy release spectrum. Since the reduced time τ is known then the variation of stored energy with time is predictable. The exponential in equation (4.29) can, to a first approximation, be replaced by a step function

$$e^{-\nu\tau} = 1, \text{ for } \nu << \tau^{-1}$$

$$e^{-\nu\tau} = 0, \text{ for } \nu >> \tau^{-1}$$

giving

$$S(t) = \int_0^{\tau^{-1}} S(\nu,0)d\nu \tag{4.30}$$

This is equivalent (Simmons, 1965) to writing

$$\frac{dS}{dt} = f(S)e^{-\frac{E}{kT}} \tag{4.31}$$

The activation energies or frequency factors must be obtained experimentally and only a few measurements have been published of such determinations.

Åström (1961) measured stored energy release rates during isothermal annealing on samples irradiated to low doses (10^{17} - 10^{18} n.cm^{-2}) at 35 °C. Activation energies were determined in two temperature ranges, 70-100 °C and 130-270 °C. In the lower range he found that the activation energy increased with the radiation dose, increasing from ~0.4 to 1.0 eV. In the higher temperature range he found values of 1.2-2.0 eV, but with no clear dependence on dose or measurement temperature. Rimmer (1959) made measurements on higher dose samples irradiated at 40 °C in the annealing temperature range 25-400 °C and obtained values of 1.15-1.6 eV.

All of the theoretical studies have considered the situation for graphite containing a sharp peak in the energy release rate at 200 °C and thus it is generally assumed that a reasonable approximation is to assume a constant activation energy. Solutions of equation (4.31) have been given by Cottrell *et al* (1958) using two sets of data corresponding to low doses and high doses at an irradiation temperature of 30 °C. In some cases it was found that the graphite temperature T stayed close to the coolant temperature T_c, but in other cases T

exceeded T_c. The difference in behaviour depends upon the strength of coupling between the graphite temperature and the coolant temperature. Detailed analysis of the results showed that the strong coupling condition corresponds to

$$a_c q < 1\,°\mathrm{C}$$

while for loose coupling

$$a_c q > 10\,°\mathrm{C}$$

where a_c is the rate of rise of coolant temperature and q is a time constant (see equation (4.33)).

Cottrell *et al* (1958) also studied the effect of a sudden increase in graphite and coolant temperatures on subsequent graphite temperatures. It was concluded that unless the graphite and coolant temperatures were raised by more than 70 °C in full channel flow or 50 °C in partial (8%) flow the graphite - coolant temperature difference remains small. Simmons (1965) presents simple approximate methods for analysing the effects of stored energy on moderator temperature. A separate but important problem is the propagation of stored energy release through the graphite moderator of a reactor. In the case of gas-cooled reactors, the only important practical situation, the release may spread by conduction or heat exchange with the reactor coolant gas. It is possible to make detailed calculations of the variations of coolant and moderator temperature with time in reactor fuel channels.

The effect of stored energy on the heat balance in the unit cell of a graphite moderated reactor is considered by Simmons (1965) and the details of the kinetics by Cottrell *et al* (1958).

The heat balance is given by

$$C_p \rho A \frac{dT}{dt} = A\rho \frac{dS}{dt} + hP\left(T_c - T\right) \qquad (4.32)$$

where A is the cross-sectional area of the graphite in a reactor unit cell
ρ is the graphite density
C_p is the specific heat of graphite
h is the heat transfer coefficient per unit length of channel
P is the perimeter of the fuel channel
T_c is the coolant temperature and T is the graphite (surface) temperature

Introducing a time constant $q = A\rho C_p/hP$, equation (4.32) becomes

$$\frac{dT}{dt} = \frac{1}{C_p}\frac{dS}{dt} + \frac{T_c - T}{q} \qquad (4.33)$$

Simmons notes that it is useful to consider two special cases, rather than attempt a completely general discussion. The first case neglects the effect of thermal conduction. The stored energy release is then propagated by heat exchange with the coolant gas. Suppose the coolant gas entering a fuel channel is rapidly raised in temperature, then the graphite temperature near the coolant inlet will increase more rapidly than that further along the channel. If the stored energy is fairly constant along the channel (actually not a very realistic case because of the cosine dependence of the axial flux and the steadily rising temperature which tends to produce a peak in the stored energy in the cooler half of the reactor), the energy release will start at the lower temperature end. In the condition of loose coupling to the gas temperature the graphite temperature will then rise above the gas temperature and transfer heat to the coolant gas. The resulting rise in coolant temperature will then reduce the time required for the energy release to occur further along the channel; that is the spread of energy release is governed by the heat exchange between the graphite and coolant.

In the second case the heat transfer between the graphite and coolant is completely neglected and the release spreads by conduction only. Assuming that the stored energy is uniform, the thermal conductivity is constant, the initial temperature is uniform at a value T_1 and that heat losses from the channel ends can be neglected, then the heat balance equation is

$$C_p \frac{\partial T(z,t)}{\partial t} = \frac{dS}{dt} + \frac{\partial T(z,t)}{\partial z} \tag{4.34}$$

where z is the axial position.

In this case the graphite temperature would rise slowly due to the energy release and an adiabatic release would take place simultaneously throughout the graphite. If some heat is applied, say at $z = 0$, the release will start at the point and spread axially by conduction. Foreman (1959) has shown that if the stored energy is large enough the release will propagate as a temperature wave with a well-defined front at a velocity of a few cm.min^{-1}. It can be shown that the temperature in the wave front is a function of $y = z - vt$ where v is the velocity of the wave front. A point at temperature T_m is located on the wave front where $d^2T/dz^2 = 0$. For $T < T_m$ heat is supplied to the graphite, while for $T > T_m$ there is a net forward propagation of heat. The effect of spatial variation in stored energy or non-uniform temperature is to cause the wave to build up or decay. Foreman and Curtis (1960) have examined the effect of uniform cooling for this case. It was shown that propagation does take place provided the constant is above a critical value, but for lower values the wave is heavily damped. In practical cases the critical time constant was 2 - 4 hours.

The early air-cooled graphite moderated reactors accumulated large amounts of stored energy. A number of reactors employed the method of controlling stored energy by regular anneals. The first reactors to be annealed were those at Windscale and BEPO in the United Kingdom. The method used was to shut off the coolant flow and then operate at low power in order to raise the graphite temperatures to ~ 100 °C following which the power was cut off and the temperature allowed to rise due to the stored energy release which then spread through the reactor. The reactor graphite temperatures rose rapidly to levels between 300 °C and 400 °C. In order for this technique to work it was necessary to choose the time of the anneal carefully so that there was enough energy to produce successful propagation but not so much that excessive temperatures would arise. The amount of nuclear heating applied needed to be carefully controlled.

Eventually annealing became regarded as a potentially dangerous operation in air-cooled reactors because of the graphite-air reaction, which was enhanced by irradiation damage. In

1957 one of the two Windscale Production Piles caught fire during an annealing operation and the annealing process was reviewed as a result and improved methods devised. Dickson *et al* (1958) describe an improved technique used on the BEPO reactor in which a flow of pre-heated air at 140 °C was maintained to the reactor throughout the anneal, permitting quasi-adiabatic anneals. Similar techniques were applied in France and the USA (see Simmons, 1965). The effect of repeated anneals on the long term changes in dimensions and properties has been reported by Woodruff (1959).

The Thermal Conductivity of Graphite

The thermal conductivity of a graphite crystal has two principal tensor components, measured parallel and perpendicular to the basal plane. The conductivities are both dominated by lattice vibrations (phonons) except at very low temperatures (~1 K) and possibly at very high temperatures where the electronic component is significant (see Kelly (1969) for a review). The conductivities are controlled at low temperatures by the scattering of the phonons at crystal boundaries, whereas at high temperatures they are scattered by other phonons. In the former case the conductivity increases with temperature and in the latter decreases with increasing temperature, so that there is a peak at intermediate temperatures for not too imperfect materials where the first process dominates. The conductivity is much higher parallel to the basal planes than perpendicular to them. In all except very well oriented materials it is found that the conductivity is dominated by the basal conductivity of the component crystallites (Taylor, Gilchrist and Poston, 1968; Kelly, 1981). It is generally possible to write, for a direction *x*:

$$K_x = \frac{K_a}{\beta_x} \qquad (4.35)$$

where β_x is a constant and K_a is the basal conductivity of the component crystallites. For low density poorly crystalline carbons the matrix conductivity is low because of the small crystallite size and the conductivity is dominated by heat transfer across the pores, either by radiation or gaseous conductivity, so that, strictly speaking, equation (4.35) must be verified for each new material. It is known to be well obeyed for well-graphitised materials with up to 50% total porosity. The basal conductivity K_a of a graphite crystal for temperatures greater than 1 K is given by (Kelly, 1969):

$$\frac{1}{K_a} = \frac{1}{K_B} + \frac{1}{K_U} + \frac{1}{K_D} \qquad (4.36)$$

where

$1/K_B$ is the thermal resistance due to crystallite boundary scattering,
$1/K_U$ is the thermal resistance due to phonon scattering,
$1/K_D$ is the thermal resistance due to lattice defects.

The thermal resistance due to crystallite boundary scattering may be written

$$\frac{1}{K_B} = \frac{1}{F(T)} L_a \qquad (4.37)$$

where L_a is the crystallite size measured parallel to the basal planes and $F(T)$ is a function of measurement temperature and the crystal elastic constants. $1/K_U$ has been derived from measurements of conductivity over a wide temperature range and is roughly of the form $AT^n \exp[\theta/T]$ where n and θ are constants. $1/K_D$ is not usually significant in unirradiated graphite.

The effect of irradiation is to increase the thermal resistance term. It would be expected that different lattice defects would scatter phonons, with different dependencies on the phonon frequencies leading to different temperature dependencies for the thermal resistances. It is difficult to develop appropriate theories of the scattering because of the anisotropic nature of the crystal lattice, although some attempts have been made (Dreyfus and Maynard, 1967; Kelly, 1969; Klemens, 1953). The assumption is always made that the lattice vibration spectrum is not changed by the presence of the crystal lattice defects, which is probably not correct at high damage levels.

In order to make progress with understanding the changes in thermal resistance under irradiation it has become customary to plot the fractional change in thermal resistance against dose for fixed irradiation temperatures at a particular measurement temperature. This is

$$\frac{\dfrac{1}{K_x(\gamma,T_m)} - \dfrac{1}{K_x(0,T_m)}}{\dfrac{1}{K_x(0,T_m)}} = \frac{K_x(0,T_m)}{K_x(\gamma,T_m)} - 1 \tag{4.38}$$

$$= \frac{K_a(0,T_m)}{K_a(\gamma,T_m)} - 1$$

if $ß_x$ does not change and where $K_a(0,T_m)$ is the basal conductivity at measurement temperature T_m for zero dose.

$1/K_a(\gamma,T_m)$ is the thermal resistance at dose γ, measurement temperature T_m. Fig 4.7 shows the fractional changes in thermal resistance at ambient temperature of Pile Grade A graphite irradiated with reactor neutrons over a wide range of irradiation temperatures. The changes are independent of direction of cut of the samples, as expected from equation (4.38), and strongly dependent on the irradiation temperature, decreasing with increasing temperature. The changes bear a strong resemblance to the variation of total stored energy with dose and irradiation temperature.

Bell *et al* (1962) compared their measurements of thermal resistivity change in Pile Grade A at ambient temperature with total stored energy, S, measured on the same samples and obtained a good correlation

$$S = 26.1\left|\frac{K_0}{K} - 1\right| \quad \text{J.g}^{-1} \tag{4.39}$$

for irradiation temperatures between 150 and 350 °C. The total stored energy and thermal resistivity changes are available for CSF graphite irradiated at 30 °C and a similar correlation

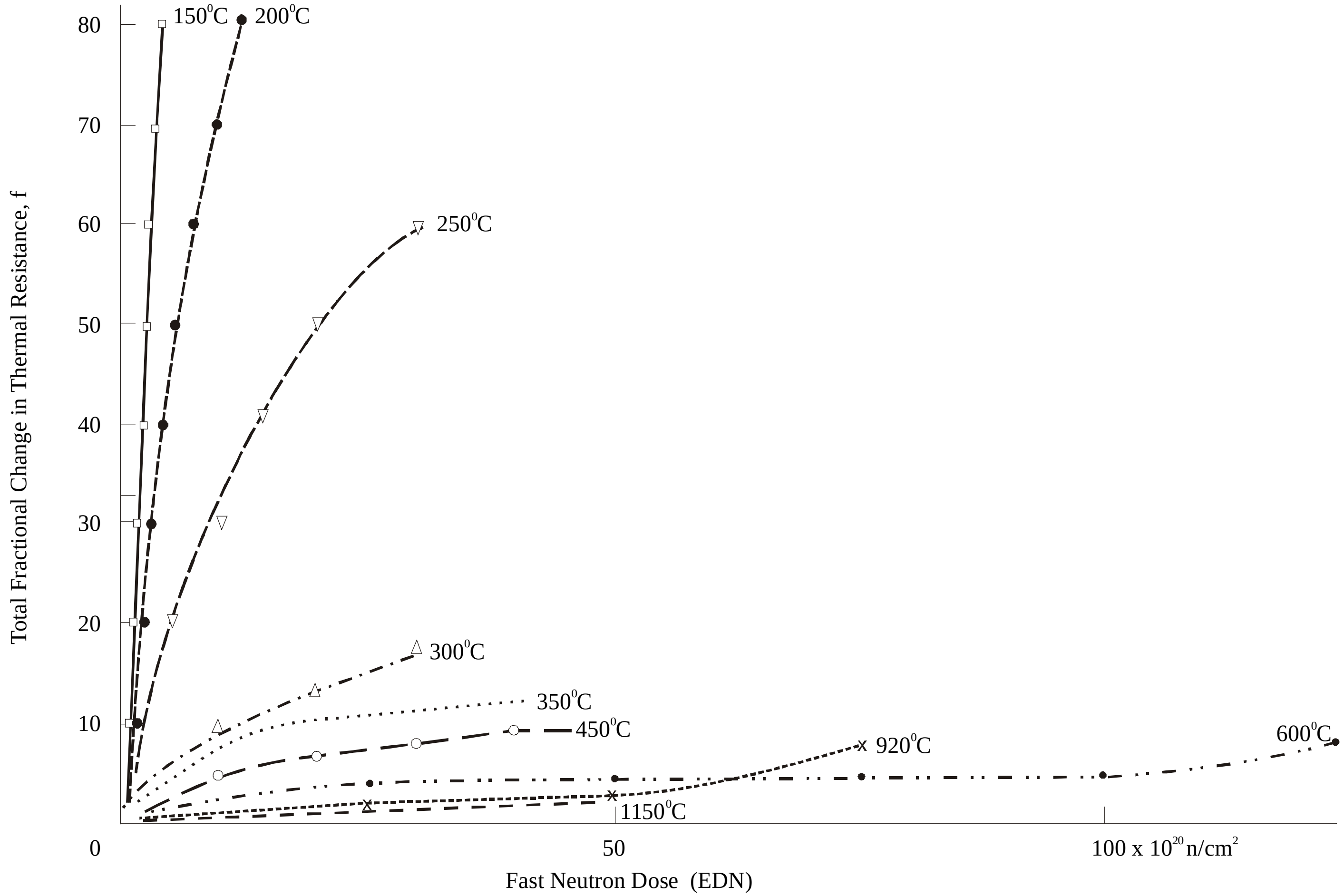

Figure 4.7 Fractional changes in thermal resistance of PGA graphite at various irradiation temperatures

is obtained (see Bell *et al*, 1962). Smith and Rasor (1956) report data on a number of graphites irradiated at 30 °C.

Measurements of the temperature dependence of thermal conductivity post-irradiation have been surprisingly rare. Mottershead and James (1967) reported data on Pile Grade A graphite and data on CSF graphite are reported by Carter (1959). The temperature dependence post-irradiation is much reduced, tending in the extreme to lead to proportionality to the specific heat. Taylor, Kelly and Gilchrist (1969) have made measurements on highly oriented pyrolytic graphite parallel and perpendicular to the deposition plane (or basal planes) from which the additional thermal resistance may be derived for both crystallographic directions.

A detailed analysis of the effect of irradiation on the temperature dependence of thermal conductivity was given by Carter (1959) who assumed that the scattering of phonons is independent of temperature, an assumption which at the time was apparently supported by the evidence. A similar method was described by Simmons (1965). Simmons noted that because of the near two-dimensional nature of the crystal lattice it is a good approximation to write

$$K_a = \frac{1}{2}\rho C_p V l \tag{4.40}$$

where l is the phonon mean free path and V is the mean phonon group velocity parallel to the basal planes. In considering the effect of irradiation on thermal conductivity it is convenient to write

$$\frac{1}{l} = f\left(T_m\right) + G \tag{4.41}$$

where $f(T_m)$ is proportional to the scattering power in the unirradiated state and G represents the additional scattering due to the radiation induced lattice defects. The term $f(T_m)$ includes phonon-phonon scattering and pre-irradiation lattice defects (crystal boundaries, etc). Assuming that to a good approximation the specific heat is unchanged by irradiation (true for temperatures above ambient, but not for low temperatures) then

$$\frac{K(0,T_m)}{K(\gamma,T_m)} - 1 = \frac{G}{f\left(T_m\right)} \tag{4.42}$$

If G is independent of temperature then it is possible to relate values of fractional change measured at two different temperatures, that is

$$\left| \frac{K(0,T'_m)}{K(\gamma,T'_m)} - 1 \right| = \left[\frac{f\left(T_m\right)}{f\left(T'_m\right)}\right]\left[\frac{K(0,T_m)}{K(\gamma,T_m)} - 1\right] \tag{4.43}$$

It may be deduced that because $f(T_m)$ contains the effect of defects present pre-irradiation then the fractional changes in thermal resistance will be less in an imperfect graphite, for the same defect content, than in a perfect graphite.

Taylor, Kelly and Gilchrist (1969) reported measurements of the thermal resistance produced by irradiation in highly oriented pyrolytic graphite parallel and perpendicular to the deposition planes (ie basal planes). This amounts to examining the same defects with phonons propagating in different directions. The results show that the thermal resistance added by irradiation at temperatures in the range 30-450 °C is not independent of temperature. In the direction parallel to the basal planes the additional resistance is fairly constant for measurement temperatures greater than 300 K, (there is a shallow minimum at about 550 K), but increases with decreasing temperature at low temperatures. The shape of this curve is apparently independent of temperature and also of the annealing condition. In the direction perpendicular to the deposition plane the temperature dependence was similar. The apparent insensitivity of the temperature dependence of the irradiation induced thermal resistance parallel to the basal planes means that given the fractional changes in thermal resistance at ambient (here denoted by *f*) the thermal conductivity in direction *x* of the polycrystal at temperature T_m K is given by

$$K_x(T_m) = K_x(0,T_m)\left[1 + f\ \delta(T_m)\ \frac{K_x(0,T_m)}{K_x(0,300)}\right] \tag{4.44}$$

where $\delta(T_m)$ is the temperature dependence of the thermal resistance due to irradiation normalised to unity at 300 K (see Fig 28 of Kelly, 1969). Later work due to Binkele (1972, 1978) and to Brown *et al* (1990) has shown that $\delta(T_m)$ is not independent of irradiation temperature, showing less temperature dependence for irradiation temperatures greater than 450 °C. It should be noted that some care is necessary in interpreting plots of thermal resistance with dose because of changes in the parameter β_x due to structural changes.

Taylor, Kelly and Gilchrist (1969) have tried to relate the changes in thermal resistance parallel to the basal planes to concentrations of defects estimated from the crystal dimensional changes and lattice parameter changes. The concentrations of various defects were estimated by Henson *et al* (1968). It was assumed that for irradiations at temperatures below ~ 450 °C only the sub-microscopic(4 ±2 atoms) interstitial groups and point vacancies contributed significantly to the irradiation induced thermal resistance, the interstitial dislocation loops and collapsed vacancy lines being relatively insignificant. Given these assumptions, for a polycrystalline graphite in direction *x*

$$\Delta\left|\frac{1}{K_x}\right| = \alpha_x\left[\delta\ x_i\ S_i^2 + \beta\ C_v\ S_v^2\right] \tag{4.45}$$

where δ and *ß* are numerical constants appropriate to ambient temperature, α_x is a factor allowing for porosity and tortuosity, x_i and C_v are the concentrations as before and S_i and S_v are the scattering parameters, of order unity. Using the estimated defect concentrations it is possible to plot $\Delta(1/K_x)/C_v$ against x_i/C_v and then, given theoretical estimates of δ and *ß*, to obtain S_i^2 and S_v^2 . Kelly (1969) obtained S_i^2 and S_v^2 and found 3.2 and 0.72 respectively, in fair agreement with expectation. Thermal resistance changes in Pile Grade A graphite following irradiation at 650, 900 and 1350 °C requires an additional contribution which has been attributed to the presence of small uncollapsed vacancy loops which lead to a thermal resistance

$$\Delta\left(\frac{1}{K_x}\right) = \alpha_x\left[C_v \beta S_v^2 + \eta\frac{C_{v,Loop}}{r_0}\right] \qquad (4.46)$$

where r_o is the loop radius, $C_{v,Loop}$ the concentration of vacancies in such loops and η a constant appropriate to room temperature.

It is possible to compare measurements of the changes in thermal resistance parallel to the basal planes with predictions from lattice parameter changes which are used to estimate the point defect concentrations x_i and C_v. The results are presented by Taylor, Kelly and Gilchrist (1969). The agreement is good.

The situation for this range of irradiation temperature is apparently quite satisfactory, however comparison with inferences from the stored energy and dimensional changes shows that there are difficulties. If the total stored energy is written in the form

$$S = 19.4 \times 10^2\left[x_i E_{fi} + C_v E_{fv}\right] \quad \text{cal.g}^{-1} \qquad (4.47)$$

where E_{fi} and E_{fv} are the energies of formation of the interstitial atoms in the groups and point vacancies in eV, the energy of defects which constitute interstitial and vacancy loops is neglected. The experimental data are such that for all except small doses x_i/C_v is small and equation (4.47) becomes, on combination with equation (4.45)

$$S = 5f\ E_{fv} \quad \text{cal.g}^{-1} \qquad (4.48)$$

for Pile Grade A graphite. The experimental value is 6.5*f* leading to E_{fv} ~1.3 eV, which is much less than the expected value of about 7 eV for a single vacancy. An analysis by Henson and Reynolds (1965) showed that the apparent formation energy of the vacancies decreased substantially for apparent concentrations greater than 1%. It was suggested that this was due to long range attractive interactions between vacancies and the formation of small uncollapsed vacancy loops, but the rate of formation of collapsed vacancy lines would be much greater than is observed if the point vacancy concentrations that are estimated are real. The alternative view is that phonon scattering and in-plane ($\Delta a/a$) lattice parameter changes are in part due to the ends of the collapsed vacancy lines (which strictly are two-dimensional dislocation dipoles one layer thick). The scattering by such dipoles has been considered by Kelly (1969) but has not been applied to the data in detail. There are two obvious simplifications, where the phonon wavelength is much greater or less than the dipole separation, but there is difficulty in making the calculations (Kelly, 1969).

The phonon scattering due to point defects can be considered as the result of three factors, assuming that the phonon wavelength is much larger than the defect size:

(i) The mass defect associated with the presence of the defect.

(ii) The change in strength of the local interatomic bonds.

(iii) The strain field of the defect.

The major difficulty in assessing the scattering of phonons by defects in graphite is the fundamental separation of the phonons into two groups, one in which the atomic motion is perpendicular to the layer planes and the other in which it is parallel to the layer planes. This latter group can be further sub-divided into longitudinal and transverse components. The scattering of phonons into the same polarisation is relatively easy but the scattering of in-plane states to out-of-plane states and vice versa is dependent on the details of the defect structure, a subject not yet satisfactorily resolved for point defects or small defect groups. It would, for instance, be expected that the scattering would decrease as the temperature falls and the mean phonon wavelength increases. The data apparently show that the opposite is true. Recent studies on irradiated graphite at low measurement temperatures show that this increase in scattering is resonant in form, although the mechanism is unclear. It remains difficult to understand why varying proportions of interstitial and vacancy defects produce the same or closely similar scattering curves, although this may be due to the relative paucity of data at low temperature on graphite irradiated at ambient or higher temperatures. This general area of defect scattering in an anisotropic lattice requires a great deal of work.

There are many calculations of the lattice vibration spectrum of graphite (see Kelly, 1981) but for most purposes the semi-continuum model due to Komatsu (1955, 1958, 1964), Komatsu and Nagamiya (1951) and Nagamiya and Komatsu (1954) is adequate. In this model the basal planes are replaced by elastic sheets, the sheets interacting through forces which resist shear and compression-tension forces. The equations of motion of the layers are readily soluble and lead to the following frequency-wave number relations for the three acoustic modes:

$$\nu_1^2 = V_L^2\left[\sigma_x^2+\sigma_y^2\right] + \left| \frac{\zeta}{\pi^2 d^2} \right| \sin^2\left(\pi d\sigma_z\right)$$

$$\nu_2^2 = V_T^2\left[\sigma_x^2+\sigma_y^2\right] + \left(\frac{\zeta}{\pi^2 d^2} \right) \sin^2\left(\pi d\sigma_z\right) \qquad (4.49)$$

$$\nu_3^2 = 4\pi^2\delta^2\left[\sigma_x^2+\sigma_y^2\right]^2 + \left(\frac{\mu^2}{\pi^2 d^2} \right) \sin^2\left(\pi d\sigma_z\right) + \zeta\left[\sigma_x^2+\sigma_y^2\right]$$

where ν_1 and ν_2 are the in-plane longitudinal and transverse mode frequencies and ν_3 is the frequency of the out-of-plane mode; σ_x, σ_y and σ_z are the wave number components parallel to the principal co-ordinate axes with the *z*-axis parallel to the hexagonal axis; and *d* is the interlayer spacing. The parameters V_L, V_T, μ and ζ are related to the crystal elastic constants as follows:

$$V_L^2 = \frac{C_{11}}{\rho}$$

$$V_T^2 = \frac{1}{2\rho}\left(C_{11} - C_{12}\right)$$

$$\mu^2 = \frac{C_{33}}{\rho} \qquad (4.50)$$

$$\zeta = \frac{C_{44}}{\rho}$$

where the C_{ij} are the usual elastic constants (see Chapter 5). The parameter δ (value 6.11 x 10^{-3} $cm^2.s^{-2}$) is a bond bending resistance in a single layer plane which is characteristic of layer lattices. The unusual dependence of the term containing δ on a wave number is very important for explanation of the properties of graphite. The wave numbers may be written in terms of $\sigma^2_a = \sigma^2_x + \sigma^2_y$ and σ^2_z.

The near two-dimensional nature of the graphite lattice reduces the frequency dependence of the scattering processes compared to the well-understood three dimensional case. For point defects the scattering is dependent on the third power of the frequency rather than the fourth power and for sessile dislocations is frequency independent rather than a first power dependence. Scattering by grain boundaries and extended defects remains describable by a constant mean free path.

Dreyfus and Maynard (1967) considered the effect of an interstitial atom which couples adjacent layer planes, a model which has been proposed by various authors (see Heggie, 1992, for a summary of models). There is a need for further studies of phonon scattering in a highly anisotropic lattice.

Hove (1959) and Deegan (1956) described the effect of annealing on thermal conductivity post-irradiation at low temperatures (~100 K). Their results showed that as annealing proceeds the thermal resistivity decreases and then increases again. This phenomenon also appears in low temperature electron irradiations, showing an inverse annealing peak between 220 and 270 K (Goggin and Reynolds, 1963).

The effect of annealing on thermal resistivity following irradiation at ~30 °C and measured at room temperature has been described (Kinchin, 1956; Woods, Bupp and Fletcher, 1956). Pulse annealing experiments have been described by Hook (1952), and Austerman (1955) has measured the activation energies for annealing using thermal conductivity. In graphite irradiated at ambient temperature to moderate doses the annealing is very similar to the recovery of stored energy, showing a peak in the annealing rate at 200 °C. High dose samples irradiated at 150, 200, 250 and 350 °C show steady annealing with increasing temperature, with an increased rate at high temperatures and complete recovery (in the absence of structural damage) at 1850 °C, the peak temperature tending to be higher for higher total damage.

The effect of annealing on the principal thermal conductivities of highly oriented pyrolytic graphite irradiated at various temperatures between 150 °C and 450 °C was described by Kelly (1969). The annealing is gradual up to 900 °C and then increases, being complete by 1700 °C. The temperature dependence of the principal conductivities was also examined after annealing at various temperatures and the additional thermal resistance determined as a function of temperature. The same unusual temperature dependence was found, simply reduced in magnitude with increasing annealing temperature. It was shown that the changes on annealing were predictable, using the same relationships as those for continuous irradiation with estimated interstitial and vacancy concentrations.

The analysis of irradiation annealing of graphite following irradiations at 150 °C and 225 °C by Gray *et al* (1969) led to the following relationship for Pile Grade A graphite:

$$\frac{K_o}{K} - 1 = 25x_i + 6C_v + 11C_{2v} \tag{4.51}$$

where C_{2v} is the di-vacancy concentration (x_i, C_v and C_{2v} are in units of %), the numerical values being based on the work of Kelly (1967) and Taylor, Kelly and Gilchrist (1969).

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