

CHAPTER 3

DIMENSIONAL CHANGES IN GRAPHITE AND THE THERMAL EXPANSION COEFFICIENT

Irradiation of graphite with energetic neutrons over a range of irradiation conditions leads to dimensional changes of considerable magnitude which must be accommodated in reactor design. The behaviour of graphite is regarded as being that of an aggregate of crystallites (including carbon-carbon composites), generally with identical properties. Irradiation experiments with energetic neutrons have been carried out at temperatures from 5 K to 1700 K. In each case it has been observed that the irradiated graphite crystals grow in the direction perpendicular to the basal planes and contract in the direction parallel to them, although the relative magnitudes of the changes depend upon the exposure conditions.

In a free graphite crystal it is possible to define two distinct measures of dimensional changes. The first is the change in the mean interatomic spacing parallel and perpendicular to the hexagonal axis (denoted by $\Delta d/d$ and $\Delta a/a$ respectively) measured by X-rays (neglecting for the moment the deduction of the appropriate values from the measurements). The second is the change in dimensions of gauge lengths embedded in each crystallite parallel and perpendicular to the hexagonal axis (denoted by $\Delta X_c/X_c$ and $\Delta X_a/X_a$ respectively). These two measures of the dimensional change do not have to be the same. It is found that for all conditions:

$$\frac{\Delta X_c}{X_c} \geq \frac{\Delta d}{d} \quad \text{and} \quad \left| \frac{\Delta X_a}{X_a} \right| \geq \left| \frac{\Delta a}{a} \right|$$

the relationship between the two measures depending upon the type of lattice defects created in the irradiation. The lattice parameter changes can be measured, given sufficient material, but the crystal strains $\Delta X_c/X_c$ and $\Delta X_a/X_a$ can be measured on single crystals or highly oriented pyrolytic graphite samples, or deduced from the dimensional changes of ordinary polycrystalline graphite using a theoretical relationship between the macroscopic and microscopic dimensional changes.

In this chapter measurements of the changes in crystal lattice parameters and crystal strains are reviewed, followed by the dimensional changes observed in polycrystalline graphites subjected to extensive studies. The theory of the relationship between the macroscopic and microscopic changes is then presented and the application of these relations and their verification considered.

Application of X-ray crystallographic methods to the measurement of irradiation damage in graphite was first reviewed by Bacon and Warren (1956) and Bacon (1959,1960). Unirradiated polycrystalline graphites as well as the more perfect crystals and highly oriented pyrolytic graphite show many lines in the diffraction pattern (Fig 3.1). Exposure to neutron irradiation at about ambient temperature results in the diffraction lines becoming fainter and more diffuse until eventually only the $\{0002\}$ and $\{10\bar{1}0\}$ lines can be used for measurement. The centres of the $\{0001\}$ lines are displaced to smaller angles, as illustrated in Fig 3.2, showing that the average interlayer spacing $\Delta d/d$ has increased, while the $\{10\bar{1}0\}$ line is displaced to larger angles, indicating that $\Delta a/a$ has decreased. (θ_0 is the peak unirradiated intensity position, θ_1 the centre of the half-peak-intensity position after irradiation, and θ_2 the

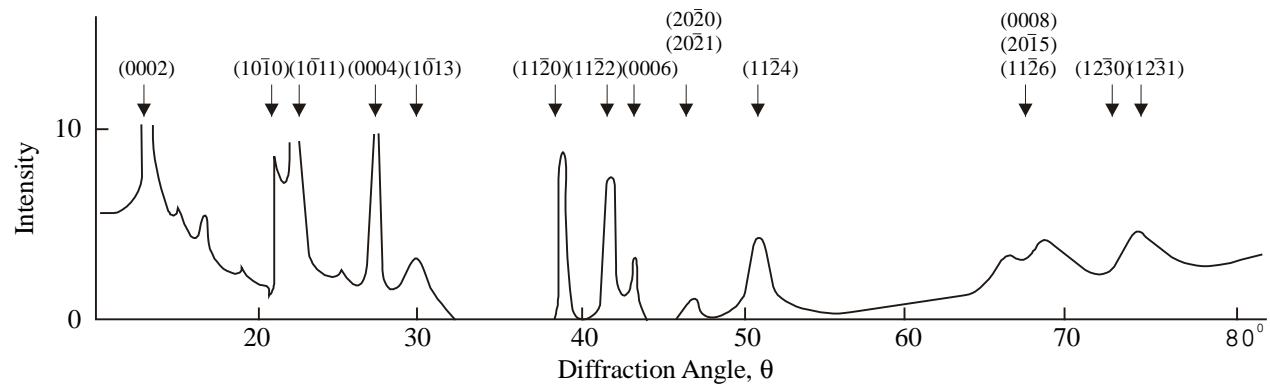


Figure 3.1 X-ray diffraction pattern of artificial graphite in Cu K α radiation

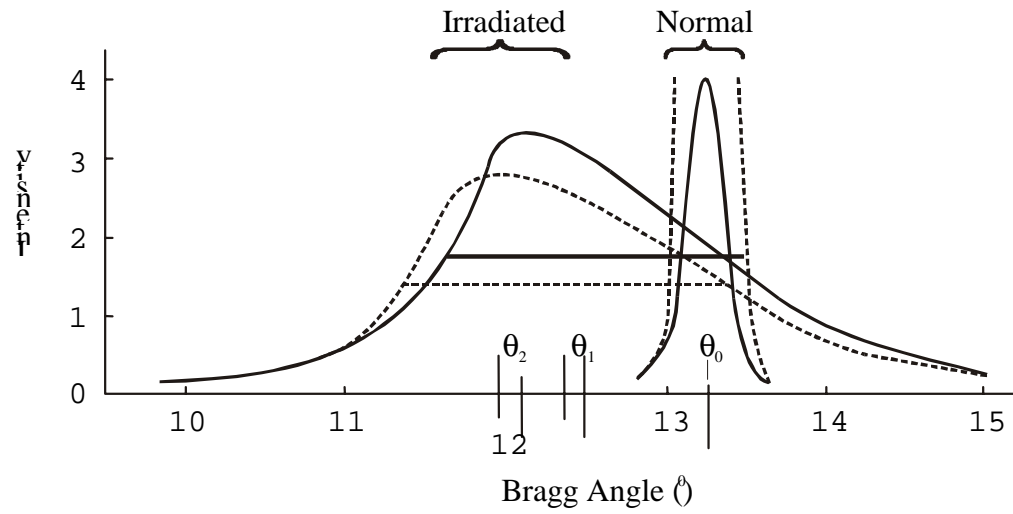


Figure 3.2 {0002} line shapes for normal and heavily irradiated graphites of differing perfections (p=0.20 for solid line, p=0.02 for broken line)

peak intensity position after irradiation.) The lines are very broad and asymmetric at high doses showing that the degree of crystalline order has decreased. Heat treatment of the materials to very high temperature restores the diffraction pattern.

Fundamental studies on a wide variety of properties after irradiation at very low temperatures indicated that, although there was some movement of interstitial atoms below 80 K, there was no significant interstitial-vacancy recombination and thus the number of interstitial atoms is expected to be the same as the number of vacancies. Studies of lattice parameter and dimensional changes at 77 K have been made by Keating (1955), Austerman (1958), Pluchery (1963) and Chinaglia et al (1965). Maeta et al (1975) measured changes in the lattice parameter $\Delta d/d$ following neutron irradiation at 5 K in a fission spectrum. The changes in the d-spacing are not expected to be sensitive to the presence of vacancies and for not too large doses to be proportional to the concentration of interstitial atoms x_i . It was found that the changes in $\Delta d/d$ were linear with dose, for doses up to $3 \times 10^{17} \text{ n.cm}^{-2}$ (instantaneous flux $1.1 \times 10^{13} \text{ n.cm}^{-2}.\text{s}^{-1}$, $E_n > 0.1 \text{ MeV}$), in both virgin and pre-irradiated samples. In this case the volume change of the graphite crystallite is given by

$$\frac{\Delta V}{V} = K x_i + 2 \left| \frac{S_{13}}{S_{33}} \right| \frac{\Delta d}{d} \quad (3.1)$$

where K is a constant and S_{13} and S_{33} are the elastic compliances of the crystal at zero dose. The value of x_i was estimated using essentially the model of Norgett, Robinson and Torrens (see Chapter 1) with a displacement energy of $28 \pm 2 \text{ eV}$, taken from the work of Iwata and Nihira (1971) at 6 K. The calculation leads to $x_i = 0.92 \pm 0.3 \times 10^{-4}$ for a dose of $1 \times 10^{17} \text{ n.cm}^{-2}$ in the fission neutron spectrum. The values of x_i would be reduced by (28/60) using the usual value for E_d of 60 eV. Comparison of the results with the theory using the measured ratio of (S_{13}/S_{33}) of -0.012 leads to $\Delta V/V = 3.3x_i$. Analysis of the thermal expansion coefficients of graphite crystals (Kelly, 1981) leads to a maximum value for (S_{13}/S_{33}) of -0.066, which leads to $\Delta V/V = 3.5x_i$. Significant annealing begins at about 100 K where about 25% of the changes are recovered, thereafter the recovery is steady up to about 400 K where only about 20% of the change remains.

Pluchery (1963), Keating (1955) and Chinaglia et al (1965) measured lattice parameter changes. The lattice parameter changes measured by Pluchery were essentially linear with dose up to a dose of $3 \times 10^{18} \text{ n.cm}^{-2}$. The ratio $(\Delta a/a)/(\Delta d/d)$ was found to be low, ~ -0.1 . Direct measurements of crystal strain by Ayasse and Bonjour (1976) showed that $\Delta X_c/X_c = 1.4\Delta d/d$.

Simmons (1965) and Kelly (1981) have reviewed lattice parameter measurements following irradiation at temperatures from 30 °C to 1050 °C. The changes in $\Delta d/d$ are very large at the lower temperatures, values of up to 15% being recorded (Nightingale, Davidson and Snyder, 1958). The changes in the a-spacing are smaller and the ratio

$$\delta' = \frac{\left| \frac{\Delta a}{a} \right|}{\left(\frac{\Delta d}{d} \right)}$$

varies with dose and irradiation temperature.

Irradiation at temperatures at and below ambient give $d' = -0.09$ approximately, but the distortion of the diffraction pattern quickly becomes too large for accurate determination. The rate of change of $\Delta d/d$ decreases with increasing dose. Detailed data were obtained by Simmons and co-workers for temperatures ≤ 150 °C. The results at 150 °C showed an increase of about 13% in $\Delta d/d$ at a dose of 1.6×10^{21} n.cm⁻² (EDN) and it was still increasing at a reducing rate. Data taken in the same series of experiments at 200 °C showed changes in $\Delta d/d$ of similar magnitude but taking place more slowly, however the dose dependence was clearly sigmoid. The change $\Delta d/d$ saturates at ~8%, accompanied by a change in $\Delta a/a$ of about -2% at a dose of 2.5×10^{21} n.cm⁻² (EDN). The results at higher temperatures show saturating changes with dose for both $\Delta d/d$ and $\Delta a/a$, the saturation levels decreasing with increasing irradiation temperature, but with the ratio d' decreasing (magnitude increasing) to about -0.6 at 500 °C and then reaching a peak at irradiation temperatures between 1000 °C and 1200 °C.

The analysis of line widths and shapes in terms of the distribution of lattice parameters in irradiated graphite has not made significant progress since the early work of Chipman and Warren (1952), Warren and Chipman (1953) and Austin and Harrison (1959). Figs 3.3 and 3.4 summarise the results for mean lattice parameter changes with dose.

In a direct analogy with the theory of thermal expansion the presence of crystal lattice defects can be represented as a source of internal pressure, that is

$$\frac{\Delta d}{d} = S_{33}P_c + 2S_{13}P_a \quad (3.2)$$

$$\frac{\Delta a}{a} = (S_{11} + S_{12})P_a + S_{13}P_c$$

where the S_{ij} are the usual crystal elastic compliances and P_a and P_c are the internal pressures acting parallel and perpendicular to the basal planes. Analyses have been given by Temkin (1970) and Stoneham (1973).

Stoneham considers a block of material with flat orthogonal surfaces. The insertion of an anisotropic defect which produces forces F_i on the lattice atom i distorts the crystal. If the crystal has hexagonal symmetry with the hexagonal axis parallel to one of the cube edges, then it is possible to apply the Betti reciprocity theorem (assuming harmonic forces). Applied external forces P produce displacements U in the solid, while in the absence of applied forces the defect forces F produce surface displacements d_l normal to surfaces l . The reciprocity theorem gives

$$P_l \cdot \delta_l = F_i \cdot U_i \quad (3.3)$$

If the stresses P are assumed uniform over the surfaces then only mean displacements apply to the left hand side of equation (3.3). The right hand side may be evaluated for various F representing interstitial and vacancy defects.

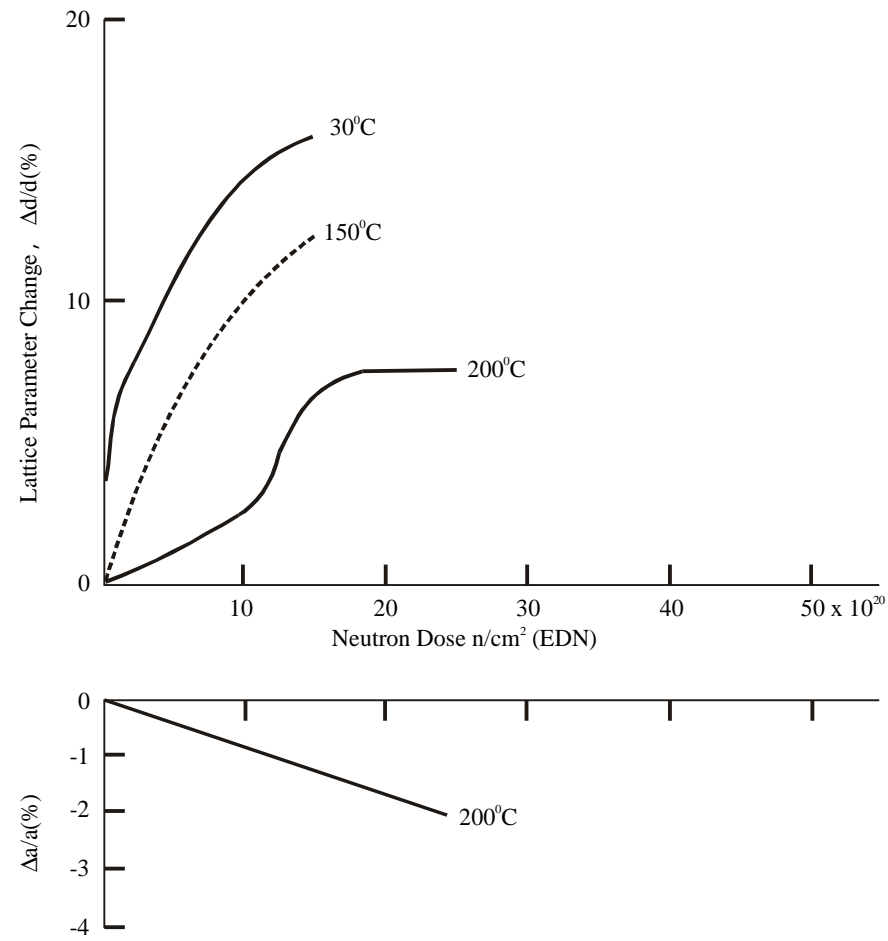


Figure 3.3 Lattice parameter changes in low temperature irradiations

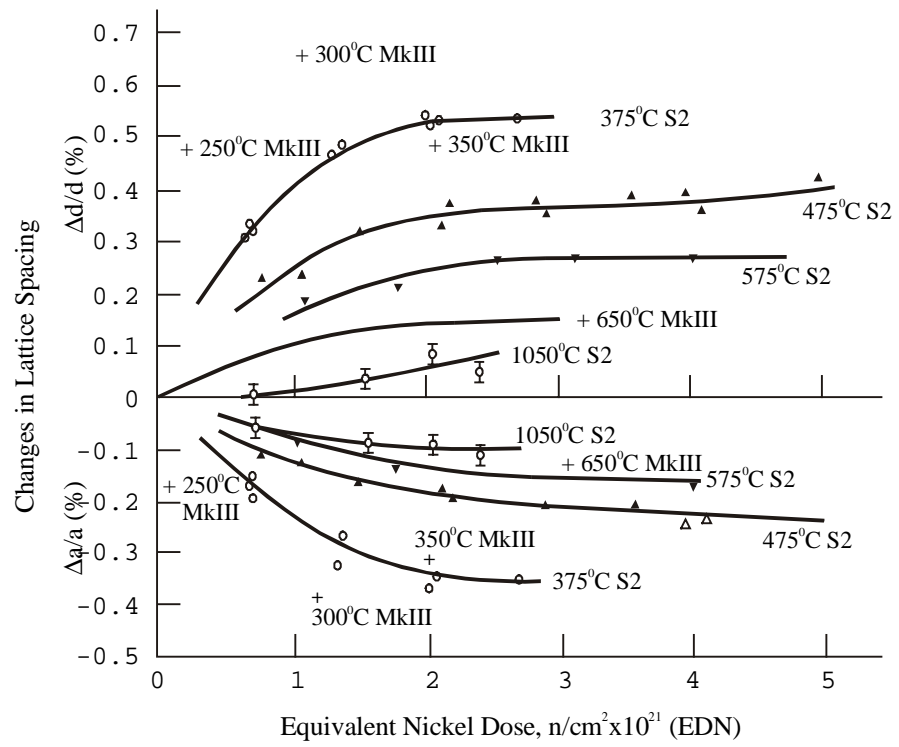


Figure 3.4 Lattice parameter changes in MTR irradiations

The analysis of lattice parameter changes in irradiation experiments between 150 °C and 650 °C for doses up to 5×10^{21} n.cm⁻² (EDN) assumes:

- (i) Small interstitial groups of $\sim 4 \pm 2$ atoms, as derived from neutron scattering experiments by Martin and Henson (1964, 1967), produce lattice parameter changes $\Delta d/d$.
- (ii) Small uncollapsed vacancy groups contribute to the basal lattice parameter changes $\Delta a/a$.
- (iii) Interstitial loops do not contribute to the lattice parameter changes.
- (iv) Collapsed vacancy lines do not contribute to lattice parameter changes.

Equation (3.2) can be written

$$\frac{\Delta d}{d} = K_i x_i + \frac{K_v c_v}{\sigma_v} \quad (3.4)$$

$$\frac{\Delta a}{a} = K_i \sigma_i x_i + K_v c_v$$

where x_i and c_v are the interstitial and uncollapsed vacancy concentrations, K_i and K_v are "effectiveness" factors for the interstitial and vacancy, and

$$\sigma_i = \frac{(S_{11} + S_{12}) P_{ai} + S_{13} P_{ci}}{S_{33} P_{ci} + 2S_{13} P_{ai}} \quad (3.5)$$

$$\sigma_v = \frac{(S_{11} + S_{12}) P_{av} + S_{13} P_{cv}}{S_{33} P_{cv} + 2S_{13} P_{av}}$$

These equations imply that

$$K_i x_i = S_{33} P_{ci} + 2S_{13} P_{ai} \quad (3.6)$$

$$K_v c_v = (S_{11} + S_{12}) P_{av} + S_{13} P_{cv}$$

For an irradiation in which $x_i = c_v$, as might be appropriate for low temperature and low dose irradiations, $d' = s_i$.

Earlier work by Kelly (1972) had shown that $(S_{11} + S_{12}) P_{av} \sim -0.14c_v$ and $S_{33} P_{ci} \sim 1 - 5x_i$, suggesting that $K_i \gg K_v$. Pluchery's data showed that $d' = -0.086$, which is close to the value for $s_i = S_{13}/S_{33}$ of -0.075 due to Spence (1963) and -0.066 due to Kelly and Walker (1970) and Morgan (1972). Henson and Reynolds (1965) thus assumed $P_{ai} \ll P_{ci}$ and therefore

$$K_i x_i = S_{33} P_{ci} \quad (3.7)$$

The values of d' obtained varied from -0.25 to -0.47 which implies that P_{cv} cannot be neglected, contradicting the assumption made by Kelly that $P_{cv} = 0$. A value of $s_2 = -0.56$ was

obtained which gave $K_v = -0.11$. The concentrations of defects can then be estimated from the equations

$$x_i = \frac{1}{0.865K_i} \left| \frac{\Delta d}{d} + 1.8 \frac{\Delta a}{a} \right|$$

$$c_v = \frac{1}{0.865K_v} \left[\frac{\Delta a}{a} + 0.075 \frac{\Delta d}{d} \right]$$
(3.8)

The concentrations of defects calculated from these changes are compatible with those obtained by other methods, but there are some changes in interpretation. A comparison with the stored energy in the graphite shows that the apparent energy per vacancy decreases with increasing concentration, from 7 eV to 1 eV. Henson, Perks and Simmons (1968) showed that the derived concentrations of vacancies would lead to excessive concentrations of collapsed vacancy lines. Both observations can be rationalised to some degree by assuming that the collapsed vacancy lines do cause lattice parameter changes (negative) and thus the observed changes in $\Delta a/a$ contain contributions from point vacancies and vacancy lines. If this is the case the interpretation of other property changes, such as thermal conductivity, must also be modified.

The first attempt to compare the crystal lattice parameter changes observed by X-rays with the direct dimensional changes of the crystals was made by Simmons (1959) who obtained a relationship between the unirradiated thermal expansion coefficients of a series of graphites and the initial rates of dimensional change on irradiation at temperatures of 30, 80 and 180 °C. Simmons obtained a theoretical relationship between the thermal expansion coefficient and the dimensional change rate (following earlier attempts, summarised by Kelly, 1981) as follows:

Dimensional change rate with dose in direction x:

$$\frac{dG_x}{d\gamma} = A_x \frac{1}{X_c} \frac{dX_c}{d\gamma} + (1 - A_x) \frac{1}{X_a} \frac{dX_a}{d\gamma}$$
(3.9)

Thermal expansion coefficient in direction x:

$$\alpha_x = A_x \alpha_c + (1 - A_x) \alpha_a$$
(3.10)

Given the thermal expansion coefficients of the graphite crystal ($\alpha_c = 26 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_a = -1.1 \times 10^{-6} \text{ K}^{-1}$) and data for two directions x which give significantly different changes and expansion coefficients, then equations (3.9) and (3.10) become four simultaneous equations which can be solved for the two rates of crystal dimensional change. Good agreement was found between the X-ray lattice parameter changes and the changes calculated from equations (3.9) and (3.10). Bridge, Kelly and Gray (1962) carried out a similar study on samples of polycrystalline graphite irradiated at Hanford over a range of irradiation temperatures from 30-306 °C. The application of equations (3.9) and (3.10) to the two

directions of Pile Grade A graphite again led to values of $\Delta d/d$ and $\Delta a/a$ in good agreement with $\Delta X_c/X_c$ and $\Delta X_a/X_a$ respectively.

In this review it is assumed, following Kelly, Martin and Nettley (1966a), Yoshikawa (1964) and Price (1974), that the dimensional changes of graphite crystallites can be observed directly on highly oriented pyrolytic graphite or on crystal flakes. Measurements of the thermal expansion coefficients of pyrolytic graphite parallel and perpendicular to the deposition plane correspond closely with those of single crystals and thus reflect strains parallel and perpendicular to the basal planes of the component crystallites. The perfection of the crystallite size can be varied by changing the final heat treatment temperature from ~2200 °C, the deposition temperature, to 3600 °C. Materials of this type were included in irradiation experiments at 150, 170, 200, 250, 300, 350, 450 and 650 °C by Kelly, Martin and Nettley (1966a) who measured the dimensional changes parallel and perpendicular to the deposition plane, together with the principal thermal expansion coefficients. The results are summarised in Figs 3.5 and 3.6.

The crystal dimensional changes $\Delta X_a/X_a$ parallel to the deposition plane (negative) and $\Delta X_c/X_c$ perpendicular to the deposition plane (positive) show a sigmoidal dependence on dose for the irradiations at temperatures below 300 °C, but at the higher temperatures the changes are essentially parabolic. The lower temperature data show large volume changes at low doses, but the results at the higher temperatures show dimensional changes at constant volume. It is appropriate to define a parameter

$$\delta = \frac{\frac{1}{X_a} \frac{dX_a}{d\gamma}}{\frac{1}{X_c} \frac{dX_c}{d\gamma}} \quad (3.11)$$

which can vary with dose and temperature. In the low temperature irradiations δ is low at low doses and increases with dose to a value of -0.5, corresponding to changes at constant volume. The irradiations at higher temperatures take place at essentially constant volume, except for a very low dose period.

The irradiations of highly oriented pyrolytic graphite were extended to very high doses by Kelly and Brocklehurst (1971) and more detailed results at temperatures of 430 and 600 °C on samples heat treated to different final temperatures, and hence crystal sizes, presented by Brocklehurst and Kelly (1993a). The results showed that the dimensional changes were insensitive to the crystal size for irradiation below 600 °C, but increased with decreasing crystal size at higher temperatures. The earlier observation that the change at ~400 °C took place at constant volume was confirmed, but at 600 °C a small continuous volume increase was observed. Figs 3.7 and 3.8 illustrate these results.

Price (1974) exposed highly oriented pyrolytic graphite of varying perfection at 1300 - 1500 °C and again found that the changes were larger in the less perfect materials. Table III.1 shows values of the parameter δ obtained in the higher temperature irradiations where it remains constant as a function of dose.

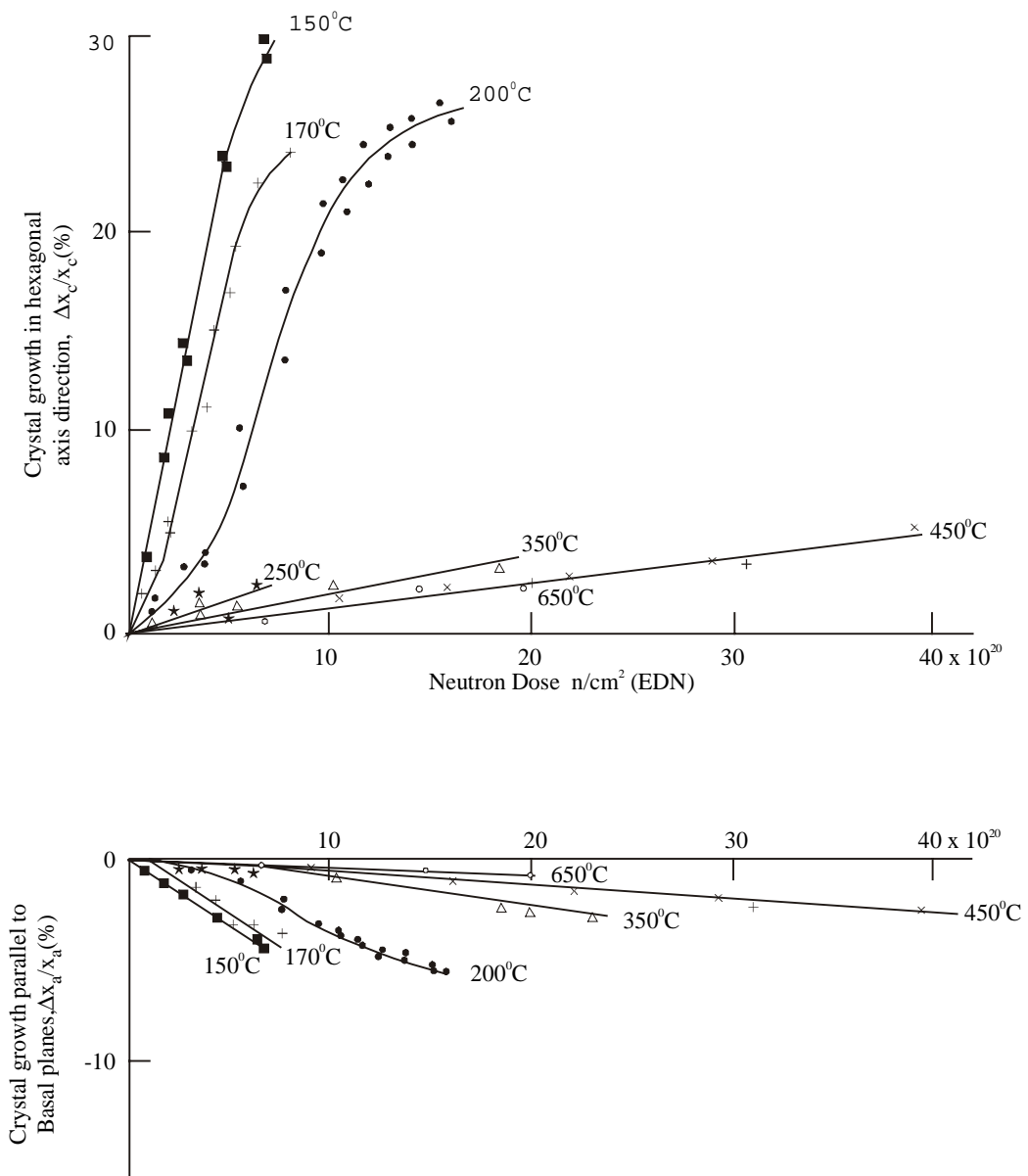


Figure 3.5 Dimensional changes of pyrolytic graphite:low temperature

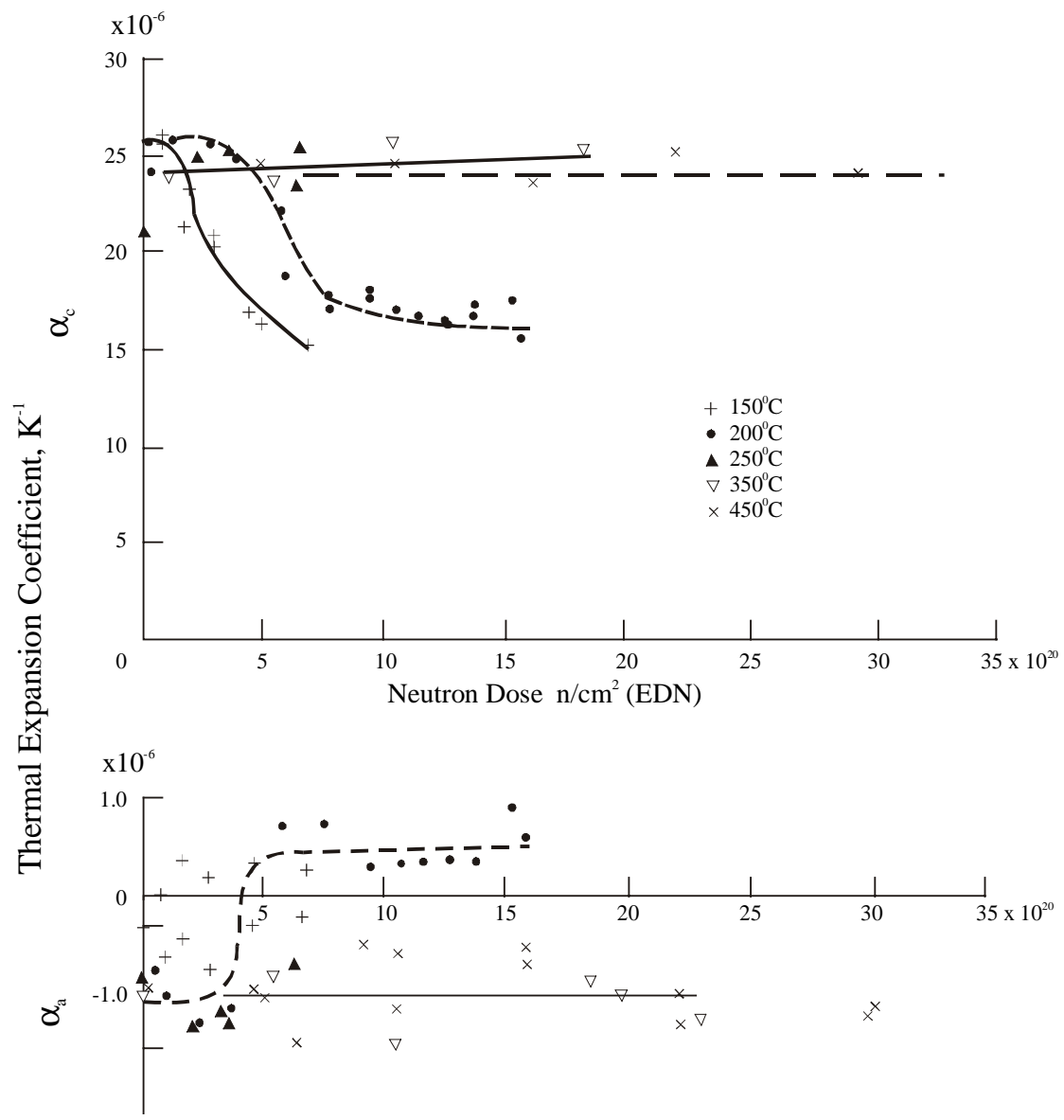


Figure 3.6 Principal thermal expansion coefficients of highly irradiated oriented pyrolytic graphite

TABLE 3.1. VALUES OF d OBSERVED IN HIGH TEMPERATURE IRRADIATIONS

Irradiation Temperature °C	Heat treatment temperature °C	d
430	2800	-0.50
600	2800	-0.47
	2000 (as deposited)	-0.49
	2000 (HTT)	-0.49
600 800 900 1000 1100 1200 1350	3000 - 3300	-0.4
		-0.2
		-0.3
		-0.4
		-0.4
		-0.4
		-0.35

The irradiations below 300 °C, where d varies with dose beginning at a low value characteristic of point defects and then increasing to the constant volume condition similar to the high temperature experiments, also show large changes in the principal thermal expansion coefficients which correspond closely with a_c and a_a . The expansion coefficient perpendicular to the deposition plane shows a decrease from $\sim 26 \times 10^{-6} \text{ K}^{-1}$ to $\sim 14 \times 10^{-6} \text{ K}^{-1}$ while the coefficient parallel to the deposition plane increases from a small negative value to a small positive value.

A comparison of the X-ray crystal lattice parameters with the direct measurements of crystal dimensional changes shows that they agree well at low doses, but the latter are larger as the dose increases. For irradiations at temperatures greater than 300 °C the lattice parameter changes saturate while the crystal dimensional changes continue at least linearly with dose.

The changes in the crystal thermal expansion coefficients are apparently correlated with the changes in crystal lattice parameters, a_c decreasing when $\Delta d/d$ exceeds about 5% and ceasing when the changes stop (observed in irradiations at 200 °C). In irradiations at temperatures greater than 300 °C the lattice parameter changes are small and thus a_c and a_a do not change. The expansion $\Delta d/d$ may be assumed to absorb the "out-of-plane" lattice vibration amplitudes which are responsible for a_c (see Kelly, 1981). The expansion coefficient a_a consists of two parts, one positive and one negative. The latter is due to the Poisson's ratio effect of the large expansion perpendicular to the layers and may also contain another negative contribution due to anharmonicity (Kelly and Walker, 1970; Harrison, 1977). The increase in the interlayer spacing eventually decouples the layer planes and permits the positive terms which are insensitive to the d -spacing to dominate.

The dimensional changes of polycrystalline graphite, which is an aggregate of crystallites with varying degrees of orientation, are a complicated mixture of the crystallite changes and porosity changes. In irradiations at constant temperature a number of authors have observed a linear correlation between the initial rates of dimensional change and the unirradiated thermal expansion coefficient (see Simmons, 1965). This relationship extends, for irradiations below ~ 600 °C, from the extreme growth of highly oriented pyrolytic graphite

perpendicular to the deposition plane to contraction parallel to the deposition plane. Other graphites have intermediate thermal expansion coefficients and intermediate dimensional changes, either positive or negative. The correlation is different at each irradiation temperature (see Simmons, 1965, for the correlations obtained at 30, 80 and 180 °C). Experimentally, at each temperature the rate of dimensional change with respect to dose is given by

$$\frac{dG_x}{d\gamma} = A\alpha_x + B \quad (3.12)$$

At each temperature there is a value of α_x for which the graphite is dimensionally stable and this observation was used to specify graphites with improved dimensional behaviour for use in the United Kingdom Advanced Gas-cooled Reactors (UKAEA, 1965; Hutcheon, 1966). Equations (3.9) and (3.10) may be combined by eliminating the parameter A_x to yield

$$\begin{aligned} \frac{dG_x}{d\gamma} &= \frac{(\alpha_x - \alpha_a)}{(\alpha_c - \alpha_a)} \left| \frac{1}{X_c} \frac{dX_c}{d\gamma} - \frac{1}{X_a} \frac{dX_a}{d\gamma} \right| + \frac{1}{X_a} \frac{dX_a}{d\gamma} \quad (3.13) \\ &= A\alpha_x + B \quad \text{as required} \end{aligned}$$

Equation (3.12) requires that all graphite crystallites behave the same way under the same irradiation conditions. The pyrolytic graphite data show that this is true for irradiations below 600 °C but not at higher temperatures. In higher temperature irradiations the crystallite dimensional changes increase with decreasing crystallite size and so equation (3.12) is not satisfied.

The relationship between the rate of dimensional change and the thermal expansion coefficients was examined for several graphites at 170 and 200 °C, by Kelly, Martin and Nettley (1966b). Given that the pyrolytic data give the rates of crystal dimensional change and thermal expansion coefficients it was shown that the values of A_x were the same for both up to a critical dose g^* after which the value of A_x for dimensional changes becomes larger than for thermal expansion. Detailed analysis of the data on one graphite, Pile Grade A, together with measurements of the density of ground up samples showed that the difference was due to the generation of new pore space which was interpreted as an apparent increase in A_x in equation (3.9). Because of this an additional positive term was added to the macroscopic dimensional changes. Pile Grade A graphite shows (Table 2.1) an anisotropy of around 2 to 1 in properties and the pore generation term in the graphite proves to have the same anisotropy, the effect being larger perpendicular to extrusion.

A large volume of data has been accumulated on a few nuclear graphites over a very wide range of irradiation temperatures. In the United Kingdom, Pile Grade A graphite used in the Magnox Reactor power stations and two near identical grades of Gilsonite coke-based graphites used in the later Advanced Gas-cooled Reactors. In the United States the CSF grade, closely similar to Pile Grade A, has also been irradiated over a wide range of temperatures. Henson et al (1968) reported data on Pile Grade A graphite at temperatures from 300 - 1350 °C, obtained in the PLUTO and DIDO reactors at Harwell, and using the very high fluxes in the Dounreay Fast

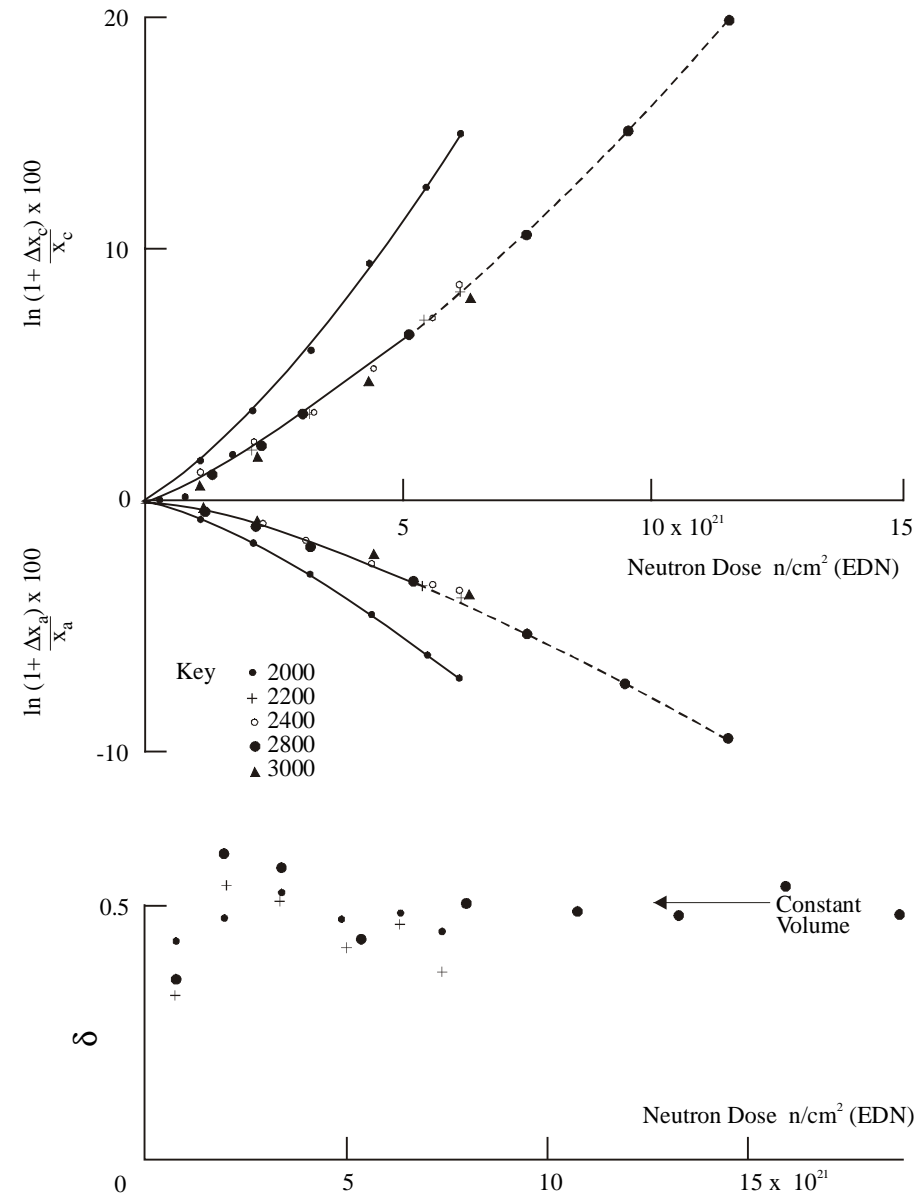


Figure 3.7 Dimensional changes of highly oriented pyrolytic graphite irradiated at 430°C for different heat treatment temperatures

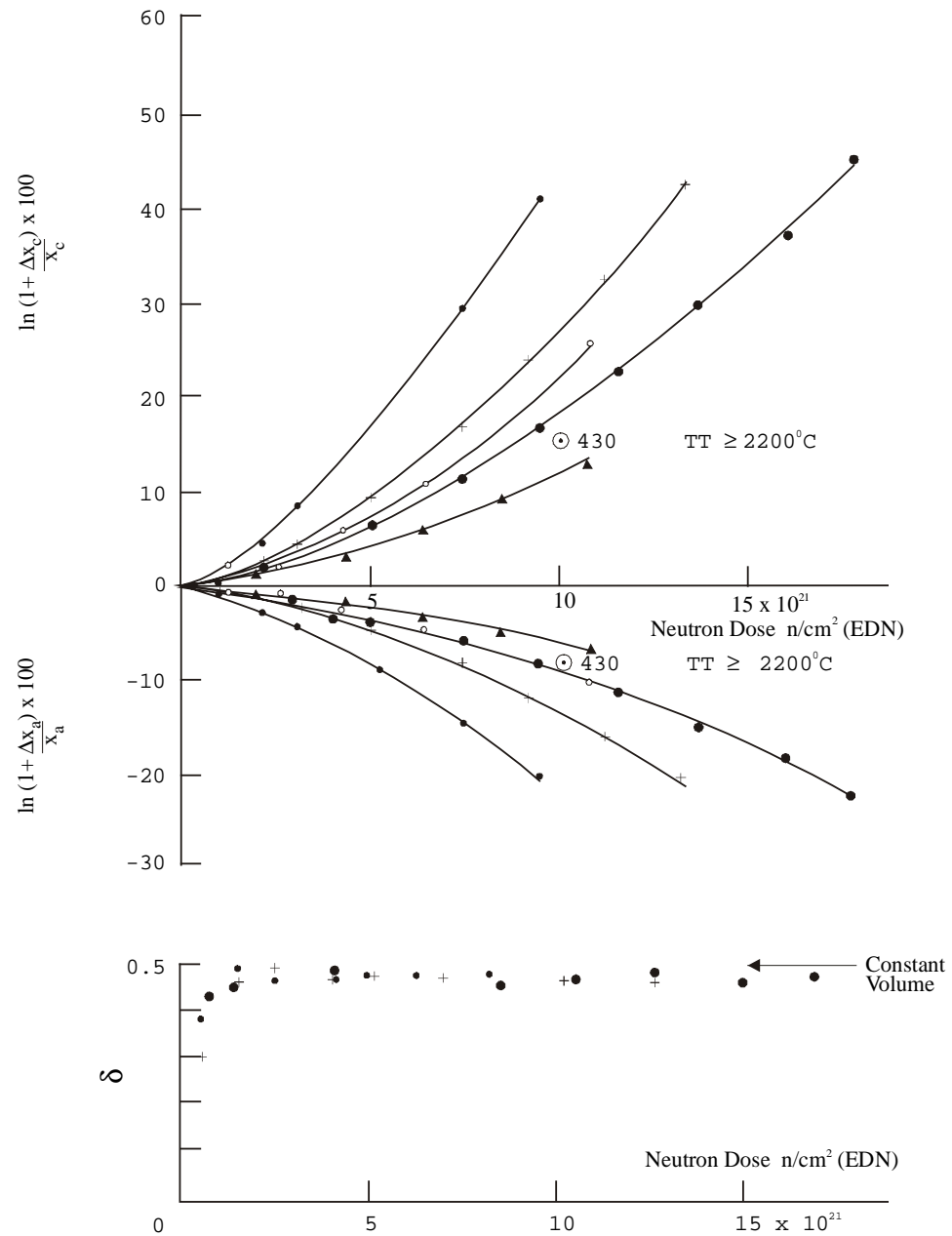


Figure 3.8 Dimensional changes of highly oriented pyrolytic graphite irradiated at 600°C for different heat treatment temperatures

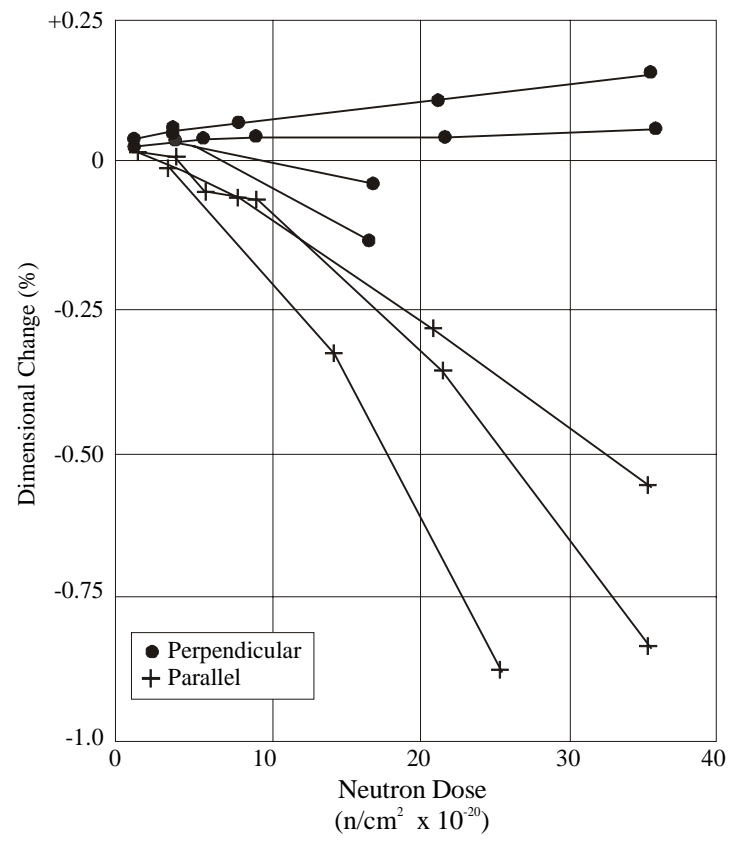


Figure 3.9 Dimentional changes of PGA graphite irradiated at 900°C in PLUTO

Reactor. These results are shown in Figs 3.9 - 3.13. Gray and Pitner (1971) reported data on CSF graphite irradiated in the GETR, shown in Fig 3.14. The high temperature irradiations were extended to higher doses and tabulated by Morgan and Gray (1972).

The dimensional changes of Pile Grade A graphite and CSF graphite are very similar. At low temperatures ($< 300\text{ }^{\circ}\text{C}$) the direction perpendicular to extrusion shows growth with the growth rate increasing with decreasing temperature, whilst the direction parallel to extrusion shows high shrinkage. The data at high temperatures show a smaller shrinkage parallel to extrusion, but perpendicular to extrusion there is an initial shrinkage which changes to growth, the change occurring at lower doses the higher the irradiation temperature.

The thermal expansion behaviour of Pile Grade A graphite is complicated. Irradiation at the lower temperatures shows, for both directions relative to extrusion, an increase followed by a decrease. At the higher irradiation temperatures the thermal expansion coefficient shows an increase in the perpendicular to extrusion direction in two stages, the first when the crystallite parameter $\Delta X_c/X_c$ reaches a value of about 5% (Simmons and Reynolds, 1962). This is interpreted as the closure, by the crystallite dimensional changes, of the cracks parallel to the basal planes created on cooling from the final heat treatment temperature and which can be directly observed (Thrower and Reynolds, 1963). These cracks, which have been postulated to be responsible for the difference between the volume thermal expansion coefficient of polycrystalline graphite and single crystal graphite, are known as Mrozowski cracks (Mrozowski, 1956). The large increase at high doses brings the volume expansion coefficient of the graphite close to that of a single crystal in spite of being accompanied by a large volume expansion due to pore generation. This has not been explained.

Brocklehurst and Kelly (1993a, 1993b) have presented data from irradiations at $600\text{ }^{\circ}\text{C}$ on Pile Grade A graphite heat treated to different final temperatures and also doped with boron to accelerate the damage rate and hence the dimensional changes. The irradiations included highly oriented pyrolytic graphite heat treated to different final temperatures to provide crystal dimensional changes. Detailed thermal expansion measurements were made on the Pile Grade A graphite in both directions relative to extrusion. The heat treatment series showed that the maximum volume shrinkage was independent of the heat treatment (ie degree of perfection). The maximum volume change of the boron-doped samples decreased with increasing boron content indicating an increasing crystal volume change; the expected acceleration of the damage was obtained.

The dimensional changes of an isotropic Gilsocarbon graphite irradiated at temperatures between 430 and $600\text{ }^{\circ}\text{C}$ are shown in Fig 3.15. Very similar results were obtained (see Brocklehurst, 1984) on a pitch coke graphite known as VQMB. Brocklehurst and Kelly (1993b) presented data on Gilsocarbon graphite doped with two levels of boron-11. The maximum volume changes were less the higher the boron content, as observed in Pile Grade A graphite, but the volume changes at $430\text{ }^{\circ}\text{C}$ were greater than those at $600\text{ }^{\circ}\text{C}$. The initially relatively high thermal expansion coefficient was found to decrease to a considerably lower value.

Data on the fine grained isotropic POCO graphite grades have been summarised by Kelly (1989). The behaviour of grades AXZ-5Q1 and AXF-8Q1 is summarised in Figs 3.16 -

3.19. These graphites are unusual in showing volume growth or a high degree of stability at most irradiation temperatures. The initially high thermal expansion coefficients fall to very low values at each irradiation temperature. There does not appear to be any low temperature data but large growths would be expected on the basis of the thermal expansion coefficients.

GRAPHNOL N3M is, as already noted, a fine grain graphite developed for aerospace and fusion reactor applications. It has a high strength and strain to failure but a lower thermal expansion coefficient than the POCO grades to give an improved thermal shock resistance. It is finally heat treated at temperatures greater than 3000 °C and is well graphitised and pure. The dimensional changes under irradiation have been examined at temperatures of 600 °C and 875 °C by Burchell and Eatherly (1991). The behaviour is similar to other isotropic graphites, showing a linear contraction of 2 - 3%, followed by expansion and a large decrease in thermal expansion coefficient at high dose.

Theory of Dimensional Changes in Irradiated Graphite

The theory of dimensional changes in irradiated graphite was originally developed to understand the relationship between crystal dimensional changes and macroscopic dimensional changes and thus to permit the specification of graphites with improved behaviour. A number of authors suggested that a relationship

$$\alpha_x = A \alpha_c + B \alpha_a \quad (3.14)$$

where A and B are constants (see Kelly, 1981, for a detailed review) existed between the thermal expansion in direction x of a polycrystal and the principal expansion coefficients of a graphite crystal. Simple models, such as a mechanical stack of crystallites, give $A + B = 1$. This relationship also holds for a non-porous body. Simmons (1965) showed that it could be shown thermodynamically that

$$\alpha_x = A_x \alpha_c + (1 - A_x) \alpha_a \quad (3.15)$$

and that the same relationship could be extended to dimensional changes using the relationship

$$\frac{dG_x}{d\gamma} = \frac{\partial^2 F}{\partial \gamma \cdot \partial T_{xx}} = A_x \frac{1}{X_c} \frac{dX_c}{d\gamma} + (1 - A_x) \frac{1}{X_a} \frac{dX_a}{d\gamma} \quad (3.16)$$

where F is the free energy per unit volume and T_{xx} is a component of the macroscopic stress tensor.

In spite of the proof given by Simmons, this relationship is still not completely accepted. Kelly, Martin and Nettley (1966b) showed that this relationship broke down above a critical dose g^* which depended on the graphite and the irradiation temperature. The generation of new pore space can be included in equation (3.16) by adding a term f_x . Equation (3.15) for thermal expansion is unchanged. Removal of the A_x term leads to

$$\frac{dG_x}{d\gamma} = \left| \frac{\alpha_x - \alpha_a}{\alpha_c - \alpha_a} \right| \left(\frac{1}{X_c} \frac{dX_c}{d\gamma} - \frac{1}{X_a} \frac{dX_a}{d\gamma} \right) + \frac{1}{X_a} \frac{dX_a}{d\gamma} + f_x \quad (3.17)$$

or

$$\frac{dG_x}{d\gamma} = \left| \frac{\alpha_x - \alpha_a}{\alpha_c - \alpha_a} \right| \frac{dX_T}{d\gamma} + \frac{1}{X_a} \frac{dX_a}{d\gamma} + f_x \quad (3.18)$$

where

$$X_T = \frac{\Delta X_c}{X_c} - \frac{\Delta X_a}{X_a} \quad (3.19)$$

Modelling of the internal processes in polycrystalline graphites suggested (Perks and Simmons, 1966) that the dimensional changes should depend on $dX_T/d\gamma$ as well as X_T . However Kelly, Martin and Nettley (1966b) proposed that the structure dependent factors in equation (3.18), α_x and f_x , depend only on X_T .

Equation (3.18) may be written in the form

$$G_x = A_x(X_T) \frac{dX_T}{d\gamma} + \frac{\Delta X_a}{X_a} + F_x(X_T) \quad (3.20)$$

where

$$F_x = f_x d\gamma$$

This equation can be applied to the two directions relative to the extrusion direction and then used to show that it should be possible to obtain two unique functions of X_T from the experimental data:

$$f_1(X_T) = G_{\perp} - G_{\parallel} = (A_{\perp} - A_{\parallel}) \frac{dX_T}{d\gamma} + (F_{\perp} - F_{\parallel}) \quad (3.21)$$

$$f_2(X_T) = 2G_{\perp} + G_{\parallel} - 3\frac{\Delta X_a}{X_a} = (2A_{\perp} + A_{\parallel}) \frac{dX_T}{d\gamma} + (2F_{\perp} + F_{\parallel})$$

The parameter X_T can be obtained, together with $\Delta X_a/X_a$, from simultaneous irradiations of pyrolytic graphite. Brocklehurst and Kelly (1993b) have shown that for Pile Grade A graphite the two functions $f_1(X_T)$ and $f_2(X_T)$ are the same for irradiations at 200 °C and 600 °C, although the macroscopic dimensional change behaviour is quite different, that is a volume expansion at the lower temperature and a volume contraction followed by expansion at the higher temperature. The analysis of the higher temperature data extends well into the pore

generation regime and thus accords with the idea of dependence on X_T only. A change in the final heat treatment temperature of the Pile Grade A graphite modifies the dimensional changes as a function of dose at 600 °C substantially, but the two functions of X_T are unchanged, essentially demonstrating that the terms F_x depend principally upon X_T and weakly, if at all, on dX_T/dg .

For an isotropic graphite $f_1(X_T)$ is zero. The equation for $f_2(X_T)$ may be written as

$$f_2(X_T) = \frac{\Delta V}{V} - 3 \frac{\Delta X_a}{X_a} = 3 A_x \frac{dX_T}{d\gamma} d\gamma + F_v \quad (3.22)$$

where $\Delta V/V$ is the bulk volume change of the graphite and F_v is the pore volume generated. Equation (3.22) can be re-written in the form

$$\begin{aligned} f_2(X_T) &= \frac{\Delta V}{V} - \left| \frac{\Delta X_c}{X_c} + 2 \frac{\Delta X_a}{X_a} \right| + \left(\frac{\Delta X_c}{X_c} - \frac{\Delta X_a}{X_a} \right) \\ &= \frac{\Delta V}{V} - \frac{\Delta V_c}{V_c} + X_T \end{aligned} \quad (3.23)$$

where $\Delta V_c/V_c$ is the volume change of the crystallites. Re-arranging equation (3.23) leads to

$$\frac{\Delta V}{V} = \Phi(X_T) + \frac{\Delta V_c}{V_c} \quad (3.24)$$

This equation is useful because if dimensional change data are available at an irradiated temperature of 400-450 °C then $\Delta V_c/V_c$ is approximately zero and $\Delta V/V$ is a unique function of X_T identical to $F(X_T)$. Given $\Delta V_c/V_c$ for other conditions it is then possible to predict $\Delta V/V$. Calculations of this kind have been made by Kelly and Burchell (1994) assuming that the ratio d (equation (3.11)) is constant with dose at a given irradiation temperature.

It is possible to analyse data taken at irradiation temperatures greater than 600 °C where the crystallite dimensional changes depend upon their perfection (provided that all crystallites in the material behave the same). It has not been established that a single parameter which can be measured pre-irradiation, such as L_a , determines the dimensional changes under irradiation, and it is uncertain whether d is independent of dose. The crystal volume change, if d is constant, can be written

$$\frac{\Delta V_c}{V_c} = \frac{\Delta X_c}{X_c} + 2 \frac{\Delta X_a}{X_a} = X_T \left| \frac{1+2\delta}{1-\delta} \right| \quad (3.25)$$

and then, given $F(X_T)$, curves of $\Delta V/V$ as a function of X_T can be constructed. Each curve of this type has two well defined points: the first the value of X_T for which

$$\frac{1}{V} \frac{dV}{dX_T} = 0$$

and the second the value of X_T at which $\Delta V/V = 0$, determined from the calculated curves.

The assumption of constant d is not valid for irradiations below 300 °C, but it does appear to be reasonable for higher temperature irradiations (Brocklehurst and Kelly, 1993a).

Simmons (private communication, 1991) has made two more recent analyses of the relationship between crystal dimensional changes and macroscopic dimensional changes in order to extend his earlier theory to higher doses (and hence pore generation). The first method is based on a stress analysis of a polycrystal including the presence of irradiation creep in basal slip. This analysis leads to the standard relationship for the thermal expansion coefficient, but shows that a further term must be added to equation (3.10) as postulated, but related to the irradiation creep in basal shear. The second model, based on a Fourier transform of stress, leads to similar conclusions.

The inherent simplicity of the atomic displacement process in graphite, which may be treated approximately as if individual atoms are displaced at random, has stimulated attempts to calculate the concentrations of individual lattice defects and hence property and dimensional changes. The calculations, in parallel with the data, are rather different for irradiation temperatures below 300 °C, where large crystal volume changes occur, than those at higher temperatures where they do not.

The most comprehensive attempt to model the data at low temperatures was made by Woolley (1963), subsequently modified by Horner and Williamson (1966), while modelling of the higher temperature behaviour was undertaken by Kelly, Martin and Nettley (1966a) following analysis of the growth of interstitial dislocation loops in graphite by Lidiard and Perrin (1966). The Woolley model assumed that the damage can be described as single immobile vacancies, small mobile interstitial groups and larger sessile interstitial clusters assumed to occur at random in space and time, which correspond to the processes of recombination, nucleation and cluster growth respectively. (The phenomenon of irradiation annealing is omitted - this is the process of distribution of suitably sized interstitial groups by displacement collisions.) In order to explain the very large contractions parallel to the basal planes exceeding the changes in the nearest neighbour spacing $\Delta a/a$, Kelly, Martin and Nettley (1966a) introduced the concept of the collapsed vacancy lines created by random displacement sequences which prevented interstitial-vacancy recombination. This effect was incorporated into the Woolley model by Horner and Williamson and similar modifications were made by and Lidiard and Perrin. The effect of the vacancy collapse was to accelerate the accumulation of interstitials, which since they lead to the growth e_{zz} parallel to the hexagonal axis and the accompanying lattice parameter changes $\Delta d/d$ improve agreement with experiment. The basal plane contraction also accelerates. Comparison with the crystal dimensional changes showed good agreement, given appropriate proportionality between concentrations and dimensional changes. However, as we shall see, the Woolley model gives much larger concentrations of sessile interstitial clusters ($\times 10$) than observed in the electron microscope.

The other models assume two types of interstitial group can be formed from the initially displaced atoms. The first, later identified as consisting of 4 ± 2 atoms, ceases to grow once a particular configuration is achieved; and the second, interstitial dislocation loops, are homogeneously nucleated for irradiations below $450\text{ }^{\circ}\text{C}$ and then grow by two-dimensional diffusion of interstitials through a surrounding field of uncollapsed vacancies in which they may be absorbed. Lidiard and Perrin (1966) solved the equation and showed that in order to conform to the experimental data on the dimensional changes and lattice parameter changes at $200\text{ }^{\circ}\text{C}$ it was necessary to assume that the recombination rate of interstitials and vacancies quickly reached a constant level, in spite of the increasing total of interstitials. This was readily explained by the model of vacancy collapse, provided it is significant for tri-vacancies. The contributions of the two types of interstitial groups were separated, it being assumed that the concentrations of interstitials in growing loops was given by

$$C_i = e_{zz} - \frac{\Delta d}{d} \quad (3.26)$$

and the concentration of interstitials in small (4 ± 2) groups by

$$x_i = \frac{1}{K_i} \frac{\Delta d}{d} \quad (3.27)$$

as approximations.

For irradiations at temperatures greater than $300\text{ }^{\circ}\text{C}$ the lattice parameter changes are small and it is readily shown that the growth of a constant number of interstitial loops by diffusion for a constant vacancy concentration leads to a parabolic dependence of e_{zz} on the dose. This relationship is well obeyed by the results presented by Brocklehurst and Kelly (1993a). Measurement of the other properties shows that point defect concentrations are saturated, and the rate of vacancy collapse equals the rate of accumulation of interstitial atoms in loops. In irradiations below $\sim 450\text{ }^{\circ}\text{C}$ the nucleation of the loops is homogeneous and hence all crystal dimensional changes are the same, independent of perfection, for a wide range of perfections. In irradiations at higher temperatures the nucleation of the loops is heterogeneous (except for very large crystals) and the number of loops and the consequent dimensional changes depend upon the perfection. The nature of the heterogeneous nuclei is not known. They may be small interstitial carbon groups which are removed by the process of graphitisation, the temperature of removal depending upon the size of the cluster.

The experimental data show that the changes continue to very large magnitudes, suggesting that fresh nucleation may occur, although no model has ever been proposed. Attempts to observe the defect structure at high doses have not been successful.

In summary, the dimensional changes of graphite crystals are due to the accumulation of point defects and extended defects created by the interstitial atoms, and vacancies created by the irradiation. The growth in the c-axis direction is due to interstitial atom clusters which are of two kinds, the interstitial dislocation loop and a small cluster. The concentration of the basal planes is due to point vacancies at low doses and collapsed vacancy lines at higher doses. When the latter are dominant, the dimensions change at constant crystal volume. In

irradiations at high temperatures where vacancies are mobile, a proportion which increases with temperature reach crystallite boundaries perpendicular to the basal planes defining L_a , where they can collapse parallel to the basal plane producing a shrinkage equivalent to the collapsed lines. For small crystallite sizes in imperfect materials the majority of the newly created interstitials can reach such boundaries and the resulting dimensional changes approach the maximum possible.

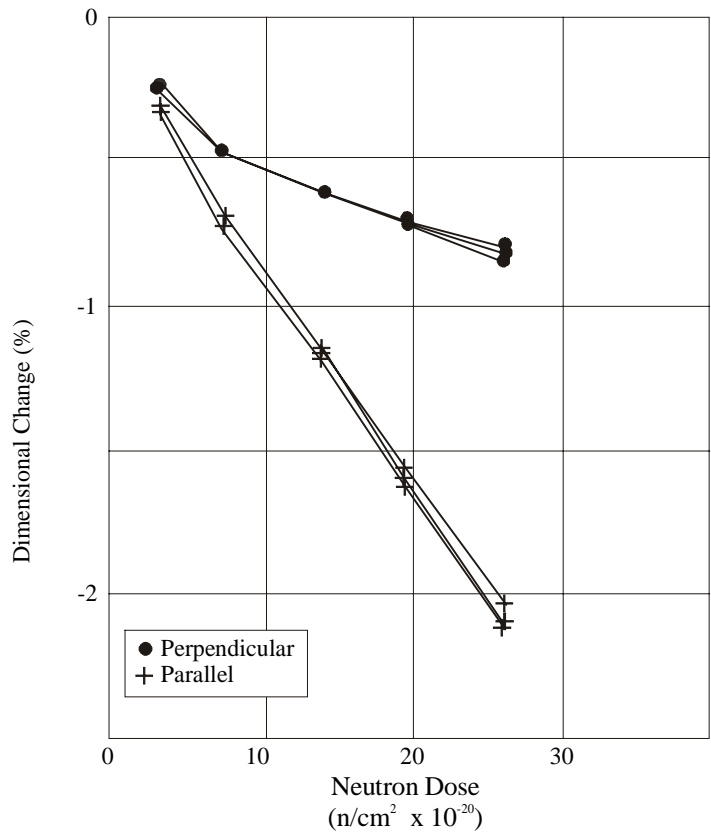


Figure 3.10 Dimentional changes of PGA graphite irradiated at 1250-1350°C in DIDO

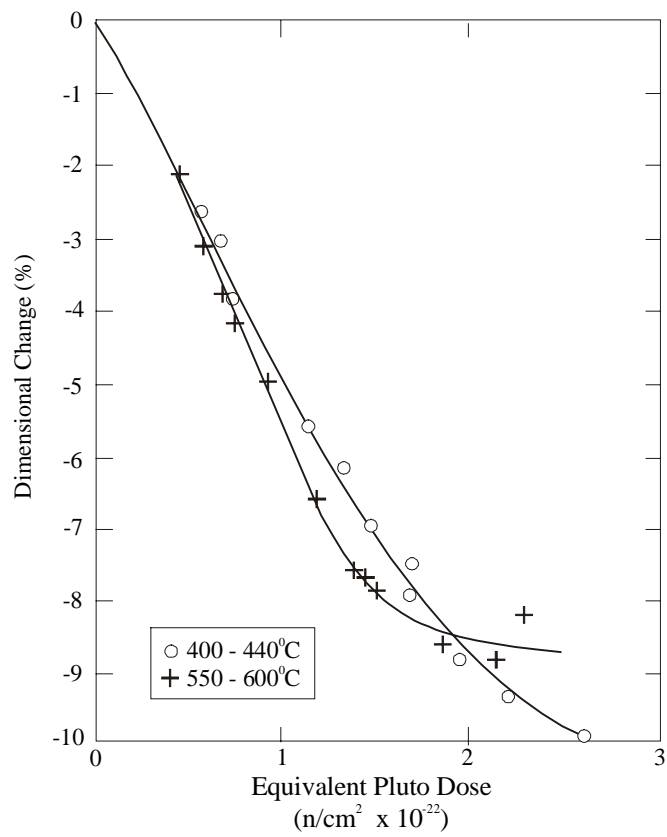


Figure 3.11 Dimensional changes of PGA graphite parallel to extrusion in DFR

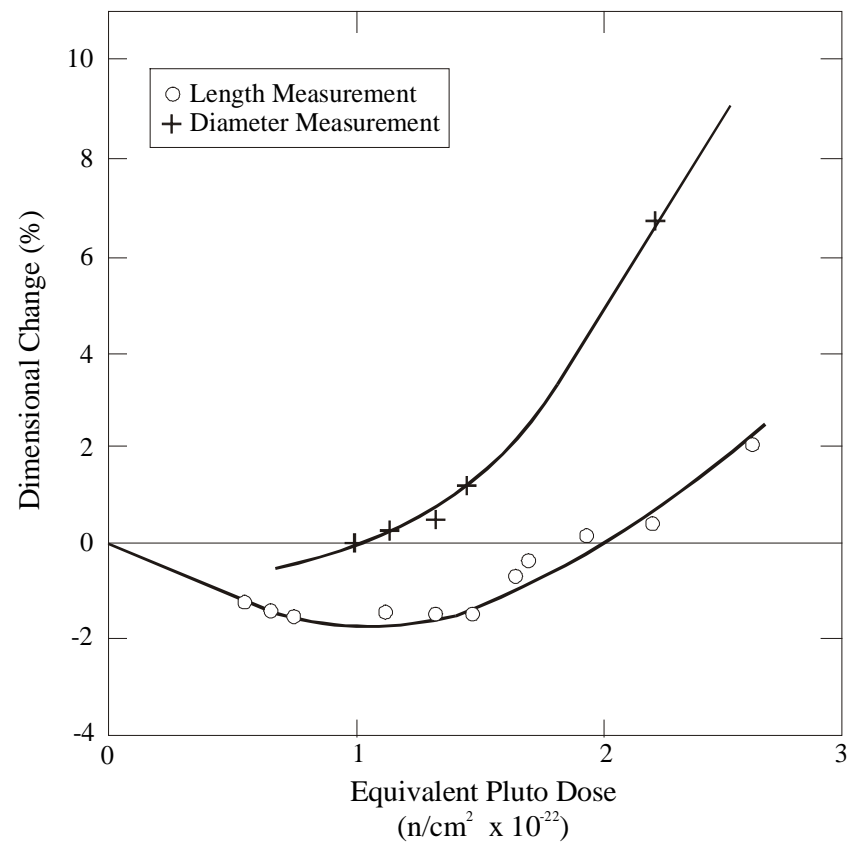


Figure 3.12 Dimentional changes of PGA graphite perpendicular to extrusion at 400°C-440°C in DFR

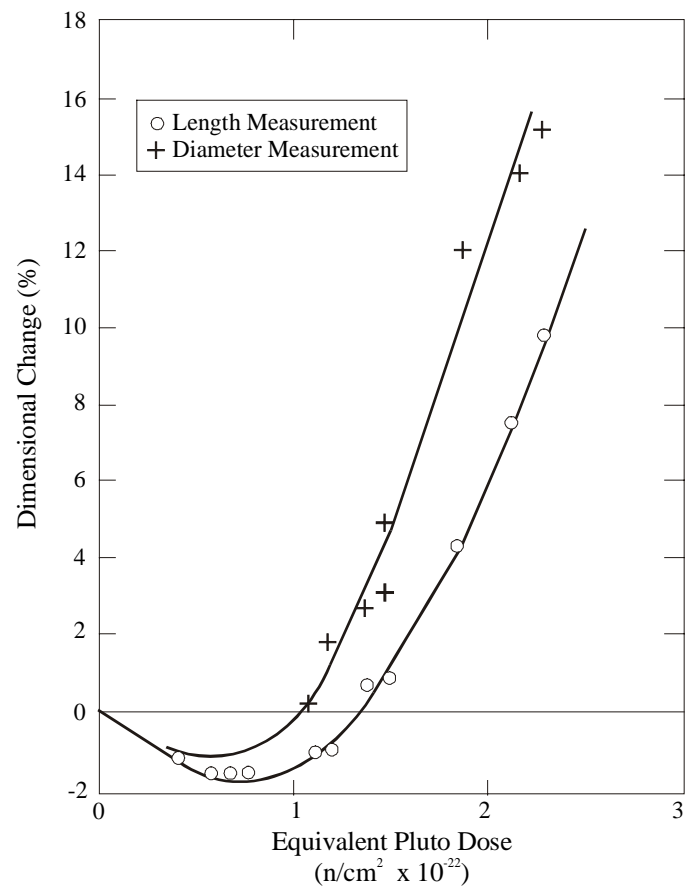


Figure 3.13 Dimentional changes of PGA graphite perpendicular to extrusion at 550°C-650°C in DFR

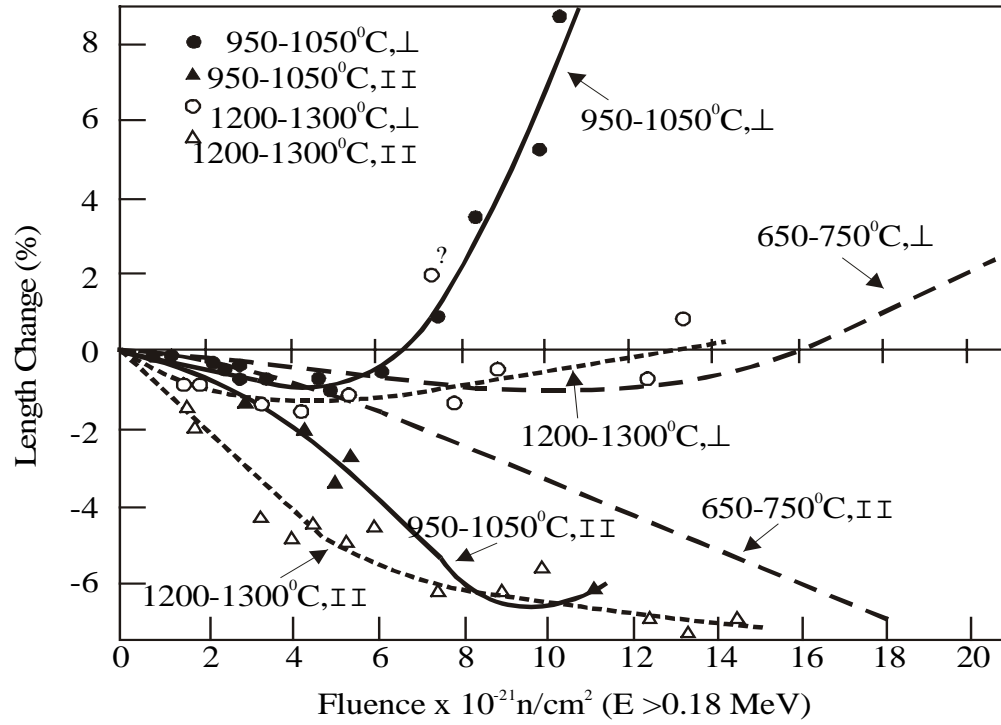


Figure 3.14 Parallel and perpendicular length changes of CSF graphite

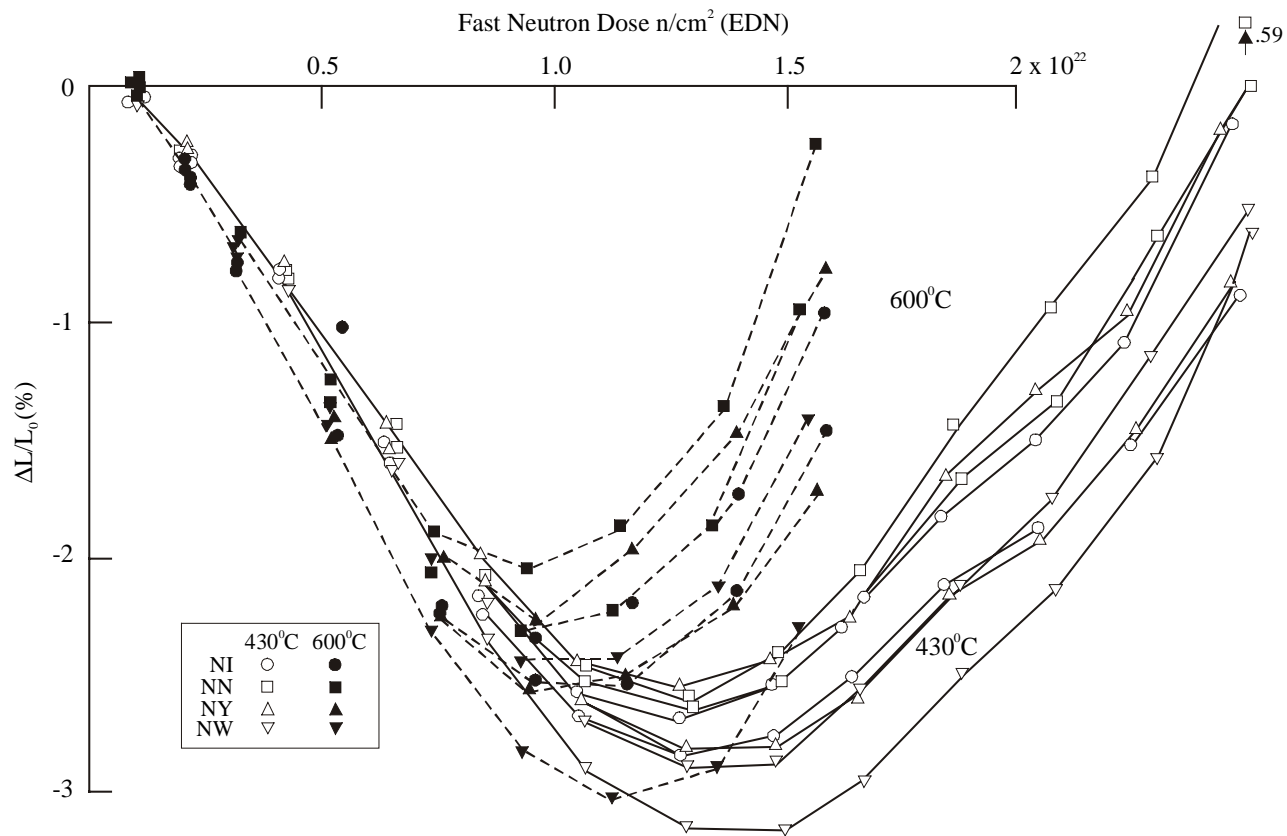


Figure 3.15 Dimensional changes of CAGR moderator graphite in PLUTO at 430 and 600°C

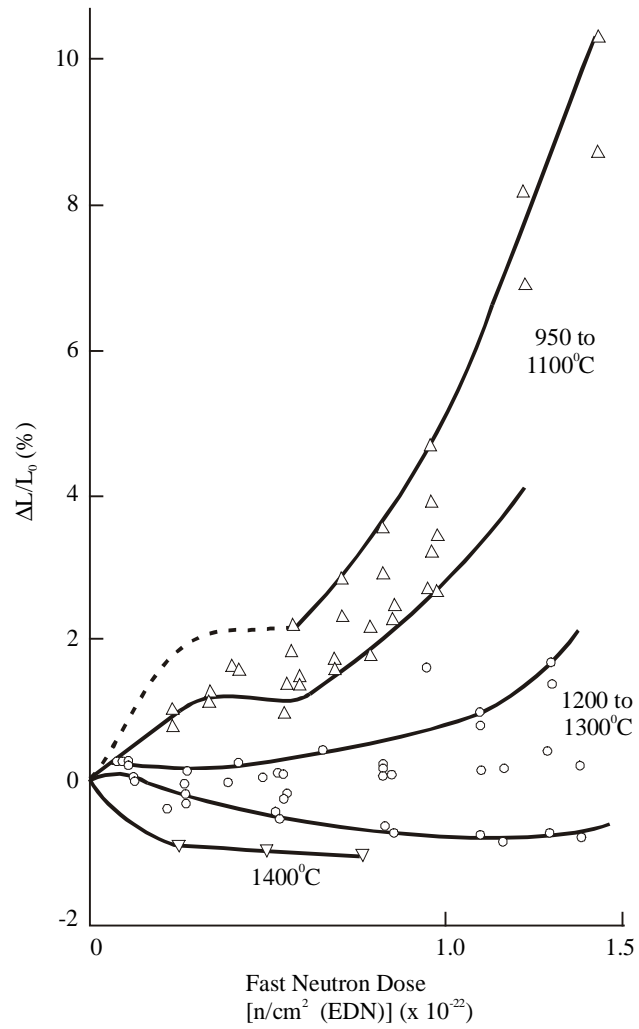


Figure 3.16 Dimensional changes of POCO graphite grade AXF-8Q1

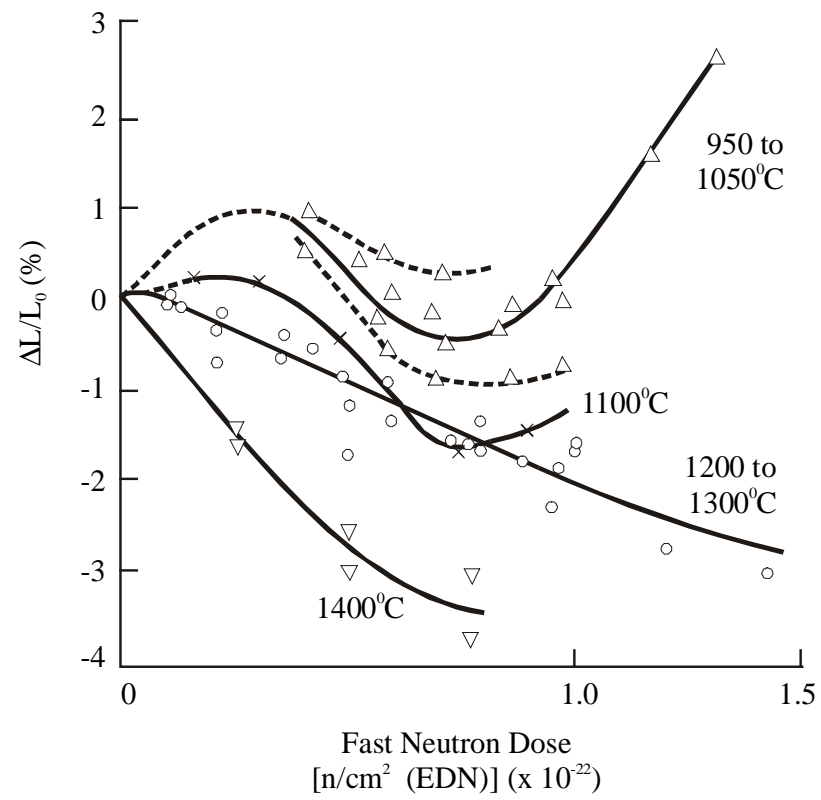


Figure 3.17 Dimensional changes of POCO graphite grade AXZ-5Q1

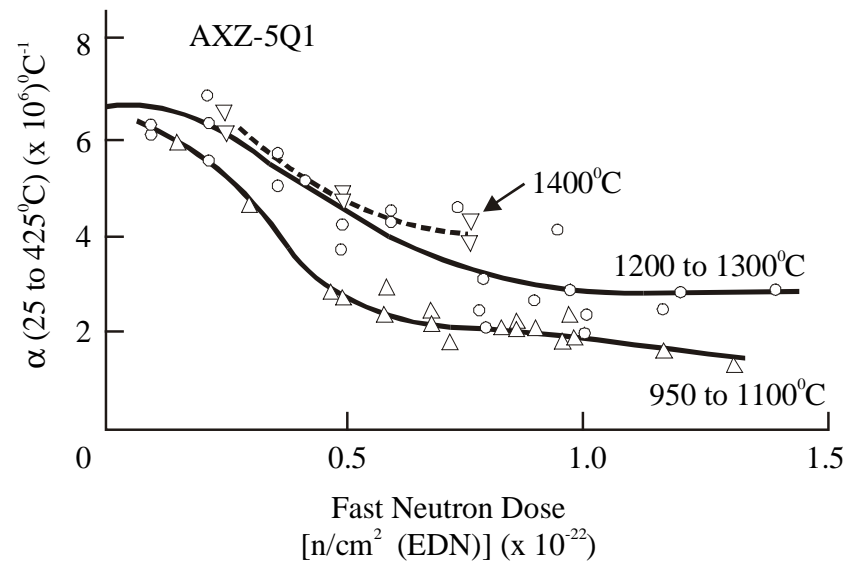


Figure 3.18 Thermal expansion coefficient for POCO graphite grade AXZ-5Q1

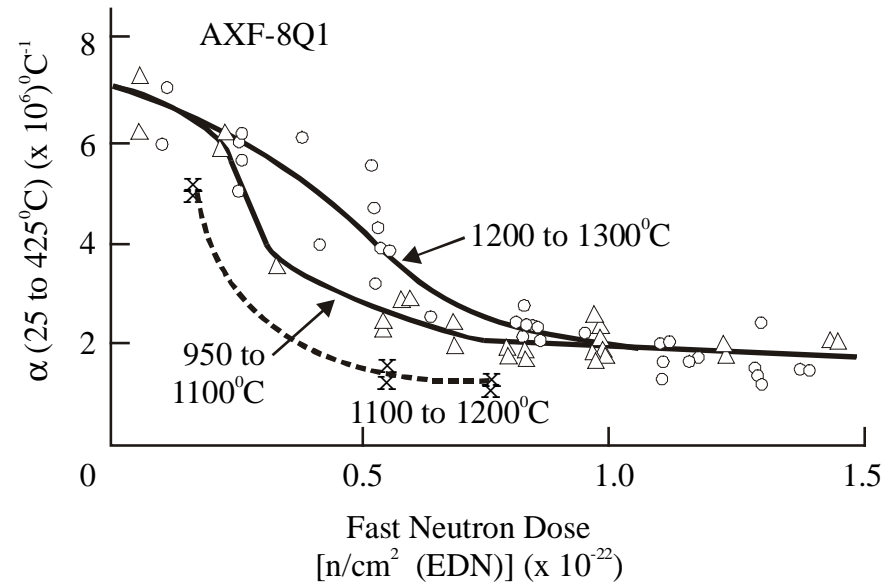


Figure 3.19 Thermal expansion coefficient for POCO graphite grade AXF-8Q1

REFERENCES

- [3.1] AUSTERMAN S.B. USAEC Report NAA-SR-2457, Atomics International (1958).
- [3.2] AUSTIN A.E. and HARRISON R.J. Proc. Third Biennial Carbon Conference, Pergamon Press, New York, p585 (1959).
- [3.3] AYASSE J.B. and BONJOUR E. Proc. Fourth SCI Conference on Industrial Carbons and Graphites, SCI, London, p620 (1976).
- [3.4] BACON G.E. Proc. Third Conference on Carbon, Pergamon Press, p475 (1959).
- [3.5] BACON G.E. J. Chim. Phys., 57, 829 (1960).
- [3.6] BACON G.E. and WARREN B.E. Acta Cryst., 9, 1029 (1956).
- [3.7] BRIDGE H., KELLY B.T. and GRAY B.S. Proc. Fifth Conference on Carbon, Pergamon Press, 1, 289 (1962).
- [3.8] BROCKLEHURST J.E. Irradiation Damage in CAGR Moderator Graphite, UKAEA Report ND-R-1117(S) (1984).
- [3.9] BROCKLEHURST J.E. and KELLY B.T. Carbon, 31, 179 (1993a).
- [3.10] BROCKLEHURST J.E. and KELLY B.T. Carbon, 31, 155 (1993b).
- [3.11] BURCHELL T.D. and EATHERLY W.P. J. Nuc. Mater., 179-181, 205 (1991).
- [3.12] CHINAGLIA B., DOMENICI M., PIERAGOSTINI F. and WALTHER H. Proc. Third Int. Conf. On the Peaceful Uses of Atomic Energy, United Nations, p399 (1965).
- [3.13] CHIPMAN D.R. and WARREN B.E. US Report KAPL-677 (1952).
- [3.14] GRAY W.J. and PITNER A.L. Carbon, 9, 699 (1971).
- [3.15] HARRISON J.W. High Temperatures - High Pressures, 9, 211 (1977).
- [3.16] HENSON R.W., PERKS A.J. and SIMMONS J.H.W. Carbon, 6, 789 (1968).
- [3.17] HENSON R.W. and REYNOLDS W.N. Carbon, 3, 277 (1965).
- [3.18] HORNER P. and WILLIAMSON G.K. Carbon, 4, 353 (1966).
- [3.19] HUTCHEON J.M. Graphite for AGR Power Stations, Paper 4, AGR Symposium, Frankfurt (1966).
- [3.20] IWATA T. and NIHIRA T. J. Phys. Soc. Japan, Vol 31, p1761 (1971).
- [3.21] KEATING D.T. Phys. Rev., 98, 1859 (1955).
- [3.22] KELLY B.T. Proc. Third SCI Conference Industrial Carbons and Graphites, SCI, London, p483 (1972).
- [3.23] KELLY B.T. Physics of Graphite, Applied Science Publishers, London (1981).
- [3.24] KELLY B.T. Fusion Technology, 16, 96 (1989).
- [3.25] KELLY B.T. and BROCKLEHURST J.E. Carbon, 9, 783 (1971).
- [3.26] KELLY B.T. and BURCHELL T.D. Carbon, 32, 499 (1994).
- [3.27] KELLY B.T., MARTIN W.H. and NETTLEY P.T. Phil. Trans. Roy. Soc. A, 260, 37 (1966a).
- [3.28] KELLY B.T., MARTIN W.H. and NETTLEY P.T. Phil. Trans. Roy. Soc. A, 260, 51(1966b).
- [3.29] KELLY B.T. and WALKER P.L. Carbon, 8, 211 (1970).
- [3.30] LIDIARD A.B. and PERRIN R. PHIL. MAG., 14, 433 (1966).
- [3.31] MAETA H., IWATA T. and OKUDA S. J. Phys. Soc. Japan, 39, 1558 (1975).
- [3.32] MARTIN D.G. and HENSON R.W. Phil. Mag., 9, 659 (1964).
- [3.33] MARTIN D.G. and HENSON R.W. Carbon, 5, 313 (1967).

- [3.34] MORGAN W.C. Carbon, 10, 73 (1972).
- [3.35] MORGAN W.C. and GRAY W.J. High Temperature Graphite Irradiations: 550 to 1450°C, BNWL-1672 (1972).
- [3.36] Mrozowski S. Proceedings of the First and Second Conference on Carbon, University of Buffalo, p35 (1956).
- [3.37] Nightingale R.E., Davidson J.M. and Snyder W.A. Proceedings of the Second United Nations Conference on the Peaceful Uses of Atomic Energy, United Nations, p295 (1958).
- [3.38] PERKS A.J. and SIMMONS J.H.W. Carbon, 4, 85 (1966).
- [3.39] PLUCHERY M. Proc. Int. Conf. Irradiation Damage in Reactor Materials, IAEA, Vienna, p523 (1963).
- [3.40] PRICE R.J. Carbon, 12, 159 (1974).
- [3.41] SIMMONS J.H.W. Proc. Third Biennial Conference on Carbon, Pergamon Press, New York, p559 (1959).
- [3.42] SIMMONS J.H.W. Radiation Damage in Graphite, Pergamon Press (1965).
- [3.43] SIMMONS J.H.W. and Reynolds W.N. Uranium and Graphite, Institute of Metals Monograph No. 27, p75 (1962).
- [3.44] SPENCE G.B. Proc. Fifth Biennial Conference on Carbon, 2, Pergamon Press, New York, p531 (1963).
- [3.45] STONEHAM A.M. J. Phys. C: Solid State Phys., 6, 223 (1973).
- [3.46] TEMKIN D.E. Sov. Phys. Solid State, 11, 1614 (1970).
- [3.47] THROWER P.A. and REYNOLDS W.N. J. Nucl. Mater., 8, 221 (1963).
- [3.48] UKAEA. Report on the Life of the Graphite Core of the Advanced Gas-Cooled Reactor,
- [3.49] Emeléus Graphite Committee, UKAEA Report (1965).
- [3.50] WARREN B.E. and CHIPMAN D.R. US Report KAPL-938 (1953).
- [3.51] WOOLLEY R.L. BRIT. J. Applied. Phys., 14, 778 (1963).
- [3.52] YOSHIKAWA H.H. Nuclear Sci. Eng., 19, 461 (1964).