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# IRRADIATION DAMAGE IN GRAPHITE

by

A. BÜRKHOLZ

1966



Report prepared at the CEN  
Centre d'Etude de l'Energie Nucléaire, Mol - Belgium

Association No. 006-60-5 BRAB

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Printed by L. Vanmelle, s.a.  
Brussels, July 1966

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## SUMMARY

From a number of easily available reports dealing with the radiation effects on graphite, we tried to trace a picture of the behaviour of graphite under irradiation. Although this review is not complete, it covers the main radiation effects and it makes available information on this vast and complicated subject. Due to the complicated structures of the graphite materials, reviews on radiation damage on graphite have very often been compilations of experimental data. Recent investigations, especially those of the British workers, allow now a deeper insight in the nature of the radiation effects.

## 1) INTRODUCTION

Graphite has been used extensively in the nuclear field, especially as a moderator material. With the development of high-temperature, gas-cooled reactors graphite has, together with beryllium oxide, found new applications as a structural, fuel matrix and container material. The advantageous properties of graphite are :

- excellent nuclear properties
- high melting point
- low vapour pressure
- rising strength at high temperatures
- good thermal conductivity

The two main disadvantages of graphite are :

- high oxidation rate above 400°C
- radiation damage

Under certain conditions, radiation damage in graphite can assume quite serious proportions. For example, exposure to  $2 \cdot 10^{21}$  nvt ( all exposures in this report are given in neutrons above 1 mev ) at 30°C resulted in doubling the mechanical strength, a factor of fifty reduction in thermal conductivity, a linear expansion of greater than 3%, an accumulation of stored energy of 500 cal/g.

## 2) FABRICATION AND PROPERTIES

The manufacture of nuclear-grade graphites may be divided into three types: (1) moderator or reflector blocks and structural components; (2) fuel-matrix graphite, the matrix in which fuel materials may be contained; (3) graphites of low permeability for fuel compact containers. The raw materials for these have in common that they are graphitisable carbons. The low permeability graphite is often manufactured from normal nuclear grade graphite by impregnation techniques to fill pores.

Manuscript received on March 10, 1966.

An even more recent development is pyrocarbon, which forms a thin-wall barrier on fuel particles (coated particles). Pyrocarbon is manufactured by passing a hydrocarbon gas over a substrate at elevated temperatures ( $1800^{\circ}$  to  $2400^{\circ}\text{C}$ ). The gas is decomposed and carbon adheres to the particles.

Reactor grade graphite is manufactured from ground or milled coke, the filler, to which has been added a suitable pitch binder. This plastic mass is shaped by extrusion or molding. The extrusion aligns the plate-like or needle-like coke particles longitudinally in the axis of extrusion, in molding the plate-like particles arrange themselves perpendicular to the direction of molding. Each particle consists of a number of crystallites, ordered layer planes a few stacks high which are highly oriented, with their c-axis perpendicular to the particle surface.

The next step is the carbonising of the pitch binder in heating it about  $1000^{\circ}\text{C}$ . Finally, the material is graphitised or recrystallised in an electric furnace at temperatures in excess of  $2000^{\circ}\text{C}$ . This process involves crystal growth in the a and c directions, and closing of the interplanar distance  $c_0$ . The growth increases the ordering of the semi-crystalline material, so that the final product is strongly preferentially oriented.

This preferential orientation results in an anisotropy of the bulk material, which mirrors to some degree the anisotropy of the single graphite crystal.

In the single graphite crystal, the carbon atoms are arranged in hexagonal rings bonded together in one plane forming layers. The layers are held together by Van der Waals forces. The interatomic distance within a layer is  $1.42 \text{ \AA}$ , the distance between the layers is  $3.35 \text{ \AA}$ . The anisotropy of the crystal lattice results in a marked anisotropy of all physical properties (electrical and thermal conductivity e.g.) of the graphite crystal.

In the whole, graphite is a very complicated material with an imperfect structure and full of macropores and micropores. There is not just one kind of graphite, but a large number of varieties, depending on raw material and fabrication

process. As many variables of fabrication have a pronounced effect on radiation sensitivity, a general statement of radiation damage was difficult.

In recent years, however, considerable knowledge on the radiation behaviour of graphite has been gained, especially through the work of British groups, and predictions on the property changes of graphite can be made with rather good confidence. Moreover, the study of defect structure by electron microscopy (transmission technique) helped much to form a picture of the damage mechanism.

The three main irradiation parameters are temperature, damage flux and time.

The problems of dimensional stability, internal stresses, changes in thermal conductivities and mechanical properties are those receiving the most attention.

### 3) RADIATION EFFECTS

#### 3.1 Dimensional changes

Irradiation at 30°C :

For samples cut perpendicular to the direction of extrusion there is always a length expansion. For samples cut parallel to the direction of extrusion, there is also a growth in length at the beginning, but contraction starts at about  $10^{21}$  nvt, fig.1. At high exposures dimensional changes seem to near saturation. Highest doses reported are about  $6 \cdot 10^{21}$  nvt, the samples exhibiting length expansions up to 6% and length contractions up to 2%. At high doses, perpendicular specimens invariably show length expansion, those cut parallel invariably contraction.(2,15)

The degree of dimensional change of graphite specimens caused by irradiation is heavily influenced by fabrication methods, the variations found are almost of the same order of magnitude as the damage itself.

The picture is rather complicated. It was found that the length changes were higher in highly graphitic materials than in

nongraphitic carbon structures. Also, the anisotropy of dimensional changes was greater in graphitic material.

Irradiation at higher temperatures:

As the temperature of irradiation is increased, the expansion perpendicular to the direction of extrusion becomes less pronounced for highly graphitic structures, until contraction occurs at about  $250^{\circ}\text{C}$  to  $350^{\circ}\text{C}$  and about  $7 \cdot 10^{20}$  nvt. Then contraction proceeds almost linear with dose. After an initial slight expansion, parallel samples also contract linear with dose, see fig. 2,3.

Dimensional changes have been studied up to exposures of  $10^{22}$  nvt. Contraction for parallel samples is more pronounced than for perpendicular samples. The perpendicular changes go rather linear with dose, whereas the parallel rate of change continues to increase. No indication of saturation could be found. The rate of contraction is a function of irradiation temperature, the contraction rate generally decreases with increasing temperature. (27,28)

There are several other factors that affect the contraction rate. Materials that are non-crystalline (e.g. as a result of poorly graphitising raw materials or low processing temperatures) contract at a high rate.

It must be mentioned that the creep rate is enhanced during irradiation, so that the graphite can accommodate to greater strain without fracturing. (29)

### 3.2 Lattice parameter changes

The changes in the lattice parameters  $a_0$  and  $c_0$  are studied by measurements of the Bragg angle reflections.

There is always an expansion of the  $c_0$  parameter and a contraction of the  $a_0$  parameter. Lattice parameter change is less sensitive to fabrication factors.

During irradiation at  $30^{\circ}\text{C}$ ,  $c_0$  increases linearly at a rate of about 1.3% per  $10^{20}$  nvt up to doses of  $6.5 \cdot 10^{20}$  nvt. At high doses (about  $2 \cdot 10^{21}$  nvt)  $c_0$  expansion reaches saturation.

Highest changes measured are about 5%  $a_0$  contraction and 18%  $c_0$  expansion.

At high irradiation temperatures (400 to 800°C)  $c_0$  expansion is almost insignificant.

### 3.3 Changes in pore volume and surface area

Analysis of nitrogen adsorption isotherms reveals that, after irradiation, total surface area of the specimen and apparent diameter of the pores have decreased. This can be attributed to the physical expansion of the individual crystallites, which amounted to 15% after exposure to  $7.5 \cdot 10^{20}$  nvt, while bulk volume expansion was as low as 0.2% to 0.6%.

The closure of cracks after irradiation has directly been observed by electron microscope replica techniques. (16)

### 3.4 Irradiation effects on electronic properties

Neutron irradiation produces marked changes in almost all the physical properties of graphite. Fig. 4 shows the effect of neutron irradiation on the electronic properties. The changes in thermoelectric power are not given but they equal those of the Hall coefficient.

Electrical resistivity:

The electrical resistivity of all graphites increases rapidly with dose to a saturation value. The relative resistivity increase  $\Delta\rho/\rho_0$  is slightly greater for the parallel cut specimens. The saturation value of  $\Delta\rho/\rho_0$  depends of the type of graphite (the highest effect showing the highly graphitised graphites with almost no change in poorly graphitised samples) and is about 3 to 4, the saturation point lies at about  $4 \cdot 10^{20}$  nvt. At higher irradiation temperatures the value of  $\Delta\rho/\rho_0$  is lower, but in general the change in electrical resistivity does not show the strong temperature dependence.

It is interesting to note that the resistance in the perpendicular direction of nearly ideal graphite is reduced after irradiation. (22)

### 3.5 Irradiation effects on mechanical and thermal properties

Hardness, strength and elastic modulus:

Young's modulus and strength are similarly affected by irradiation. Values of these properties increase and reach a maximum at about  $10^{20}$  nvt during room temperature irradiation. Saturation values, reached at about  $10^{21}$  nvt, are about a factor three above the unirradiated values. At higher temperatures, changes are much smaller.

Irradiated graphite is harder and more brittle and has good abrasive qualities.

Thermal conductivity:

The variation of thermal resistivity  $1/K$  with exposure is given in fig. 5. Fabrication history does not seem to be as important as with other property changes. The thermal resistivity increases always with exposure, although the rate of increase falls off markedly at higher doses and temperatures. Increase in thermal resistivity can be considerable. The fractional change  $K_0/K$  is the same for perpendicular and parallel samples.

Thermal expansion:

As with other properties, the effect of irradiation on the coefficient of thermal expansion is dependent on material history, direction of cut and irradiation temperature.

At room temperature, the coefficient of thermal expansion increases with dose until, at about  $5 \cdot 10^{20}$  nvt, it starts to decrease. This decrease in the thermal expansion is accompanied by a considerable increase in the rate of length growth of the perpendicular samples. (18)

At higher irradiation temperatures, the change in thermal expansion has a different character. At temperatures higher than  $300^\circ\text{C}$ , the coefficient remains unchanged up to doses of  $2 \cdot 10^{21}$  nvt. At  $250^\circ\text{C}$  the dose where increase starts is about  $6 \cdot 10^{20}$  nvt, at  $225^\circ\text{C}$  the dose is  $4 \cdot 10^{20}$  nvt. Again at the same exposures a sharp increase in length growth can be found, fig.6. (15)

### 3.6 Effects on the chemical behaviour

Investigations deal with the reactivity of irradiated graphite against oxidation by gases. (1,3)

After neutron irradiation, the rate of oxidation of graphite is increased. If this oxidation takes place the presence of ionizing radiation, the rate of oxidation is still higher. About the same increase of oxidation rate is found for graphite exposed during reactor irradiation.

The mechanism by which irradiation prior to oxidation promotes the reaction rate is not yet fully understood. Annealing at 2800°C completely removes the enhanced reactivity of irradiated specimens.

It is possible that the changed rate in oxidation is due to the change of electronic properties at the surface of irradiated graphite. Understanding of the effects is blurred by the influence of catalytic effects.

As to the effect of purely ionizing irradiation, one thinks of the formation of highly active gas compounds and oxygen atoms which attack graphite.

## 4) THE NATURE OF RADIATION DAMAGE IN GRAPHITE

### 4.1 Lattice changes

Contrary to beryllium and beryllium oxide, there is no generation of impurity atoms by nuclear reactions in graphite. Bombardment with fast neutrons displaces carbon atoms from their normal lattice sites driving them to sites between planes and leaving vacancies in the layers.

The lattice vacancies within the planes cause a marked alteration in vibrational frequencies in their vicinity, and the interstitial atoms will cause a buckling of the adjacent lattice planes which will not only change the vibration frequencies in this region, but will affect the lattice spacing as well. Buckling and warping of the lattice planes is reflected by an increase in  $c_0$  spacing and a decrease in the  $a_0$  spacing within the lattice planes.

In addition, the bending of the lattice planes by individual interstitials and complexes of interplanar atoms would tend to restrict the normally easy gliding of one lattice plane over another. This latter effect accounts for the observation that irradiated graphite becomes extremely hard and has good abrasive qualities. It also accounts for the increase in compressive strength and the initial rise, followed by a sharp decrease, in cross breaking strength as the material becomes more brittle.

The effect of irradiation on the shape and position of the (002) reflection is shown in fig. 7. The shift of the peak indicates an increase in  $c_0$ . The decrease in peak height and the asymmetric broadening of the line indicates strong distortion and strain of the lattice. The final diffuse form reflects the resulting fragmentation of the crystallites into small grains with non-graphitic structure.

#### 4.2 Growth

There are three growth phenomena due to irradiation: the growth of the lattice, of the single crystallite, and of the bulk volume.

The growth in the c-spacing can be followed by line shift measurements, until at high doses lines become too much blurred to be measured any longer.

For the individual crystallite, the expansion in the direction of the c-axis is considerably larger than that deduced from the increase in c-spacing (x-ray measurements). The reason is the formation of fragmentary new basal planes by the aggregation of interstitial defects into large clusters. The change in the crystallite dimensions can be evaluated by various methods. (18,38)

After exposure to  $10^{21}$  nvt at  $150^{\circ}\text{C}$ , the crystallites have grown about 30% in the c-direction and contracted about 10% in the a-directions. At higher irradiation temperatures, again changes are much smaller. At temperatures as high as  $1200^{\circ}\text{C}$ , however, changes are again high and comparable to those at  $250^{\circ}\text{C}$ . This is also reflected in a higher overall shrinkage in the

graphite sample. The phenomenon is explained by a different annealing mechanism at this temperature. (30)

The changes in the bulk volume of the polycrystalline samples are always much smaller than the changes of the crystallites, due to the presence of numerous macro- and micropores. Because the c-axis expansion results in filling the cracks, the overall effect in polycrystalline material is a shrinkage due to the a-axis contraction.

The partial filling of the pores by the expanding crystallites causes a tightening of the bulk material. Its influence on the thermal expansion and Young's modulus has been discussed elsewhere.

The rate of length change  $l$  of a specimen with irradiation dose  $s$  is given by

$$(1/l)dl/ds = (A/X_c)dX_c/ds + ((1-A)/X_a)dX_a/ds$$

where  $X_c$  and  $X_a$  are the c-axis and basal plane dimensions of the crystallite.  $A$  is a parameter characteristic of the type of graphite and the direction of cut of the particular specimen.

Experimental measurements, especially on pyrolytic graphite, gave support to a theory which is based on the above equation and which explains the dimensional changes in irradiated graphite. (27,30,38)

#### 4.3 Electronic properties

In a perfect graphite crystal equal concentrations of electrons and holes are available for transport of current, but because of the greater mobility of the electrons, current is mostly carried by electrons. The decrease in conductivity after irradiation can be provoked by a decrease in the concentration of the charge carriers and a decrease in mobility by additional carrier scattering.

The Hall coefficient  $R$  (and the thermoelectric power) are both inverse functions of the carrier concentration, and its sign is that of the dominant charge carrier. Before bombardment  $R$  is negative, because of the greater mobility of the electrons. After exposure to  $10^{19}$  nvt, the holes have become the dominant

charge carriers, as is indicated by the change in sign of  $R$ . The electrons must have been removed by being trapped in radiation produced defects. One believes that a vacancy can trap two electrons and a single isolated interstitial can trap one electron. Further exposure increases the defect concentration and consequently also the hole concentration toward a saturation value. As  $R$  is inversely proportional to the carrier concentration, this means a decrease in the absolute value of  $R$ . (1)

The increase in hole concentration is expected to cause a decrease in the electrical resistivity, so apparently this effect is overcompensated by an irradiation produced increase in carrier scattering centers. This is made evident by the rapid decrease in magnetoresistance, which is proportional to the carrier mobility. This sort of dynamic equilibrium is further attested by the variations of resistivity at higher exposures.

The decrease in diamagnetism is also consistent with electron trapping and hole production, as shall be only mentioned.

Although the interstitial defects are very different in character at the different irradiation temperatures, the change in electrical resistivity does not show this strong temperature dependence. So carrier scattering and trapping seems to be mainly due to the vacancies. (1)

#### 4.4 Thermal and mechanical properties

Thermal conductivity:

Only less than 1% of the thermal current is carried by electrons or holes, mostly it is carried by phonons. Like the electrical conductivity, the thermal conductivity is considerably greater along the atomic layers.

Before exposure, scattering at the crystallite boundaries constitutes most of the resistance to phonon motion. After irradiation the concentration of phonon scatterers is evidently greatly enhanced by the existence of vacancies, interstitials and interstitial complexes.

For crystallite diameters in the range from 100 to 1000 Å, the radiation introduced increment (at 260°C) of the reciprocal of conductivity ( $1/K_1$ ) is proportional to the square root of

dose and to the reciprocal of crystallite diameter. This implies that the majority of displaced atoms within a graphite crystal layer must cluster into a single defect. When the crystal diameter is greater than the separation distance between clusters, the number of clusters will be independent of crystal size. Then  $\Delta(1/K_i)$  is independent of the crystal diameter and varies as the square root of dose. When the crystal size is so small that the number of crystal layers is greater than the number of displaced atoms, clusters cannot form and  $\Delta(1/K_i)$  is directly proportional to dose. (17)

Thermal expansion:

For a well graphitised specimen, the coefficient of bulk thermal expansion is given by

$$\alpha = A \cdot \alpha_c + (1-A) \cdot \alpha_a$$

where  $\alpha_c$  and  $\alpha_a$  are the respective coefficients for a single crystallite (along the c and the a-axis). A is the same parameter as used in section 4.2.

In pyrolytic graphite it was possible to measure  $\alpha_c$  and  $\alpha_a$  directly. These values are necessary for the evaluation of growth in polycrystalline graphite. (27,38)  $\alpha_c$  was found to decrease monotonously with exposure, while  $\alpha_a$  increases slightly. (18)

The stepwise increase in  $\alpha$  (see fig. 6) must mainly be due to the closure of cracks and pore space due to c-axis growth.

Young's modulus:

The theory of the effect of radiation on the elastic moduli is rather complicated. Their increase with exposure is not only due to the closing of pores by growth of the crystallites. It is also provoked by an increase of the shear modulus of the latter consequent to the pinning down of dislocations by the clusters. (1,15)

#### 4.5 The formation of clusters

By methods of transmission electron microscopy, the existence of clusters in purified and irradiated graphite can directly be observed. (19,20) The clusters are lying on the basal planes and become larger and less dense with increasing irradiation

temperatures. From 200°C to 650°C, the cluster radius  $r_0$  varies from 40 Å to 200 Å, and the half separation distance  $r_1$  from 350 Å to 10000 Å. The separation distance seems to be independent of time of irradiation, and the diameter of the cluster increases with the square root of it.

The most striking feature is the linearity of the spot size increase with irradiation temperature. In general the spots (clusters) show a distribution of about  $\pm 30\%$  about the mean value. On annealing, the smaller defects tend to decrease and to coalesce. At temperatures above 1200°C the total amount of damage begins to decrease.

The distribution of the irradiation defects can be described by the model of homogeneous nucleation. Then  $r_1^4 \sim D/\phi_d$  and  $\phi_d t = (r_0/r_1)^2$  where  $D = D_0 \exp(-q/kT)$  is the diffusion coefficient,  $q$  the activation energy for diffusion,  $T$  the irradiation temperature,  $t$  the time of irradiation,  $\phi_d$  the damage flux and  $r_0$  and  $r_1$  as above.

At room temperature  $r_1$  is small and nucleation is in small unresolvable clusters, which aggregate only on annealing to coarser defects. Spike formation as found in metals is not to be expected in graphite because of the low mass and large lattice spacing of the carbon atoms in graphite. Each spike is spread over a large volume and so production of interstitials is more homogeneous.

The activation energy  $q$  is about 1.27 eV in the 150°C to 250°C temperature range. The value of  $q$  is too high for the migration of interstitial atoms and too low for the migration of single vacancies, so one thinks of the motion of small groups of interstitials.

If  $r_1$  becomes greater than the crystallite radius, homogeneous nucleation is impossible and the flux-temperature relationship is changed.

The activation energy and the given equations which were derived from electron microscopy studies, are in good agreement with other experimental results. (21,17)

The theory of homogeneous nucleation has been substantiated by seeding experiments, this is, short irradiations followed by an irradiation at a higher temperature. (20)

During irradiation at the lower temperature numerous invisible nucleation sites are produced, which grow to visible clusters during the subsequent high temperature irradiation. So after seeding irradiations much more clusters are found in transmission electron micrographs than without seeding.

As a consequence, the rate of the c-axis expansion and a-axis contraction of the lattice is much considerably increased. Effects are greatest in large single crystals, where natural nucleation sites (as grain boundaries, lattice defects, etc.) are rare. After very long exposure times seeding is reduced in effectiveness because of the (low) mobility of defects which reduces their number.

Although a complete understanding of the phenomenon is not yet possible it is clear that, by means of the seeding process even short variations (lowering) of the irradiation temperature can wholly alter irradiation damage.

#### 5) THE INFLUENCE OF FLUX LEVEL AND IRRADIATION TEMPERATURE ON DAMAGE

To compare the irradiation results obtained in different reactors or reactor positions with different flux spectrum, the damage flux has been defined by

$$\phi_d = \int_0^{\infty} \gamma(E) \phi(E) dE$$

where  $\gamma(E)$  represents the variation of atomic displacement rate with neutron energy. As variations in  $\phi(E)$  affect  $\phi_d$ , for each radiation facility  $\phi_d$  should be compared to a  $\phi_d$  standard. This intercorrelation of the various experimental facilities can be found by measuring the change in electrical resistivity of selected specimens or by calculation of the flux spectra.

During irradiation at higher temperatures, considerable annealing occurs simultaneously with damage production. Two irradiations will be equivalent, if the defects are identical. So the distribution and the size of the clusters must be the same for both irradiations:

$$(r_1)_1 = (r_1)_2 \quad (r_0)_1 = (r_0)_2$$

from which follows that

$$D/\phi_d \quad \text{and} \quad (\phi_d) \cdot t = \text{dose}$$

must be invariants ( $t$ =irradiation time). The required invariance of  $D/\phi_d$  gives a relation between damage flux and irradiation temperature for two irradiations:

$$1/T_1 - 1/T_2 = (k/q) \ln ((\phi_d)_2/(\phi_d)_1)$$

(  $k$  = Boltzmann's constant).

By means of the equation one can refer different irradiation facilities to a standard irradiation facility.

The above deduction implies that the immediate recombination of interstitials with vacancies is not very much affected by the irradiation temperature. (19,21)

## 6) ANNEALING OF RADIATION DAMAGE

The annealing mechanism of irradiated graphite is not yet completely understood. Annealing during irradiation is much more effective than post-irradiation annealing. So the radiation must have a direct influence on the annealing mechanism, and the activation energies are not the same.

At low temperatures and low damage levels the damage consists mainly of small groups of interstitial atoms and single vacancies. At higher temperatures or at high damage levels, simple defects are unstable and the formation of larger groups is favored. During thermal annealing, simple defects break up and the interstitial atoms diffuse to vacancies, crystallite edges and the more stable groups.

The annealing process is presumed to be due to the diffusion of interstitial atoms and groups of them. The activation energy depends on the size of the diffusing group. There are different annihilation and complexing reactions with different kinetics. The activation energy for diffusion of interstitial groups will change during the course of annealing because it depends on the spacing between the graphite layers, which in turn, is influenced by the number and size of the interstitial clusters. The instantaneous activation energy therefore depends on the amount of

damage and the extent of annealing.

Activation energies found by post irradiation annealing are higher than those found during irradiation. One may ascribe the annealing effects to the motion of large clusters, the activation energy increasing with the size. At annealing temperatures above 1200°C the increasing mobility of the vacancies enables them to attack the interstitial groups which therefore begin to decrease and disappear.

For short exposures at low temperatures, annealing at 200°C reduces considerably most of the property changes (as stored energy, electronic and thermal properties), except for  $c_0$ -spacing and volume changes. This suggests that some relatively simple process occurs in the interval from 100°C to 200°C which not only decreases the concentration of scattering centers for both phonon and charge carriers but reduces the stored energy as well. As little or no annealing of the  $c_0$ -spacing occurs around 200°C, the annealing process can not be a simple recombination of interstitials and vacancies, but must involve some clustering of interstitials (vacancies are not mobile at this temperature) into less mobile and more stable complexes. The consequence would be a release of trapped electrons and a reduction of charge and phonon scatterers. In heavily irradiated material this clustering occurs already at lower temperature during irradiation.

To anneal dimensional changes or  $c_0$ -spacings, one has to break up these more stable complexes, which can only be done by heating to a high temperature.

On annealing the samples at their original graphitisation temperature (2800°C), the contraction of the parallel cut samples anneals almost completely, but not the contraction of the perpendicular cut samples (irradiated at high temperature). Some authors ascribe this permanent contraction to the graphitisation of non-graphitised material under the action of the radiation. This ordering of the formerly poorly organised regions (which are mostly in the direction parallel to extrusion) should cause a densification and permanent shrinkage of the material. (3,4)

Annealing between 1500°C and 2000°C reestablishes the initial unirradiated values for the  $c_0$  and  $a_0$  spacing and line breadth. Electron micrographs show the disappearance of defect clusters. Yet there remains a permanent growth in the (low temperature irradiated) and perpendicular cut specimens, as well as a permanent change in the coefficient of bulk thermal expansion. This may be explained by the formation of cracks during annealing, due to the contraction of the individual crystallites.(16)

Much more effective than annealing after irradiation is annealing during irradiation, that is to irradiate the sample for a short time at a temperature higher than the previous exposure temperature. Irradiation annealing works at a much lower temperature than annealing without irradiation.

Irradiation annealing must be regarded as the breaking up of multiple defects, by a process involving the bombarding particles, the diffusion of the resulting interstitial atoms being enhanced by the elevated temperature.

## 7) STORED ENERGY

The study of stored energy in graphite is of great practical importance for graphite power reactors. On the average, every atom in the central region will be knocked out of position twice during the lifetime of a reactor. At low temperatures and after a dose of  $4 \cdot 10^{20}$  nvt, the quantity of displaced atoms is about 2%.

Defects increase the energy content of the lattice, the increase being the product of the defect concentration and the energy of defect formation. Much of the stored energy can be removed by annealing after low exposure, the excess energy content becomes increasingly stable after bombardment in excess of  $5 \cdot 10^{20}$  nvt.

After irradiations at 350°C stored energy is only 0.01% of that after 30°C irradiations to the same dose. At 750°C irradiations, stored energy is always negligible. Fig. 8 gives an example of the build-up of total energy.

Another parameter is the release of stored energy on annealing. Fig. 9 shows the effect of irradiation temperature on stored energy release. From annealing temperatures of 400°C onward, energy release has reached a constant level. The value of this constant level increases with dose and decreasing irradiation temperature. Energy release begins essentially at 200°C.

For samples with low exposure at low irradiation temperatures, energy release has a sharp peak at 200°C. This result suggests again that some relatively simple process occurs in the interval from 100°C to 200°C, if the defects have not yet clustered to more stable complexes.

Energy storage and energy release is not much affected by the type of graphite.

The release of stored energy arising from a rapid rise in the moderator graphite temperature can lead to a dangerous situation when  $dE/dT$  exceeds the specific heat of the graphite and the heat release thus becomes self-sustaining.

ANNEX

BIBLIOGRAPHY

- 1) Radiation damage in solids  
D.S. Billington J.H. Crawford  
Princeton University Press 1961
- 2) TID-3314                    1962  
Graphite    A selected bibliography  
T.F. Davies
- 3) GA-2802                    1962  
High energy neutron induced changes in carbon and graphite  
G.B. Engle

Radiation damage in reactor materials:

IAEA    1963

- 4) Radiation effects in carbon and graphites  
H.H. Yoshikawa et al.
- 5) Comparison of irradiation damage in artificial and natural graphite at different radiation temperatures  
R. Gain
- 6) Irradiation damage in graphite  
W.N. Reynolds P.A. Thrower
- 7) An effect of flux level and flux spectrum on the accumulation of damage in reactor irradiated graphite  
H. Bridge et al.
- 8) Evolution des propriétés physiques du graphite sous l'effet d'irradiations et de recuits successifs  
J. Rappeneau et al.

- 9) Etude comparative des effets des neutrons rapides sur le graphite monocristallin et le graphite nucléaire  
J. Blons et al.
  
- 10) Irradiations neutronique à 78°K de graphites polycristallin  
L. Bochirol et al.
  
- 11) CEA-2241            1962  
Mésure de l'énergie emmagasinée par le graphite irradié  
P. Gelin et al.
  
- 12) CEA-2242            1962  
Réalisation d'un appareil de mesure de la conductibilité thermique du graphite irradié ou non irradié  
M. Bocquet G. Micaud
  
- 13) CEA-2243            1963  
Méthode de mesure dynamique du module d'Young, application aux graphites nucléaires  
F. Pattou J.C. Trutt
  
- 14) ZfK-WF 16           1962  
Reaktorbestrahlung von Graphit  
O. Hauser M. Schenk
  
- 15) TRG Report 567 (c)   1963  
The effect of high-flux fast-neutron irradiation on the physical properties of graphite  
H. Bridge B.T. Kelly P.T. Nettley
  
- 16) AERE-R 4007        1962  
Microstructural changes in neutron-irradiated graphite  
P.A. Thrower W.N. Reynolds
  
- 17) AERE-R 4184        1962  
The influence of crystallite size on the thermal conductivity of irradiated polycrystalline graphite  
I.B. Mason R.H. Knibbs

- 18) AERE-R 4243 1963  
Dimensional changes in the irradiated graphite lattice  
P.R. Goggin et al.
- 19) AERE-R 4316 1963  
The flux-level effect in radiation damage  
W.N. Reynolds P.A. Thrower
- 20) AERE-R 4345 1963  
Enhanced nucleation of radiation damage in graphite  
W.N. Reynolds P.A. Thrower
- 21) Nuclear Engineering 7 70 March 1962  
Stored energy in graphite and reactor design  
H. Bridge B.T. Kelly B.S. Gray
- 22) Proc. Phys. Soc. 78 504 Nov. 1961  
Radiation damage in well oriented pyrolytic graphite  
L.C. Blackman et al.
- 23) BNL 745 (T-270) 1962  
Fundamental studies of radiation damage in graphite  
D.G. Schweitzer
- 24) Kerntechnik 1963 4  
Untersuchung der Porenstruktur von Graphit

Radiation damage in reactor materials:

IAEA 1963

- 25) A model of radiation damage in graphite  
T. Iwata H. Suzuki
- 26) The behaviour of various graphites under neutron irradiation  
E. Fitzer O. Vohler

- 27) A/Conf.28/P/163      1964  
The irradiation behaviour of graphite  
J.H. Simmons et al.
- 28) A/Conf.28/P/254      1964  
Developments in solid moderator materials  
R.E. Nightingale C.G. Collins
- 29) AERE-R 4372            1963  
Radiation induced creep in graphite  
A.J. Perks J.H.W. Simmons
- 30) DW (64) 20            1964  
Radiation damage in graphite at 1200°C  
W.N. Reynolds et al.
- 31) A/Conf.28/P/470      1964  
Influence of various parameters on the behaviour of  
graphite under neutron irradiation
- 32) AERE-R 4701            1964  
A new damage function for predicting the effect of reactor  
irradiation on graphite in different neutron spectra  
M.W. Thompson S.B. Wright
- 33) AERE-R 4612            1964  
Interstitial and vacancy loops in graphite irradiated  
at high temperatures  
P.W. Thrower

Second industrial carbon and graphite conference:  
London April 1965

- 34) Fast-neutron-induced dimensional changes in graphites  
and carbons  
B.T. Kelly et al.

- 35) The effects of fast-neutron irradiation on the thermal conductivity of reactor graphite  
D. Mottershead A. James
- 36) Stored energy in reactor irradiated graphite  
J.G. Tindle H. Sorensen
- 37) Dimensional stability of low permeability graphites during high temperature irradiations  
R.E. Dahl
- 38) Variations dimensionnelles des graphites sous l'effet des rayonnements neutroniques  
J. Rappeneau et al.
- 39) A statistical study of thermal expansion and irradiation growth behaviour of reactor graphite  
B.S. Gray et al.

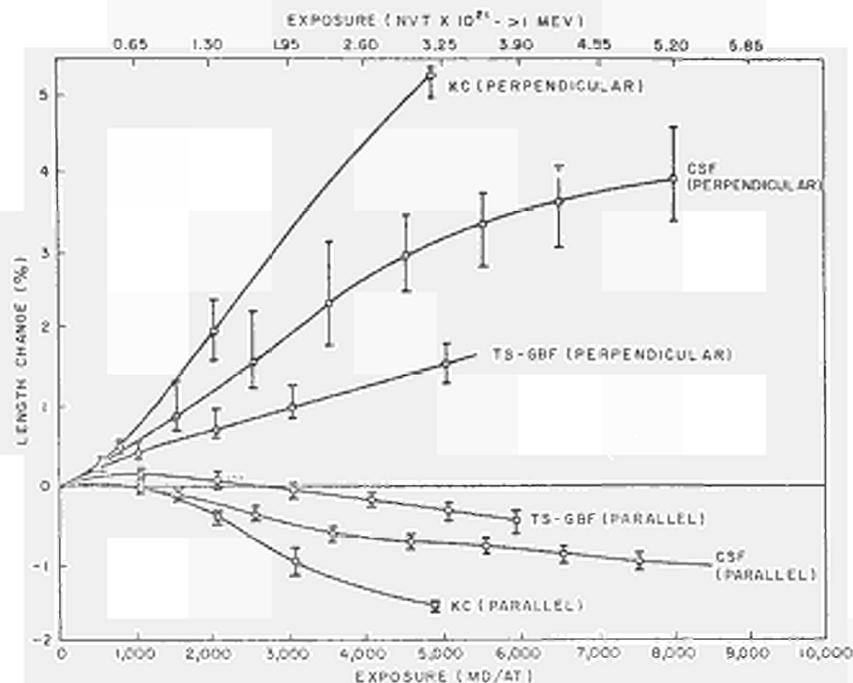


Fig. 1 --Dimensional change of typical commercial nuclear graphites irradiated at 30°C

From N.W. 57.90 Rev. 6 J.L. D'AMICO, G.L. ROSENTHAL and I.R. YOSHIZAWA

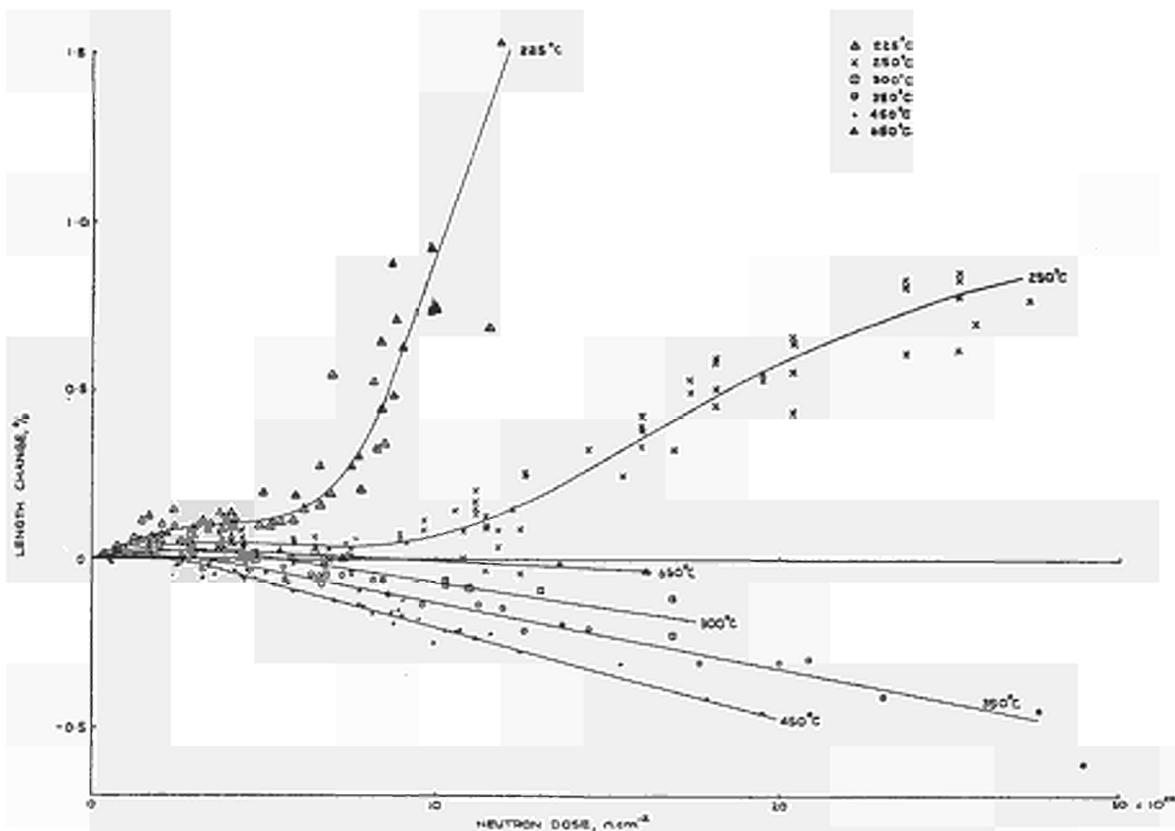


FIG. 2 DIMENSIONAL CHANGES IN PILE GRADE A GRAPHITE PERPENDICULAR TO EXTRUSION WITH NEUTRON DOSE.

From The effect of high-flux fast-neutron irradiation on the physical properties of graphite by H. BRIDGE, B.T. KELLY and P.P. MOTTLEY - Reactor Materials Laboratories, Culcheth - TRG Report 567 (C)

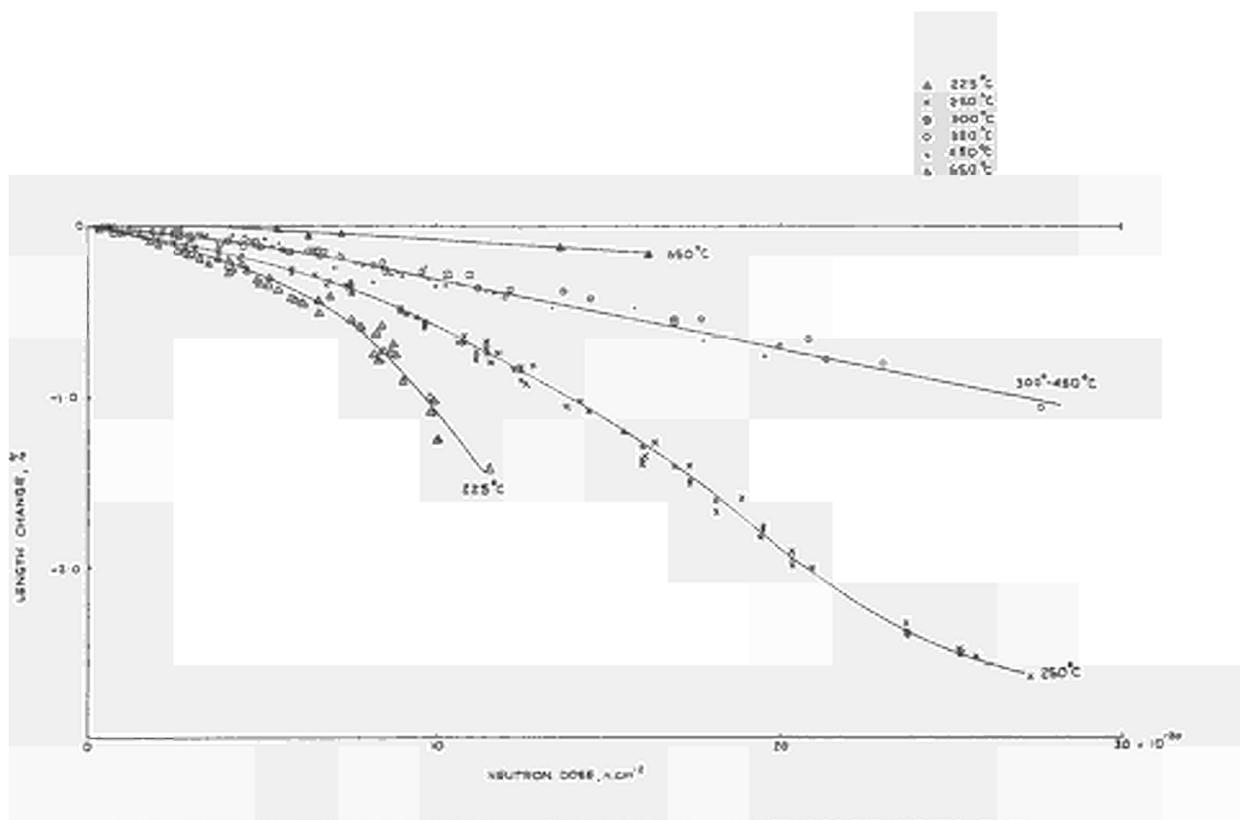


FIG 3 DIMENSIONAL CHANGES IN PILE GRADE A GRAPHITE PARALLEL TO EXTRUSION WITH NEUTRON DOSE.

From The effect of high-flux fast-neutron irradiation on the physical properties of graphite by H. BRIDGES, Miss HOLBY and Miss. McTIGUE - Reactor Materials Laboratories, Culcheth - FRG Report 567 (C)

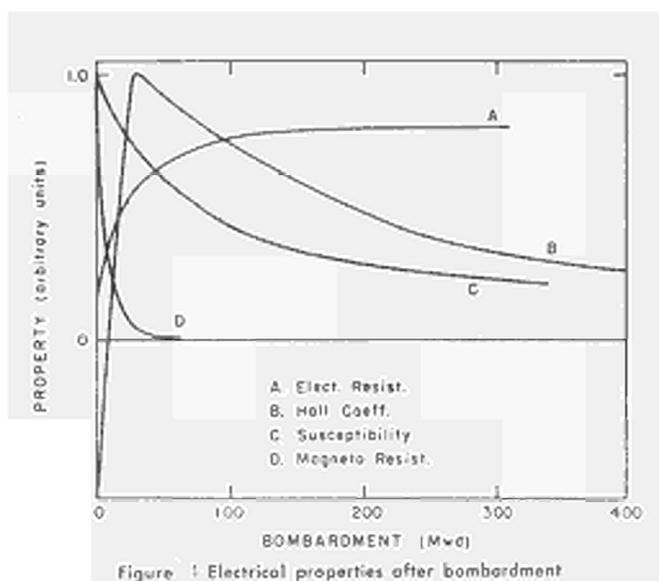


Figure 4 Electrical properties after bombardment

From Interpretation of radiation damage to graphite by Miss Leung and Miss Hove - Proceedings of the International Conference on the Peaceful uses of Atomic Energy - Vol. VII - 1/2/53 - p. 669

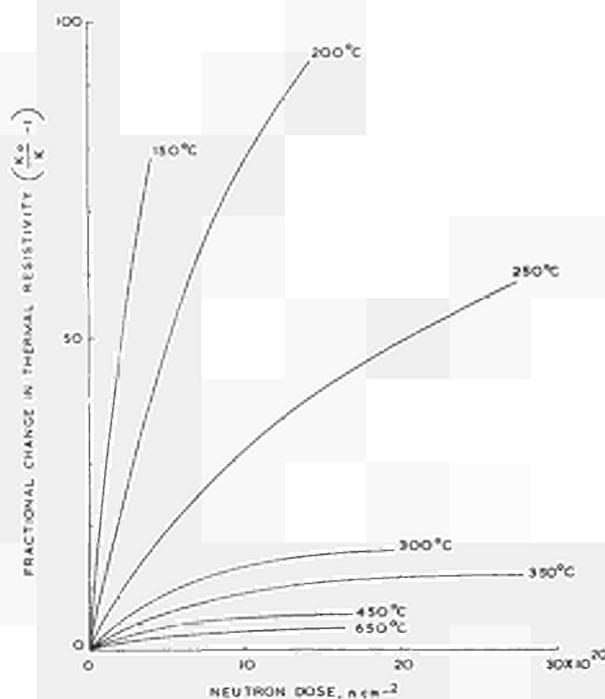


FIG 5 FRACTIONAL CHANGES IN THERMAL RESISTIVITY OF P.G.A.

GRAPHITE WITH NEUTRON DOSE

From the irradiation behaviour of graphite by J.E.W. Simons\*,  
B.T. Kelly†, P.T. Nettley† and W.N. Reynolds\*

\*UKAEA, Atomic Energy Research Establishment, Harwell, Berkshire

†UKAEA, Reactor Materials Laboratory, Culcheth, Warrington, Lancs. -

Third United Nations International Conference on the Peaceful Uses of  
Atomic Energy - May 1964 - A/CONF.28/P/163

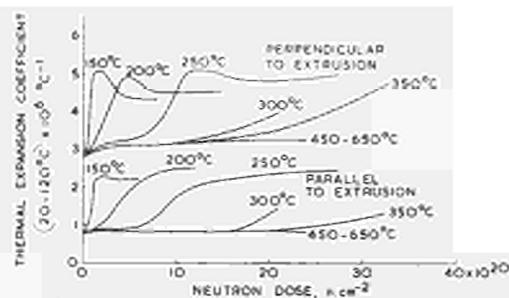


FIG 6 CHANGE IN THERMAL EXPANSION OF P.G.A. GRAPHITE  
WITH NEUTRON DOSE

From the irradiation behaviour of graphite by J.E.W. Simons\*,  
B.T. Kelly†, P.T. Nettley† and W.N. Reynolds\*

\*UKAEA, Atomic Energy Research Establishment, Harwell, Berkshire

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Atomic Energy - May 1964 - A/CONF.28/P/163

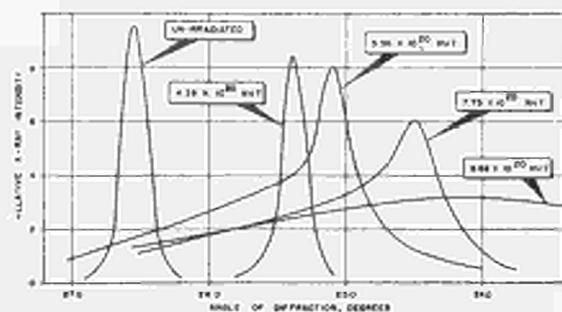


Figure 7 X-ray diffraction line shapes; graphite 002 reflection: effect from irradiation in cooled test holes

From Irradiation Damage to Artificial Graphite by G.K. Leeds, L.F. Bupp and J.W. Fletcher - Proceedings of the International Conference on the Peaceful Uses of Atomic Energy - Vol. VII - P/276 - p. 460

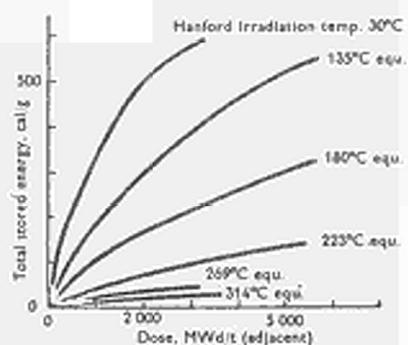


Fig. 8 - Accumulation of total stored energy.

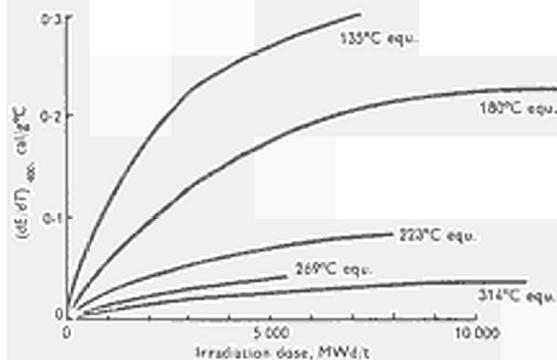


Fig. 9 - Increase of  $(dE/dT)_{eq}$  with irradiation dose.

From Stored energy in graphite on reactor design by G. Ridge, J.W. Kelly and G.W. Gray - Nuclear Engineering - Vol. 9 - March 1963 - p. 12

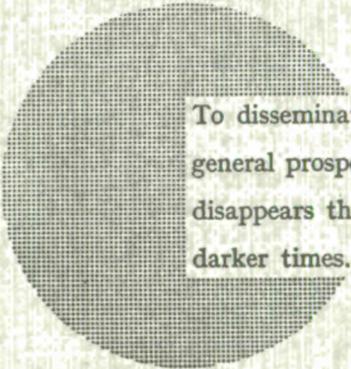
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**Alfred Nobel**

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