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REPORT ON SELECTION OF GRAPHITES

AND TESTING REQUIREMENTS

by

M W Davies

NNC Ltd, U.K.

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Summary

Graphite has been used as a neutron moderator and reflector in a variety of different reactors, and there has recently been a renewal of interest in High Temperature Reactors (HTRs) in the world. In particular the European Commission is supporting a number of projects for the development of HTR technology, with a view to creating the technological basis for an industrial emergence of HTRs in Europe by 2010.

Most of the available data on the irradiation behaviour of graphite have been obtained by irradiating small samples in MTRs. Unfortunately, most of the data have been obtained at temperatures <550^{o}C, whereas HTRs will be operating generally at temperatures >550^{o}C. In addition, almost all the graphites previously irradiated are no longer commercially available. As a result a planned irradiation programme of some of the currently available graphites is being undertaken for the European HTR project. This will allow the ‘best’ graphite(s) to be chosen, and provide all the data necessary to allow a full core design to be carried out.

Discussions have been held with three graphite manufacturers - UCAR Carbon, SGL and Toyo Tanso, to identify suitable candiate graphites from those currently available. Five graphites have been selected from those available, two made by UCAR Carbon, two made by SGL and one made by Toyo Tanso. These will be the main focus of the experiment. In addition, three ‘minor’ graphites have been selected, one from each manufacturer. These will be included as ‘piggy back’ samples in the experiment, and will give an early indication of their suitability for inclusion in further experiments.

The material supplied will be machined into ~150 small samples (8mm in diameter, 6 or 12 mm in length) for inclusion in a specially designed carrier. The graphites will first of all be pre-characterised by measuring specific properties on all (or some) of the samples. The carrier will be loaded into the HFR, and the samples irradiated to a low/medium fluence at a temperature of 750^{o}C. The carrier will be removed at the end of the irradiation period, and the properties of the samples remeasured. This work is being carried out under HTR-M1 as part of the 5th Framework Programme. It is hoped that further funding will become available under the 6th Framework Programme, to extend the irradiation to full life fluences and to irradiated the same graphites to full life fluences at different temperatures.

1 Introduction

Graphite has been used as a neutron moderator and reflector in a variety of different reactors. These include the Advanced Gas-cooled Reactors (AGRs), Magnox Reactors, High Temperature Reactors (HTRs), RBMKs, Research Reactors and Materials Testing Reactors (MTRs). The amount of nuclear grade graphite currently manufactured worldwide is relatively small, and broadly consists of graphite for AGR fuel sleeves and prototype HTRs (one in Japan and one in China). However, there has recently been a renewal of interest in HTRs in the world. The design of the Pebble Bed Modular Reactor (PBMR), led by ESKOM (South Africa), and the Gas-Turbine Modular Helium Reactor (GT-MHR) led by an international consortium (Russia, USA, France and Japan) are at an advanced stage. The European Commission is also supporting a number of projects for the development of HTR technology, with a view to creating the technological basis for an industrial emergence of HTRs in Europe by 2010.

The behaviour of graphite in a reactor environment has been extensively studied since the early 1940s and a good understanding of the significant and complex property changes which take place in the material has been gained. Most of the available data have been obtained by irradiating small graphite samples in MTRs. Unfortunately, almost all the graphites previously irradiated are no longer commercially available. In addition, most of the irradiation temperatures investigated will have been <550^{o}C, whereas for HTRs the graphite temperatures will generally be >550^{o}C. It is known that the behaviour of most graphites varies significantly with irradiation temperature and so it is important that data are obtained over the appropriate temperature range (a review of available data on the irradiation behaviour of different graphites at high temperatures was carried out in Ref. 1).

Therefore, in order to support the development of a future European HTR, it was first of all necessary to establish what graphites are currently available. From these, a number of suitable candidates would be selected for an irradiation programme in a high flux MTR. The irradiation programme will be aimed at providing data for these selected graphites over the appropriate irradiation fluence and temperature range as required by the core designer. The selection of candiate graphites and the initial phase of the irradiation programme is being carried out under HTR-M1 as part of the 5th Framework Programme. Both of these are discussed in this report.

2 Currently available graphites

As stated above, almost all the graphites for which irradiation data are available at high temperatures are no longer commercially available. It was therefore important to establish exactly what ‘suitable’ graphites are currently being produced, and which, if any, are under development. To do this it was necessary to visit the world’s two leading graphite manufacturers, namely UCAR Carbon and SGL. The meeting with UCAR Carbon took place at their Notre Dame plant in France on 26th March 2002. The meeting with SGL took place at their Chedde plant in France on 27th March 2002. The findings of the visit are covered below. In addition, discussions were held with staff from Japanese Atomic Energy Research Institute (JAERI) who are responsible for the Japanese HTR programme, and with the Japanese graphite manufacturer Toyo Tanso, who supplied the graphite for the HTTR.

2.1 UCAR Carbon graphites

UCAR use a particular nomenclature for the different graphite grades. The first two letters are UCAR's proprietary code for the coke type. The third letter is the forming method - E for Extrusion, M for Uniaxial Moulding and I for Isostatic Moulding. The fourth letter is the number of impregnations - A for 3, B for 2, C for 1, and D for 0 impregnations. Thus grade PPEA is made using a pitch coke by extrusion and has three impregnations. The following were put forward as potential graphite grades.

Grade	Coke type	Forming method
PPEA and PPEB	Pitch	Extrusion
PAEA and PAEB	Pitch	Extrusion
PCEA and PCEB	Petroleum	Extrusion
PCMA and PCMB	Petroleum	Moulding
PCIB and PCIC	Petroleum	Iso-moulding

The potential graphite grades cover the two most commonly used coke types, namely pitch coke and petroleum coke, and three forming methods, namely extrusion, moulding and iso-moulding. In addition, the number of impregnations range from one to three.

2.2 SGL graphites

The following were put forward as potential graphite grades.

NBG-10 (previously P3XA2N) is an extruded graphite which is an upgrade on the AGR fuel sleeve material. It is made using a Japanese pitch coke on the industrial scale, but has also been produced using a USA petroleum coke on the laboratory scale, and using a South African (Sasol) coke on an industrial scale (the latter produces an isotropic graphite but has too much boron).

NBG-25 (previously R6810) is an iso-statically moulded graphite made using a USA petroleum coke on an industrial scale.

NBG-20 is an extruded graphite made using a petroleum coke (this graphite was still under development when the meeting was held with SGL, it may become an economic alternative to NBG-10).

As with the UCAR potential graphite grades, the above cover the two most commonly used coke types, namely pitch coke and petroleum coke, but only two of the forming methods, namely extrusion, and iso-moulding.

2.3 Toyo Tanso graphites

The graphite used for the Japanese HTTR was IG-110, an iso-moulded graphite made by Toyo Tanso using a petroleum coke supplied by the Nippon Steel and Chemical Company (NSCC). It was pointed out that an improved iso-moulded graphite grade, IG-430 has been developed and was also available.

3 Graphite selection

3.1 Basis for selection

Ultimately, the selection of the 'best' graphite for the design of a reactor core will be based on a number of factors including dimensional change behaviour and changes in physical/mechanical properties with irradiation, impurity levels and production cost. However, for the purposes of the irradiation programme, it was decided that a range of graphites should be tested, and the selection based on raw materials, grain size and manufacturing methods only.

3.2 Selected graphites

Of the ten potential graphite grades manufactured by UCAR, the grades put forward for selection were PPEA, PAEA, PCEA and a super-fine grade of PCIB (PCIB-SFG). The quoted density and Young's modulus for all four graphites are similar. The largest difference was in the strengths (tensile, compressive, bend). The strengths of the first three (which are all extruded graphites) are reasonably similar, although the first two (made from pitch cokes) have higher strengths than the third (made from a petroleum coke). For the fourth, which is an iso-moulded graphite, the strengths are significantly higher than all three extruded graphites. It was decided that two graphites would be selected and it was agreed that these were PCEA and PCIB-SFG. Although both are made from a petroleum coke, one is an extruded graphite and the other is an iso-moulded graphite (which is also of interest due to it having a very small grain size). The important physical/mechanical properties for these two graphites are given in Table 1.

Of the three graphite grades put forward by SGL for selection, only two are currently being manufactured on a large scale. These are NBG-10 and NBG-25 (as stated earlier, the third grade, NBG-20 is being developed as an economic alternative to NBG-10). It was therefore decided that the two currently manufactured grades would be selected. This would provide an extruded graphite made from a coal tar pitch coke, and an iso-moulded graphite using a petroleum coke. The decision also took into account the risks associated with the third grade not being available in time. The important physical/mechanical properties for these two graphites are given in Table 2.

Of the two graphite grades put forward by Toyo Tanso for selection, it was decided that IG-110 should be included. The important physical/mechanical properties for these two graphites are given in Table 3. The decision was based on the fact that it has previously been irradiated at high temperature, although only to a small/medium fluence. Nevertheless, the available data will be extremely useful for comparison with the data obtained from the 5th Framework Programme experiment. The behaviour of the graphite will then, hopefully, be determined up to the full life fluence in the 6th Framework Programme.

3.3 Additional grades

Although five (major) grades of graphite have been selected for full testing in the experiment, it was decided that it would be useful to have an early indication of the irradiation behaviour of some of the other proposed graphites. These could be included as 'piggy-back' samples in the irradiation capsule (see section 4). The (minor) graphites selected are UCAR grade PPEA, SGL grade NBG-20 and Toyo Tanso grade IG-430.

3.4 Block sizes supplied

The ‘major’ graphites to be used in the experiment were supplied by UCAR, SGL and Toyo Tanso in the following block sizes:

PCIB-SFG:	three discs with diameter of 265 mm and height of 45 mm
PCEA:	three half-discs with original diameter of 465 mm and height of 45 mm
NBG-10:	block of dimensions 305 x 320 x 95 mm
NBG-25:	block of dimensions 520 x 200 x 130 mm
IG-110:	block of dimensions 400 x 200 x 100 mm.

The ‘minor’ graphites were supplied in the following block sizes:

PPEA:	three discs with diameter of 265 mm and height of 45 mm
NBG-20:	four discs with diameter of 110 and height of 296 mm
IG-430:	two blocks of dimensions 400 x 200 x 50 mm.

4 Graphite testing requirements

In order to provide a complete database on a particular graphite it is important to determine it’s behaviour over the full range of irradiation fluences and temperatures expected for the particular HTR core design. First of all it is necessary to pre-characterise the graphite i.e. determine the unirradiated properties. It is then necessary to determine how these properties vary with irradiation over the appropriate fluence and temperature range as required by the core designer. The testing requirements for each are covered below.

4.1 Pre-characterisation

The discs/blocks supplied are first of all sectioned and machined to produce the 150 or so samples to be included in the capsule. The samples will be cylindrically shaped with a diameter of 8 mm and a length of 6 or 12 mm. Each will be uniquely identified with suitable markings. The samples will be machined from both from the central region of each block as well as from the border of each block to allow the initial property variation as a function of position in the disc/block to be determined.

For the ‘major’ grades selected, ten samples of 6 mm in length and five samples of 12 mm in length, i.e. fifteen in total, will be produced for each direction (with grain and against grain). Therefore there will be a total of thirty samples for each ‘major’ grade. The number of samples of the ‘minor’ grades depends on the space in the irradiation rig, and if there are no ‘free’ spaces, might involve substituting one or two samples for each of the major grades.

The machined samples will be used to pre-characterise each graphite i.e. to obtain the unirradiated properties. The dimensions of the samples are measured together with Young's modulus, CTE and thermal conductivity. The mass of each sample will be measured, which together with the dimensions, will allow the initial density to be determined (clearly strength cannot be measured on the samples to be irradiated as this will involve a destructive test, nevertheless, strength measurements can be made on other suitable samples obtained from a block, and the strength distribution obtained should be representative of those which will be irradiated). Details of the testing methods to be adopted are given in Appendix A. The measurements will be recorded in tabular form in an electronic spreadsheet similar to the one shown in Table 4 (details of the proposed graphite database are given in Ref. 2).

4.2 Irradiation behaviour

As stated earlier, the irradiation behaviour of graphites is generally determined using high flux MTRs. The main reason is that they have much higher fast neutron fluxes than the (commercial) power reactors and therefore a lifetime's irradiation for a particular core design can be achieved in a fraction of the time. For this irradiation experiment, the small cylindrical graphite samples (8 mm indiameter, and 6 or 12 mm in length) are located in a special carrier, designed such that the graphite is maintained at the specified temperature.

Many irradiations in the past have been carried out in stages. After each stage, the carrier is removed and the graphite properties re-measured for each sample. For this experiment, the irradiation will be carried out in two stages. At the end of each stage the results will be recorded in tabular form in an electronic spreadsheet similar to the one shown in Table 5. The fractional changes in each property will then be calculated in an electronic spreadsheet similar to the one shown in Table 6. This will allow the property variations to be obtained over the full fluence range.

[Note - If it is not possible or practical to carry out the irradiation in stages, it will still be possible to obtain data over most of the fluence range by distributing the samples over the full height of the core and making use of the axial flux shape. At the end of the (single) irradiation period, the samples near the centre of the carrier will have reached the peak fluence, whereas the samples above and below will have received a progressively lower fluence, and those at the top and bottom will have received the lowest fluence.]

It was mentioned earlier that the properties of the graphites need to be determined over the appropriate range of temperatures. In order to maximise the number of graphites tested in this first irradiation experiment, and also to maximise the number of data points obtained for each of the graphites, it was decided that only one irradiation temperature will be used. The temperature chosen was 750^{o}C, and the carrier is being designed accordingly (in subsequent irradiation programmes, it is hoped that the graphites will be irradiated at other temperatures, and that other graphites can be irradiated as well).

5 Conclusions

Most of the available data on the irradiation behaviour of graphite have been obtained by irradiating small samples in high flux MTRs. Unfortunately, most of the data have been obtained at temperatures <550^{o}C, whereas in HTRs the graphite will be operating generally at temperatures >550^{o}C. In addition, almost all the graphites previously irradiated are no longer commercially available. As a result a planned graphite irradiation programme is being undertaken for the European HTR project. This will ultimately allow the 'best' graphite(s) to be chosen, and provide all the data necessary to allow a full core design to be carried out.

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6 References

Ref	Title
1	M W Davies and G Haag. State of the art review of graphite materials and behaviour. HTR-M-02/6-D-3.1.37. NNC Report C6463/TR/011
2	M W Davies Report on database of graphite properties for use by designers. HTR-M-02/06-D-3.1.22. NNC Report C6463/TR/012.

Table 1 Typical properties of selected UCAR Carbon graphites

Property - Typical average		Units	Petroleum coke	
			Extruded	Iso-moulded
			PCEA	PCIB-SFG
Apparent density		g/cm^3	1.83	1.86
Young's modulus	WG	GPa	11	12
	AG	GPa	10	
Tensile strength	WG	MPa	20	43
	AG	MPa	16	
Flexural strength (4-point)	WG	MPa	26	53
	AG	MPa	23	
Compressive strength		MPa	67	98
Ceofficient of thermal expansion 20 - 100^{o}C (20 - 1000^{o}C)	WG	10^{-6}/K	5.1 (3.8)	5.4 (4.1)
	AG	10^{-6}/K	5.6 (4.3)	
Thermal conductivity		W/mK	165	120
Anisotropy factor			1.13	< 1.07

Table 2 Typical properties of selected SGL graphites

Property - Typical average		Units	Coal tar pitch coke	Petroleum coke
			Extruded	Iso-moulded
			NBG-10	NBG-25
Apparent density		g/cm^3	1.80	1.81
Young's modulus	WG	GPa	10.0	9.9
	AG	GPa	9.8	10.9
Tensile strength	WG	MPa	19	
	AG	MPa	20	
Flexural strength (4-point)	WG	MPa	27	44
	AG	MPa	27	48
Compressive strength		MPa	60	95
Ceofficient of thermal expansion 20 - 200^oC	WG	$10^{-6}/K$	4.2	4.3
	AG	$10^{-6}/K$	4.5	3.9
Thermal conductivity	WG	W/mK	155	112
	AG	W/mK	161	126

Table 3 Typical properties of selected Toyo Tanso graphites

Property - Typical average		Units	Petroleum coke	Coal tar pitch coke
			Iso-moulded	Iso-moulded
			IG-110	IG-430
Apparent density		g/cm^3	1.77	1.82
Young's modulus	WG	GPa	9.7	10.8
	AG	GPa		
Tensile strength	WG	MPa	29	37
	AG	MPa		
Flexural strength (4-point)	WG	MPa	40	52
	AG	MPa		
Compressive strength		MPa	79	90
Ceofficient of thermal expansion	WG	$10^{-6}/K$	4.1	4.2
	AG	$10^{-6}/K$		
Thermal conductivity		W/mK	130	145
Anisotropy ratio			1.07	1.10

Table 4 Recording of unirradiated sample dimensions/properties

Graphite materials property database

Direction: Perpendicular (Against grain)

Graphite: PPEA
Manufacturer: UCAR
Coke: Pitch
Grain size: Fine
Process: Extrusion

Rig location	Specimen code	Unirradiated properties							
		Length Lo (cm)	Diameter Do (cm)	Volume Vo (cm3)	Mass Mo (g)	Density ρo (g/cm3)	Young's modulus Eo (GN/m3)	CTE αo (x10-6/oC)	Thermal conductivity Ko (W/m/oC)

Table 5 Recording of irradiated sample dimensions/properties

Irradiation temperature (oC)	Dose EDND (x10E22)	Irradiated properties							
		Length L (cm)	Diameter D (cm)	Volume V (cm3)	Mass M (g)	Density ρ (g/cm3)	Young's modulus E (GN/m3)	CTE α (x10-6/oC)	Thermal conductivity K (W/m/oC)

Table 6 Calculation of fractional changes in sample dimensions/properties

Fractional change							
Length (L/Lo-1)	Diameter (D/Do-1)	Volume (V/Vo-1)	Mass (M/Mo-1)	Density (ρ/ρo-1)	Young's modulus (E/Eo-1)	CTE (α/αo-1)	Thermal conductivity (K/Ko-1)

Appendix A - Pre-characterisation measurements and testing methods

1 Introduction

This Appendix describes the measurements and testing methods to be used to pre-characterise the selected graphites.

2 Measurements and testing methods

2.1 Dimensions

Both length and diameter of the samples are measured using inductive tracers. The measuring range of the tracers is 4 mm, within this range the accuracy of the tracers is within 1 µm. All measurements are performed relative to a gauge length. The length measurements are carried out with a flat tracer head (flat disc, 11.3 mm in diameter). The diameter measurements are carried out by putting the samples in a V-notch to centre the tracer compared to the full diameter of the cylindrical sample. The diameters are measured by a spherically shaped tracer head with a diameter of 1.5 mm.

2.2 Density

To calculate the dynamic Young’s modulus from the sound velocity and to calculate the thermal conductivity from the thermal diffusivity, the density is needed. The density is obtained by accurately measuring the mass of the sample and using the results from the dimension measurements to calculate the volume.

2.3 Dynamic Young’s Modulus

The Dynamic Young’s Modulus (E) is determined by an ultrasonic sound measurement based on ASTM C769-80. E is related to the sound velocity according:

$$E = \frac{(1+\upsilon)(1-2\upsilon)}{(1-\upsilon)}\,\rho\, v^2$$

where v is the Poisson’s ratio, ρ the density and v the sound velocity.

The measurements are performed with 5 MHz transducers. Both transmitter and receiver have rubber heads and therefore no liquid coupling medium is needed. The measurements are performed under constant contact force and a correction is made to subtract the propagation time through the rubber transducer heads.

(Note - The ultrasonic sound velocity measurements have been cross-checked with those obtained by BNFL at their Berkeley Centre, UK.)

2.4 Coefficient of Thermal Expansion

The length of the sample as a function of temperature is measured in the temperature range of 30°C to 750°C. In this temperature range the average linear thermal expansion coefficient can be determined by:

$$\alpha(T_1, T_2) = \frac{1}{l_1} \cdot \frac{l_2 - l_1}{T_2 - T_1} = \frac{1}{l_1} \cdot \frac{\Delta l}{\Delta T}$$

where l_1 is the length at temperature T_1 and l_2 is the length at temperature T_2

Measurements are performed in a dilatometer that works according the common standards, such as DIN 51045, ASTM E 831, ASTM E 228.

The sample is contained in an Al_2O_3 sample holder that is put in a vacuum tight furnace to allow measurements in a 100% Helium environment. The length change is transmitted by a push-rod, that is pushing at to sample with a force of 30 cN, to an electronic measurement system outside the furnace. The sensitivity of the LVDT is 1.25 nm/digit. The support of the transducer is kept at a constant temperature by a thermostat bath with an accuracy of ± 0.01K. The furnace heating is controlled by measuring the temperature near the sample, resulting in linear heating of the sample. The accuracy of the temperature control is better than 0.5°C.

The average linear expansion coefficient is calculated by taking in to account the length changes of the sample holder and the push-rod.

2.5 Thermal Conductivity

The thermal diffusivity is measured by the laser pulse method described by ASTM C714 and DIN 51 936. A sample is placed in a furnace at a constant temperature. The front face of this sample is exposed to a short laser pulse. This creates a temperature pulse that is travelling through the sample. The thermal diffusivity is obtained from the thickness of the sample and from the increase of temperature as a function of time at the backside of the sample.

A Nd-YAG laser is used (wavelength is 1.06 µm) to produce a laser pulse. The pulse duration can be varied between 0.2 to 20 µs and the pulse energy can be varied between 0 to 70 J. In practice the pulse duration is between 0.5 and 1 µs and the pulse energy is between 2 and 6 J. The temperature increase at the backside of the sample is measured by a thermocouple as a function of time and loaded in an oscilloscope. The temperature versus time curve is transferred to a PC and automatically analysed to calculate the thermal diffusivity. The measurements are performed between room temperature and 700°C.

From the thermal diffusivity a, the thermal conductivity λ, can be calculated if the density ρ and specific heat C_p of the sample are known using the following equation:

$$\lambda = a \rho C_p$$