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Report on XRD on low dose irradiation experiment at 750°C

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Summary

In the European graphite irradiation programme, the irradiation behaviour of modern graphite grades is investigated at two irradiation temperatures, 750°C and 950°C. Following up on the irradiation experiments performed in the HTR-M and RAPHAEL projects, a low dose irradiation experiment at 750°C was performed to investigate materials properties changes induced by neutron irradiation. This report describes the X-Ray Diffraction measurements performed on a selection of samples from the low dose irradation experiment.

Approval

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INNOGRAPH-1C PIE

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Summary

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1 Introduction

Graphite is a suitable material to be used as a neutron moderator and reflector in nuclear reactors. Graphite has been used in Advanced Gas-Cooled Reactors, Magnox reactors, RBMK's (a Russian acronym meaning "reactor cooled by water and moderated by graphite"), Research Reactors, Materials Test Reactors and High Temperature Reactors (HTR's). Since the end of the 20th century there has been a renewed interest in HTR's. Two prototypes, one in Japan (HTTR) and one in China (HTR-10) are in operation. A demonstration plant is under construction in China (HTR-PM). The Next Generation Nuclear Plant NGNP in the US is in development. The European Commission is supporting research projects for the development of HTR technology to determine the technological requirements for designing and constructing an HTR in Europe.

Much research has been done on the behaviour of graphite grades in a nuclear reactor environment, because graphite is already being used in reactors for decades. However, these graphite grades are no longer commercially available since the raw materials no longer exist. In addition, most data from the past are from low temperature experiments (<550°C), whereas for HTR's the graphite temperatures will generally be higher than 550°C. In order to be able to design a European HTR, it was decided by the European commission to create a database that contains data of the materials behaviour of available graphite grades under neutron irradiation at temperatures relevant for the HTR's. This will allow the 'best' graphite(s) to be chosen, and provide the necessary data to allow the core design to be carried out.

The irradiation behaviour of HTR graphite grade candidates is investigated in the European programme on High Temperature Technology, started in 2001. Within the HTR-M1 and RAPHAEL-IP framework, graphite irradiation experiments were performed at 750°C and 950°C in the High Flux Reactor (HFR) in Petten. These were named INNOGRAPH-1B (750°C, high dose), INNOGRAPH-2A (950°C, medium dose) and INNOGRAPH-2B (950°C, high dose). In every experiment a few graphites were also irradiated at lower temperatures of 650°C (in the 1B) and 850°C (in the 2A and 2B). Figure 1-1 shows schematically the volume change of graphite with neutron fluence at the two main irradiation temperatures. The boxes on the curves indicate the five different irradiation experiments. Box 1A indicates the low dose irradiation at 750°C named INNOGRAPH-1A. This has been performed within HTR-M1 in the 5th Framework Programme and had a target dose of 8 dpa [1]. Box 1B indicates INNOGRAPH-1B, the high dose (up to ~25 dpa) experiment at the same temperature. Boxes 2A and 2B indicate the medium and high dose experiments at 950°C, INNOGRAPH-2A and INNOGRAPH-2B respectively. Results of these experiments are reported in [2]. Box 1C indicates the low dose irradiation experiment at 750°C, called INNOGRAPH-1C, that is performed in the framework of the ARCHER project. In this report, the results of X-Ray Diffraction (XRD) measurements on a selection of samples from the INNOGRAPH-1C experiment are presented. The XRD measurements comprise determination of coherence length (indicative for crystallite size) and lattice parameters.

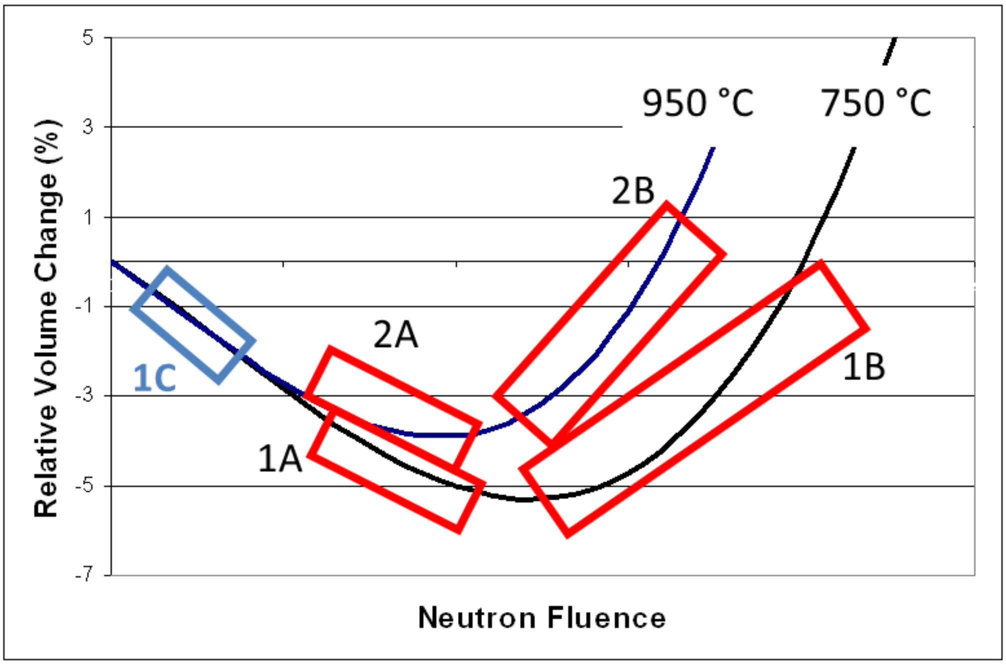

Figure 1-1 Schematic overview of the five INNOGRAPH irradiation experiments

2 Experiment and measurement technique

2.1 Irradiation experiment

2.1.1 Graphite grades

The INNOGRAPH-1C is a follow-up experiment of the INNOGRAPH-1A and -1B experiments. Therefore, graphite grades are selected based on their presence in these preceding experiments [3]. The selection of the graphite grades for the INNOGRAPH irradiation experiments is based on several factors such as thermal and mechanical properties, impurity levels and availability [1]. The four major grades, produced by SGL Carbon and Graftech are chosen in such a way that the graphites cover a variety of microstructures. This is achieved by selecting grades based on different raw materials, i.e. coal tar pitch coke or petroleum coke, and different manufacturing methods, i.e. extrusion, isostatic-moulding or fibro-moulding.

The minor grades include graphites from three different manufacturers, SGL Carbon, Graftech and Toyo Tanso. The minor grades include iso-moulded graphites and graphites based on needle coke. The graphites used in the experiments are listed in Table 1.

Next to the major and minor grades that also were presented in the preceding irradiation experiments, a number of “specials” were present in the INNOGRAPH-1C. These include fuel matrix material supplied by Furnaces Nuclear Applications Grenoble (FNAG), graphite grades supplied by GrafTech and SGL, and Highly Oriented Pyrolitic Graphite (HOPG).

Table 1 Overview of the graphite grades selected for the INNOGRAPH-1C irradiation experiment

Grade	Manufacturer	Coke	Process	Major/minor
NBG-10	**SGL**	**Pitch**	**Extrusion**	**Major**
NBG-18	**SGL**	**Pitch**	**Vibro-moulding**	**Major**
PCEA	**GrafTech**	**Petroleum**	**Extrusion**	**Major**
PPEA	**GrafTech**	**Pitch**	**Extrusion**	**Major**
IG-110	Toyo Tanso	Petroleum	Iso-moulding	Minor
IG-430	Toyo Tanso	Pitch	Iso-moulding	Minor
LPEB/BAN	GrafTech	Needle	Extrusion	Minor
LPIB	GrafTech	Needle	Iso-moulding	Minor
NBG-17	SGL	Pitch	Vibro-moulding	Minor
NBG-20	SGL	Petroleum	Extrusion	Minor
NBG-25	SGL	Petroleum	Iso-moulding	Minor
PCIB	GrafTech	Petroleum	Iso-moulding	Minor

2.1.2 Specimen geometry

All specimens loaded in the INNOGRAPH experiments are cylindrical. The diameter of all specimens is 8 mm and the length is 6 mm. Specimens of these sizes are small enough to allow a sufficient number of specimens in the irradiation rig, and large enough to perform reasonably accurate measurements. The specimens are suitable for all type of measurements (dimensional changes, dynamic Young's modulus, coefficient of thermal expansion and thermal diffusivity).

The cylindrically shaped specimens are flattened by milling a plane with a width of 3 mm along the length. Figure 2-1 schematically shows the flattening. Producing a plane with a width of 3 mm mills only 1% of the volume of the cylinders. The benefits of this plane are threefold. The first benefit is the possibility to indicate the z-direction from the original graphite blocks in the specimen. The plane is milled perpendicular to the *z*-direction if the axial direction of the cylinder is parallel to the *xy*-direction, and therefore the *z*-direction in the specimen is known after fabrication. The plane is milled on an arbitrary position if the axial direction of the cylinders is parallel to the *z*-direction, because in that case the *z*-direction is already indicated by the axial direction.

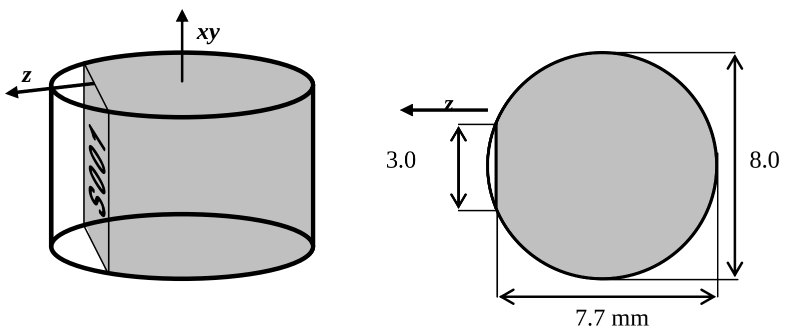

Figure 2-1 Flattening of the specimens. The figure on the left-hand side exaggeratedly shows the flatting of the cylinder. The figure on the right-hand side is a top-view of the specimen

The second benefit of the plane is that it gives an area to engrave the specimen with a unique code. This code is necessary to easily identify a specimen. The code consists of four characters. The code is formed by three numbers and one letter. The letter indicates the graphite manufacturer (S= SGL, U= UCAR (Graftech) and T= Toyo Tanso). The letter Z is used for a number of special samples by various manufacturers.

A third benefit is that the milled plane can act as a marking that defines the measuring positions during the dimensional measurements before and after irradiation.

2.1.3 INNOGRAPH-1C low dose irradiation experiment at 750°C

The INNOGRAPH-1C rig consists of a stack of eight TZM (0.5Ti, 0.08Zr, 0.42 Mo) drums that are used as specimen-holders (Figure 2-2). The rig contained seven drums with a height of 60 mm and one drum with a height of 30 mm. In each drum, three channels are present to contain the samples. In between drums, a thin graphite foil is placed to prevent specimens moving axially into the drum below. The high density of TZM makes it possible to reach the required nominal temperature of 750°C. Because of the relatively low neutron flux in the top drum, this drum cannot reach the 750°C. However, this drum is still usable to irradiate graphite specimens at a slightly lower temperature. The top drum is separated from the drums below by a thermal barrier and is designed to have a temperature of 650°C. For the rest of the rig the design temperature is 750°C. The capsule is instrumented with 24 thermocouples that are placed on different radial and axial positions to monitor the temperature during irradiation. Temperature was controlled by changing the He/Ne gas mixture in the second containment and the vertical displacement of the experiment in the reactor core. The temperature was controlled for the 750°C drums; the temperature for the top drum at 650°C is not controlled.

In the centre of each drum a hole was drilled to place neutron fluence detector sets. Five fluence detector sets were distributed axially over the rig with TZM fillers in between. Four fluence detector sets are distributed radially in two drums to monitor the radial gradients. The detector sets are analysed after the experiment to determine the neutron fluence.

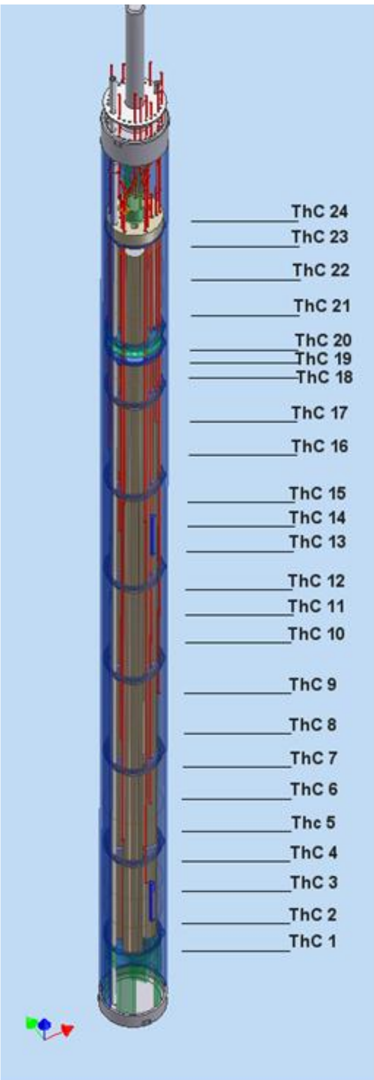

Figure 2-2 Drawing of the INNOGRAPH-1C irradiation rig

2.2 X-Ray Diffraction

2.2.1 Test matrix

Table 2 shows the samples selected for the X-Ray Diffraction (XRD) measurements. For each selected graphite grade, two samples are selected. Selected samples for each grade have as large a difference in dpa as possible. The neutron metrology data taken from the flux detector sets was not available yet for this report. Therefore, the dpa values are the a priori calculated dpa values.

Table 2 XRD test matrix for INNOGRAPH-1C samples

Specimen code	Grade	Location	Orientation	calc. dpa
0S25	NBG-10	heart	AG	1.3
0S27	NBG-10	heart	AG	2.2
1S01	NBG-17	heart	WG	1.6
1S02	NBG-17	heart	WG	2.1
2S00	NBG-18	heart	WG	1.5
2S01	NBG-18	heart	WG	2.2
0U30	PCEA	heart	AG	1.4
0U32	PCEA	heart	AG	2.2
1U05	PCIB	heart	AG	1.4
1U07	PCIB	heart	AG	2.2

2.2.2 X-Ray Diffraction

Graphite has a hexagonal crystal structure. Literature values [4] for the graphite lattice parameters are a = 2.461 Å and c = 6.708 Å, with 4 carbon atoms in the unit cell (Figure 2-3).

The XRD measurements were performed using a Bruker D8 Advance powder diffractometer. Measurements are performed in θ-2θ configuration.The 2-theta measurement range used for the measurements was 15-90° with a step size of 0.05°.

The EVA software package (Bruker) was used to determine position, peak height, and full width at half maximum (FWHM) of the (002) and (110) peaks in the XRD spectra of the graphite samples. From the FWHM values the coherence lengths in the {002} and {110} directions were derived. The coherence length can be regarded as but is not equivalent to the crystallite size in given lattice directions.

For determination of the lattice parameters from the XRD spectrum the software package TOPAS (Bruker) was used by making a whole pattern fit with the “Pawley” method. Determined parameters are the lattice parameters *a* and *c*. The TOPAS software was also used to determine the “zero error”in the XRD setup by evaluating measurements on the silicon SRM640c NIST standard.

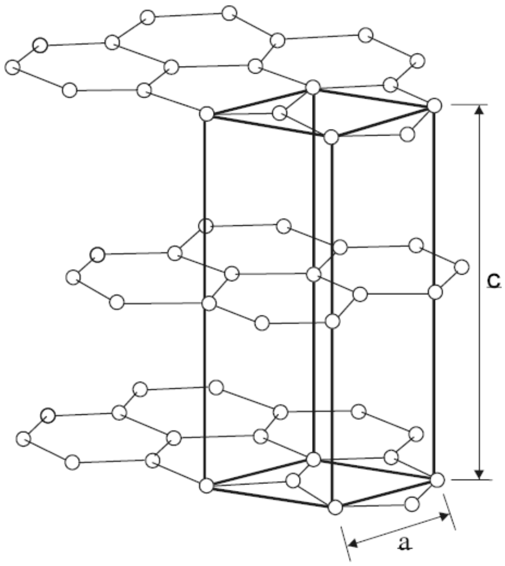

Figure 2-3 Crystal structure of graphite

3 Results

The results of the calibration and reference measurements is presented in Table 4 and Table 5 in Appendix A.

XRD measurements have been performed on virgin samples of the grades under investigation in this report in a Dutch government subsidised internal NRG project in 2008-2009. These measurements are used for 0 dpa reference values and presented in Table 6 in Appendix A. The reference measurements were made without the sample placement tools used for the current study. Thus, results show large spread in between measurements on samples of the same grade and are indicative.

The lattice parameters and coherence lengths for the INNOGRAPH-1C samples are presented in Table 3. Figure 3-1 and Figure 3-2 show graphically the results of the determination of the lattice parameters. In general, the *c*-axis expands upon irradiation. Changes in *a*-axis are too small with respect to uncertainty in fitting the peaks in the XRD spectra to discern an upward or downward trend. Results for the coherence lenghts are shown graphically in Figure 3-3 and Figure 3-4. In both *a*- and *c*-direction, the coherence length is reduced for all graphite grades. This may be attributed to the disorder in the lattice structure caused by the neutron-carbon interaction.

Table 3 Results of the XRD measurements on graphite samples taken from the INNOGRAPH-1C low dose irradiation experiment

Specimen code	Grade	Location	Orientation	Calc. dpa	Lc [nm]	La [nm]	c [Å]	a [Å]
0S25	NBG-10	heart	AG	1.3	22.032	33.727	6.748	2.457
0S27	NBG-10	heart	AG	2.2	19.961	29.636	6.751	2.456
0U30	PCEA	heart	AG	1.4	23.564	32.371	6.747	2.458
0U32	PCEA	heart	AG	2.2	21.420	31.595	6.754	2.457
1S01	NBG-17	heart	WG	1.6	20.007	30.762	6.755	2.455
1S02	NBG-17	heart	WG	2.1	18.567	29.228	6.756	2.454
1U05	PCIB	heart	AG	1.4	22.263	28.744	6.752	2.456
1U07	PCIB	heart	AG	2.2	20.246	28.209	6.755	2.455
2S00	NBG-18	heart	WG	1.5	19.592	34.395	6.758	2.455
2S01	NBG-18	heart	WG	2.2	17.941	29.062	6.752	2.454

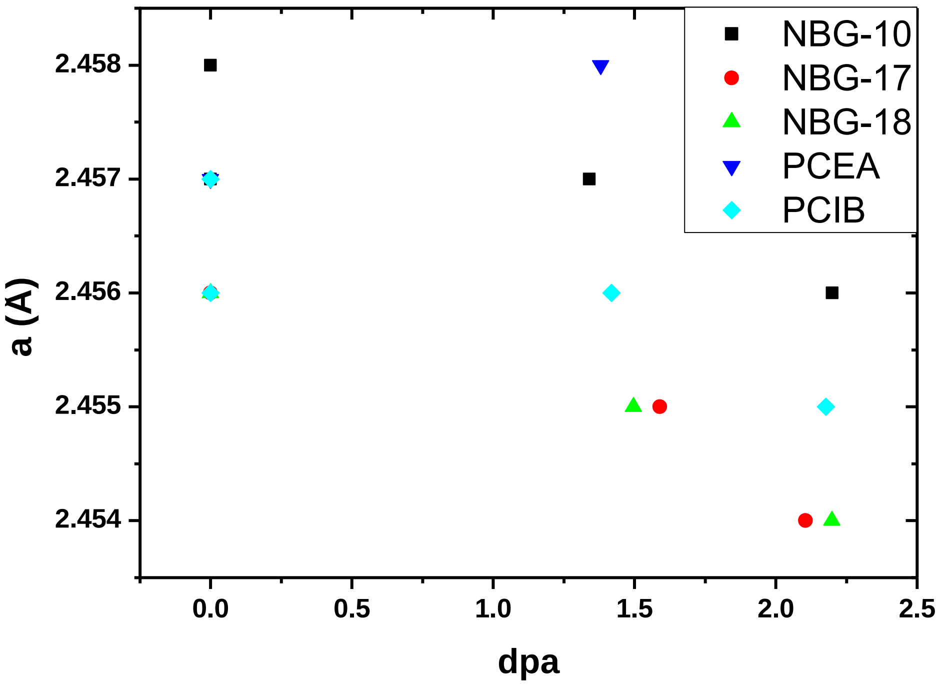

Figure 3-1 Unit cell axis *a* versus dpa

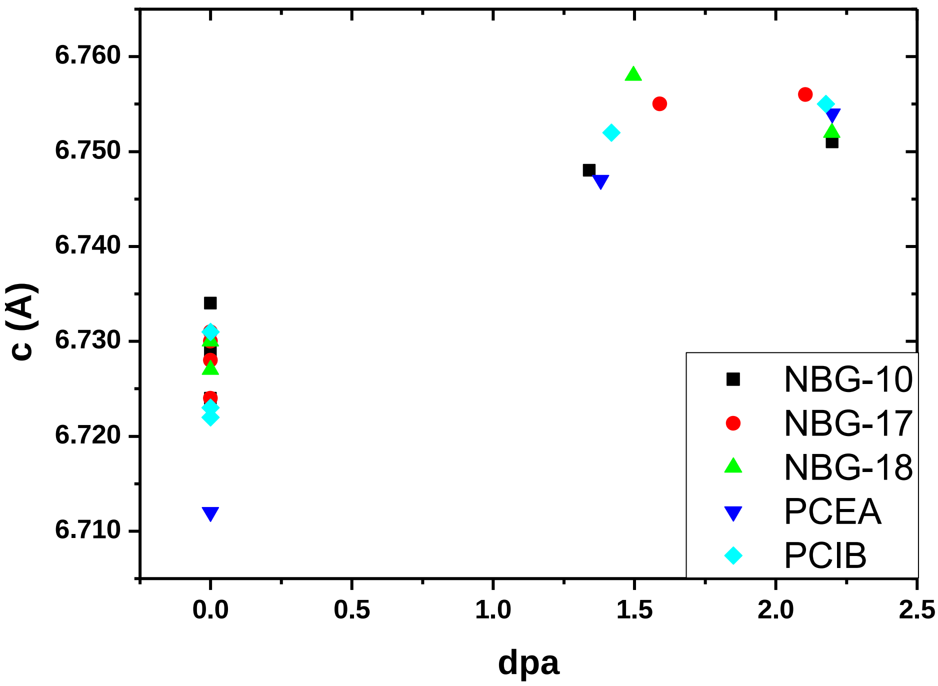

Figure 3-2 Unit cell axis *c* versus dpa

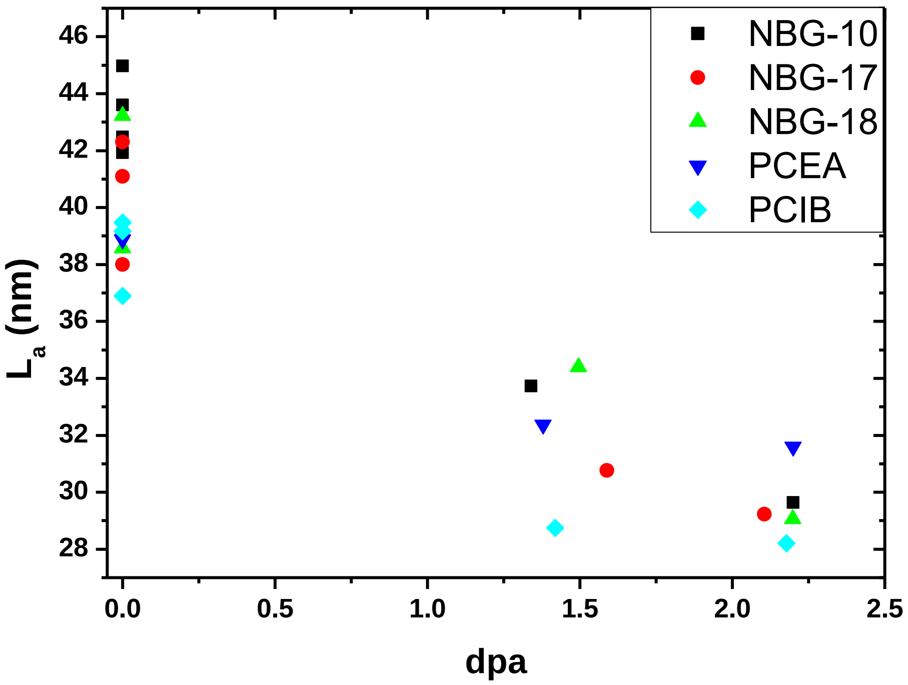

Figure 3-3 Coherence length L_a versus dpa

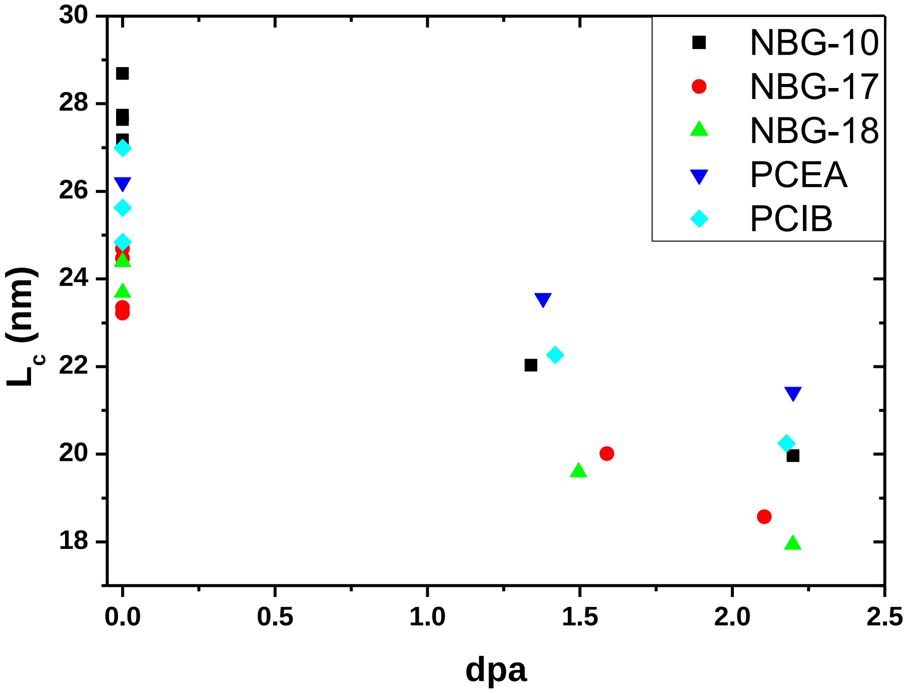

Figure 3-4 Coherence length L_c versus dpa

4 Conclusion

XRD measurements have been performed on graphite samples irradiated in the INNOGRAPH-1C low dose experiment. Results show changes in lattice parameters and coherence length. In general, the *c*-axis expands upon irradiation, while *a*-axis changes lie within the measurement uncertainty. The neutron damage causes the X-Ray coherence length to be reduced in both *a*- and *c*-direction.

5 References

[1] F. Schmalz et al., *Preliminary irradiation testing of selected graphite grades for HTR, Final report on HTR-M1 WP3*, NRG-20787/05.71179/P, 19 December 2005

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[3] M.C.R. Heijna, *D41.13 Final Design Proposal Low Dose Irradiation*, NRG-22906/12.114053, 24 April 2012

[4] R.E. Nightingale (editor), *Nuclear Graphite*, Academic Press, 1962

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Appendix A Calibration and reference measurements

Table 4 Results of the calibration measurements on aluminium oxide. Measurements are within the allowable error margin with respect to the theoretical values

Measurement	2θ		2θ	
	Measured	Theoretical	Measured	Theoretical
Before campaign	35.145	35.149 ± 0.005	127.684	127.680 ± 0.010
After campaign	35.146	35.149 ± 0.005	127.678	127.680 ± 0.010

Table 5 Results of the measurements on the silicon NIST reference sample to determine the zero-error

Measurement	2θ	FWHM	2θ	FWHM	Zero-error
Before campaign	28.441	0.070	76.372	0.075	0.048
After campaign	28.441	0.068	76.372	0.079	0.047
Averaged values		0.069		0.077	0.048

Table 6 XRD measurements on virgin graphite samples, performed as part of a Dutch government internal NRG project in 2008-2009.

Specimen code	Grade	Location	Orientation	Lc [nm] (hkl=002)	La [nm] (hkl=110)	c [Å]	a [Å]
U426	PCEA	edge	WG	26.206	38.875	6.712	2.457
S344	NBG-10	edge	WG	27.734	42.478	6.729	2.458
S368	NBG-10	edge	AG	27.639	44.976	6.729	2.458
S374	NBG-10	heart	WG	27.171	43.595	6.734	2.458
S393	NBG-10	heart	AG	28.691	41.920	6.724	2.457
S572	NBG-17	edge	AG	24.467	42.301	6.730	2.456
S581	NBG-17	edge	WG	23.217	37.992	6.724	2.456
S603	NBG-17	heart	WG	23.348	39.015	6.731	2.456
S616	NBG-17	heart	AG	24.689	41.088	6.728	2.456
S515	NBG-18	heart	WG	23.687	43.224	6.727	2.456
S525	NBG-18	heart	AG	24.393	38.569	6.730	2.456
U168	PCIB	heart	AG	26.990	39.164	6.731	2.457
U186	PCIB	edge	AG	25.624	39.478	6.723	2.456
U194	PCIB	edge	WG	24.839	36.891	6.722	2.456