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Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

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First structural data of virgin and irradiated graphite before treatment

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Document title
First structural data of virgin and irradiated graphite before treatment

Executive summary

This work package task focuses on the changes in graphite structure by irradiation and before treatment and will assist in determine the graphite final waste form behaviour by cross-linking several techniques such as Raman microspectrometry, Transmission Electron Microscopy, Scanning Electron Microscopy, confocal scanning microscopy and X-ray Diffraction. These techniques allow study to be undertaken near the atomic scale. Additional experiments are now initiated by combined Raman mapping, scanning electron microscopy and optical microscopy in order to distinguish between the binder and the filler in the nuclear graphite. The observation of the nanostructural changes caused by the ion beam irradiation at the surface or near the surface (implantation depth about 1 μm) however, was not easily achievable by the conventional techniques such as hand grinding, ultramicrotomy and mechanical abrasion or ion thinning.

The process which provided a great advance in the study of the ion-implanted graphite was the use of thin sections prepared by the Focused Ion Beam (FIB) technique. By using thin sections prepared by FIB technique, it was possible to image directly, for the first time, the structural modification due to implantation at the nanometre scale; this can be considered as a great improvement in the characterization of the ion-implanted graphite.

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1 Structural characterisation before irradiation and treatment

1.1.1 Microscopy studies

This task focuses on the changes in graphite structure before irradiation which may determine the graphite final waste form behaviour. Contributions to this report are extensive and inputs have been received from: CEA, ENRESA, ENS, IPNL and UoM. These combined efforts give a comprehensive understanding of any structural changes before irradiation and finally, of irradiated graphite waste before.

In order to study the structural modifications and to correlate them with the long term behaviour, it is necessary to address adapted analytical methods, which aid understanding, giving the scientific basis of the mechanism corresponding to the observed behaviour.

The contribution in Task 3.2 from *CIEMAT* (Partner 7) in CARBOWASTE program focuses on the structural characterisation of virgin and irradiated nuclear graphite using in order to understand the structure character of irradiated graphite. Porosity measurements have been performed in order to calculate the particle size distribution and specific surface area, Typical UNGG graphite samples show a range in specific surface area from 6.8 – 12 $m^2 g^{-1}$. The graphite samples exhibit a varied particle size distribution between 20 – 100 μm^{-1} which is typical of a nuclear graphite grade[1].

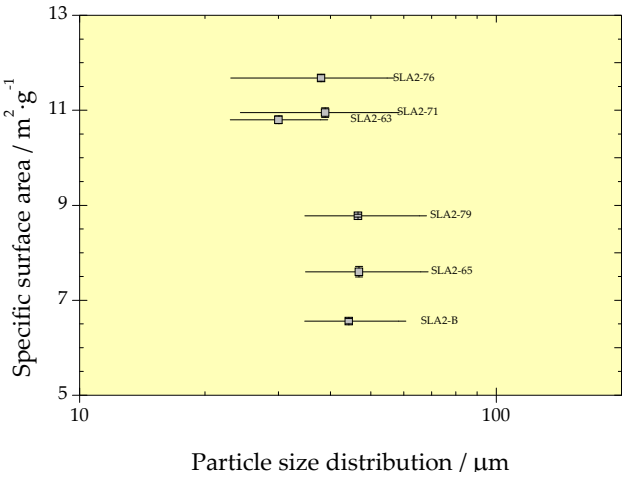

Figure 1: Particle size distribution of UNGG typical of a nuclear graphite grade.

1.1.2 X-ray Diffraction before Treatment

X-ray Diffraction has been used to determine the crystallite size of the materials. Typical MTR (JEN_A, JEN_B) graphite exhibit a crystallite size in the region of 300-314Å, and UNGG graphite is smaller at 187 - 287Å, this is expected as the small isotopic coke particles are used in the manufacturing of new MTR graphite grades.

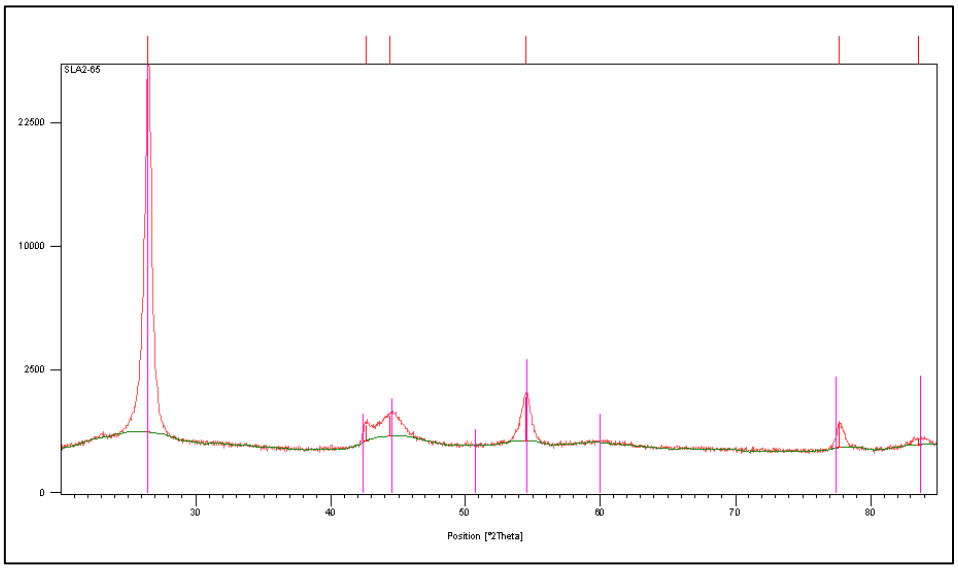

Figure 2: XRD analysis of UNGG typical of a nuclear graphite grade

The contribution of the *University of Manchester* (UoM, Partner 27) in CARBOWASTE program focuses on the structural characterisation of virgin and irradiated nuclear graphite using none destructive techniques such as Polarised optical microscopy, Focused Ion Beam-Scanning electron microscopy, Raman spectroscopy, X-ray Tomography, Scanning Electron Microscopy and X-ray Diffraction.

The UoM have undertaken detailed polarised microscopy on virgin and neutron irradiated graphite including PGA, NBG10, NBG18, AGR, Pechiney, and BEPO in order to understand irradiation damage to the graphite structure in addition to Raman spectroscopy in order to understand the structural changes in graphite before and after irradiation damage and before any treatment.

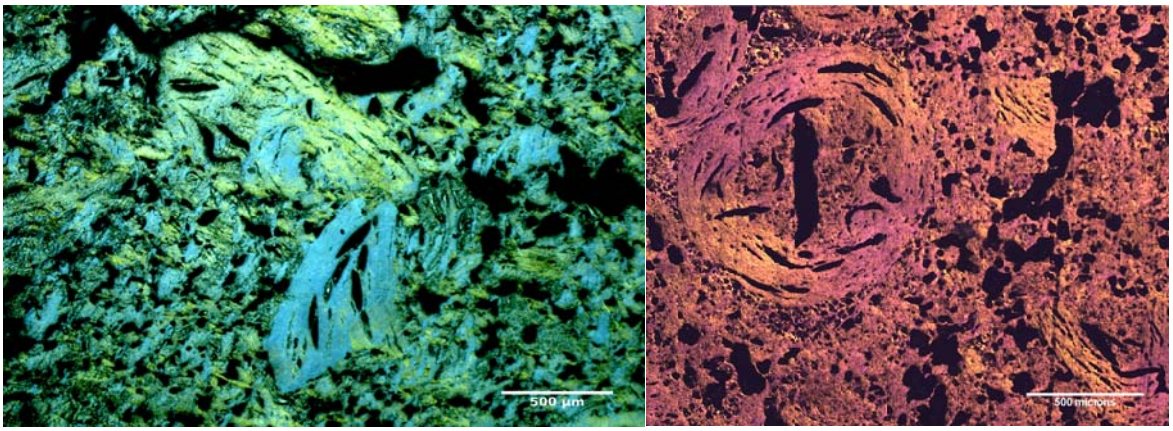

Figure 3: polarised microscopy on virgin (a) PGA Magnox and (b) Gilsocarbon AGR graphite before irradiation

1.1.3 Confocal Microscopy

Confocal microscopy is an optical imaging microscope that increases optical resolution and contrast of a micrograph by using point illumination and a spatial pinhole to eliminate out-of-focus light in specimens that are thicker than the focal plane. This enables the reconstruction of three-dimensional structures from the obtained optical and laser images. Confocal microscopy has a XY resolution down to 100 nm and a Z resolution 10 nm resulting in SEM scale accuracy being achieved. The 3D surface analysis technique allows material texture mapping and roughness analysis to be determined with a +/- 2% accuracy on measured values. This technique was used to investigate the pore structure present within BEPO graphite at increasing levels of irradiation damage. Figures 4 shows the types of images collected in the raw format prior to the 3D reconstructed image show in figure 5.

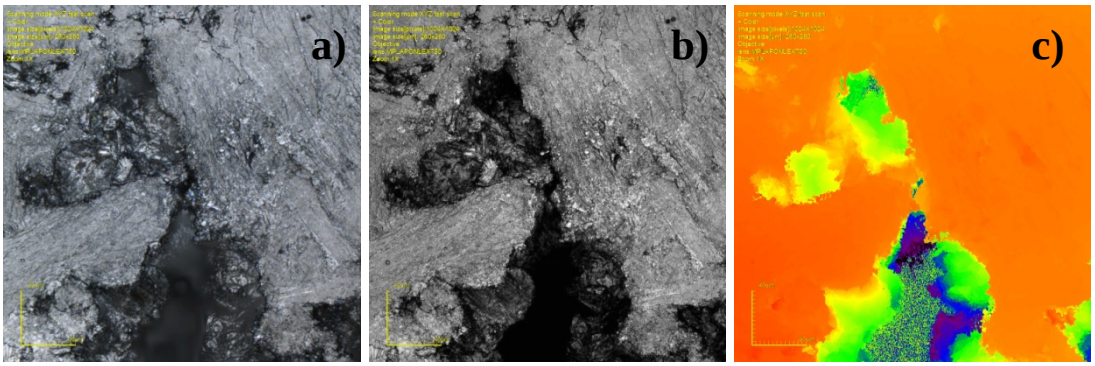

Figure 4 Shows three images collected by the confocal microscope. This allows a comparison between a) microscope, b) laser and c) height images collected by the microscope. Reconstruction of this data is used to produce a 3D profile for the material.

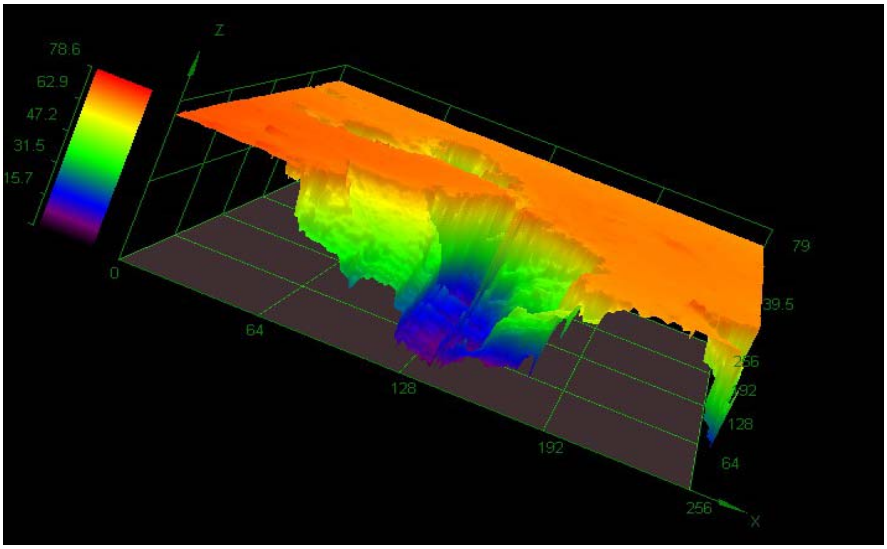

Figure 5 shows a 3D depth profile of porosity within the BEPO graphite. The pore depth is approx 60 microns and the scale bar is in microns.

1.1.4 RAMAN Spectroscopy

Raman spectroscopy is a technique which relies on the inelastic (Raman) scattering of light by the molecules within a material and is therefore, a non-destructive technique. In carbon materials[2]. Raman is used to determine the degree of crystallinity ranging from poorly ordered carbon to high order in graphite and diamond [3-9]. Principally, when a monochromatic beam of light impinges on a sample, a fraction of the light is scattered. The majority of this scattered light is elastically scattered, however, a small fraction is scattered at wavelengths different to that of the incident beam due to inelastic scattering. This change in frequency is called the Raman Effect [8]. The

resulting Raman spectrum corresponds to a particular bonding assignment. It is useful in the analysis of carbon- carbon bonding as one can ascertain information such as bonding type (sp^2/sp^3), structural characterisation, phase purity and crystallite size from the Raman spectrum.

The assignment of the band or peaks in the Raman spectrum is relatively straightforward in carbon materials and gives an insight into the molecular structure of carbon [10-11]. The G peak (located at 1580cm^{-1}) is dominant in single crystalline graphite and is due to the bond stretching of all sp^2 atoms both in the aromatic rings and chains. This peak typically exhibits a FWHM (Full Width at Half Maximum intensity) value less than 20cm^{-1} and is accompanied by the second harmonic (2D) at 2700cm^{-1} which is indicative of highly crystalline graphite[9]. In polygranular graphite and baked carbon material there is a D-peak present around 1350cm^{-1}.[9] This is assigned to the breathing node of disordered sp^2 atoms in rings and may increase in intensity relative to the G-peak with decreasing crystallite size

The degree of disorder within graphite has been studied by Tunstra and Koening [10] and noted the ratio of the D-peak intensity to that of the G-peak varied inversely with crystallite size (L_a), where crystallite size was obtained from the FWHM of x-ray diffraction peaks:

$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a} \quad \textbf{(1)}$$

Where C is the bond force constant of 4.4 nm at λ=514.5nm

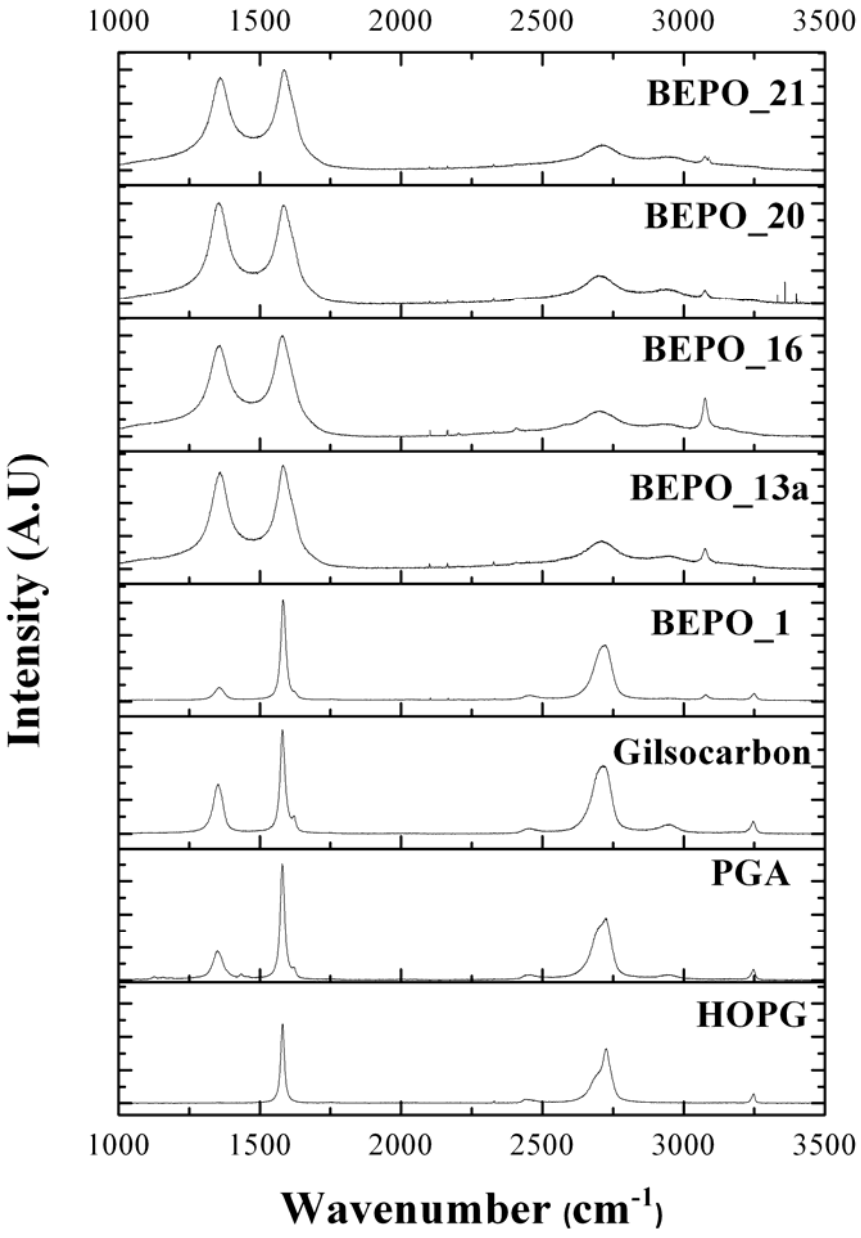

FIGURE 5- Raman Spectra of various nuclear graphite grades including UK grades and UK irradiated BEPO graphite.

Figure 5 shows the Raman spectra of several polygranular nuclear graphites and irradiated nuclear graphite from the British Experimental Pile grade Zero (BEPO)

reactor. A reduction in the G-peak intensity relative to virgin graphite and low irradiation BEPO graphite is evident with increasing fluence. The FWHM of the G-peak also increases in graphite samples which have undergone fast neutron irradiation. The irradiated graphite samples also show the magnitude of the D-peak increases with increasing fluence. This is indicative of increased structural disorder from the presence of both sp^2 and amorphous sp^3 carbon phases. The general behaviour of unirradiated polycrystalline nuclear graphite is that the FWHM is less than $20cm^{-1}$ and the $I_{(D)/(G)}$ ratio is below one. Neutron irradiated samples show larger values both in terms of FWHM and $I_{(D)/I(G)}$ ratio, similar to the baked graphite, coke and glassy carbon in which the crystal structures also exhibit a degree of disorder.. These methods are now being used to quantify the effects of fast neutron irradiation and graphite manufacture on crystallite size and order/disorder within graphite crystals after treatment.

The Raman spectra of several polygranular nuclear graphites and irradiated nuclear graphite from the British Experimental Pile grade Zero (BEPO) reactor have been obtained and show a reduction in the G-peak intensity relative to virgin graphite and low irradiation BEPO graphite is evident with increasing fluence. The FWHM of the G-peak also increases in graphite samples which have undergone fast neutron irradiation. The irradiated graphite samples also show the magnitude of the D-peak increases with increasing fluence. This is indicative of increased structural disorder from the presence of both sp^2 and amorphous sp^3 carbon phases. Figure 6 shows the Raman G-peak FWHM as a function of the $I_{(D)/(G)}$ ratio for various graphite and coke materials. Results from this group are compared with those of Knight and White[11].

The highly ordered pyrolytic graphite (HOPG) shows little peak broadening and is directly comparable with that of Knight and White.

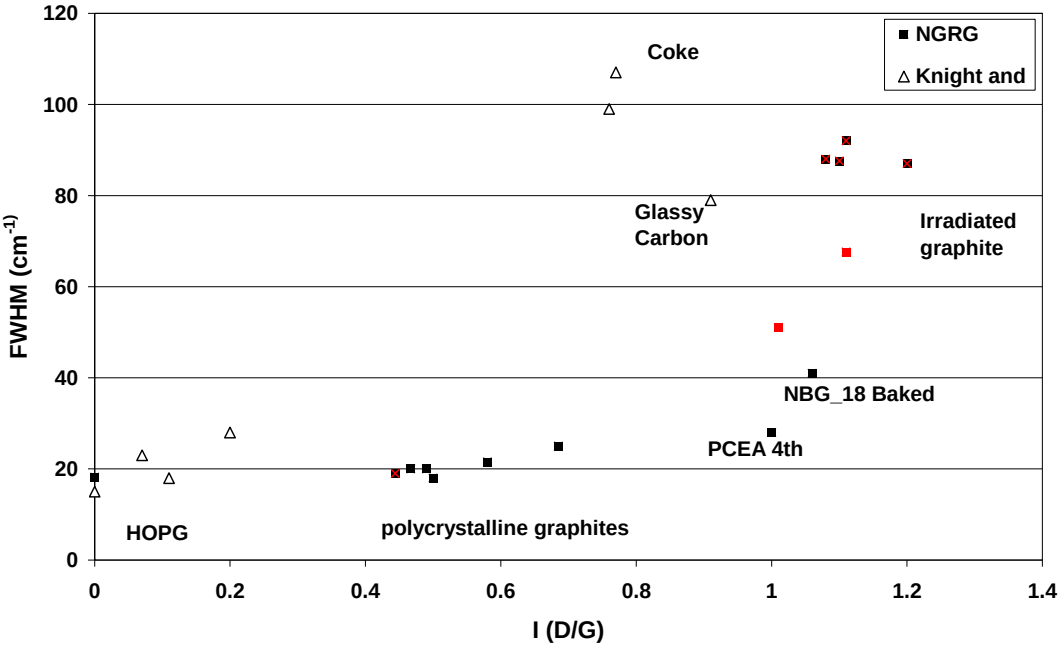

Figure 6: - Raman ratio of I(D)/(G) against Full width half maximum of the G-peak to show the structural disordered of various nuclear graphite grades including VHTR grades and UK irradiated BEPO graphite.

Neutron irradiated samples show larger values both in terms of FWHM and I(D)/I(G) ratio, similar baked graphite, coke and glassy carbon. These methods are now being used to quantify the effects of fast neutron irradiation and graphite manufacture on crystallite size and order/disorder within graphite crystals by the UoM.

Principally, ENS's work started by characterizing the virgin nuclear graphite of Saint Laurent des Eaux, France (SLA2) using Raman microspectrometry[12, 13]. This

technique was particularly attractive due to the high spatial resolution (~ 1 µm) achieved and that Raman provides less averaged information, in comparison with X-ray diffraction (XRD). Moreover, analyses were quick, operationally straightforward, non-destructive and requiring minimal sample preparation.

Compared to a single crystal of graphite (as for the Highly Oriented Pyrolytic Graphite (HOPG)), Raman spectrum of nuclear graphite exhibited additional bands labelled D for “Defect” bands, which are known to be characteristic for finite crystals of graphite. The polarization of the laser spot was used to distinguish preferentially oriented from randomly oriented crystals. Our result ensured that the nuclear graphite is composed of small crystallites more or less randomly oriented in the area of the laser spot. This aspect has been confirmed by X-ray Diffraction analyses.

Raman mapping of virgin nuclear graphite was performed, using the structural parameter R_2, (D_1 area relative to the whole bands area). Compared to HOPG, virgin nuclear graphite featured a clear repartition on the defect band area. This showed the heterogeneity of the nuclear graphite, at a micrometric scale, in terms of the organization degree. This variation could be directly related to the composition of the nuclear graphite consisting in two main phases: the binder (coal-tar pitch) and the filler (petroleum coke) heated at 2800°C. Petroleum cokes are generally the more graphitizable of the two, and this aspect could give a noticeable decrease of the defect bands in Raman spectrum. Additional experiments are now initiated by combined Raman mapping, scanning electron microscopy and optical microscopy in order to distinguish between the binder and the filler in the nuclear graphite.

In order to select any treatment option for irradiated nuclear graphite, it is necessary to obtain a comprehensive understanding of the character in terms of the nanostructure of raw and modified graphite. Ion irradiation beam (implantation) may provide an effective way of the structural modification of graphite, where the structural defect could be similar to those induced by neutrons irradiations at varying fluences and temperatures. Moreover, such implantation can introduce a wide range of defects in a controlled manner.

Raman analyses showed an increase of defect bands with fluence in room temperature conditions, resulting in a disorder increase in the graphitic structure, until a complete amorphization for higher fluences characterized by an asymmetric broad single band. Compared to X-ray diffraction, Raman microspectrometry appears as particularly sensitive to both the disorder and the amorphization, and may be achieved on very small volumes of matter (less than 0.1 μm^3).

A more interesting finding occurred when we implanted the nuclear graphite at various temperatures. At high implantation temperatures (up to 600°C), the defect band in Raman spectrum decreased significantly suggesting that graphite defects recombine as fast as they form.

1.1.5 Transmission Electron Microscopy

Analysis from Transmission electron microscopy (TEM) showed particularly interesting findings, in particular the 002 lattice fringe (LF) mode that allowed a direct imaging of

the polyaromatic layers profile and consequently the access to the multiscale organization in the nanometer-micrometer range. The observation of the nanostructural changes caused by the ion beam irradiation at the surface or near the surface (implantation depth about 1 μm) however, was not easily achievable by the conventional techniques such as hand grinding, ultramicrotomy and mechanical abrasion or ion thinning. The process which provided a great advance in the study of the ion-implanted graphite was the use of thin sections prepared by the focused ion beam (FIB) technique. In fact, its very important benefit was the easy and direct control of the choice of the area, the sample orientation according to the beam and the specimen thickness during ion milling (less than 100 nm that making it electrons transparent). By using thin sections prepared by FIB technique, we were be able to image directly, for the first time, the structural modification due to implantation at the nanometre scale; this can be considered as a great improvement in the characterization of the ion-implanted graphite[13].

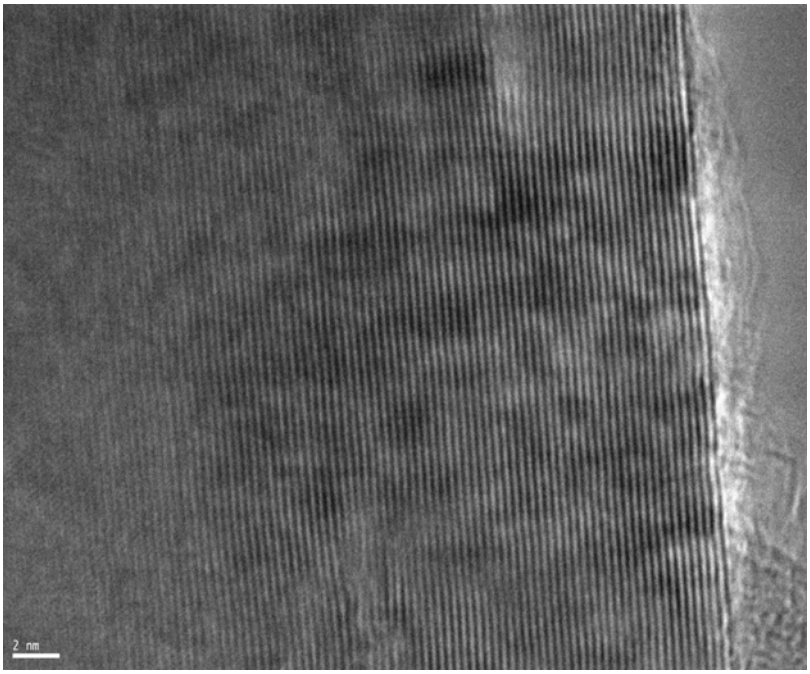

Figure 7: TEM of UNGG graphite prepared by FIB

The results shown in Figure 7 display a dramatic change of the polyaromatic layers organization at the surface, where the density of ^{37}Cl implantation was maximal. The graphite structure was strongly damaged without being completely amorphous: only short nanometer sized fringes forming small BSU (stacks of 2-3 layers) were visible and these stacks were strongly disoriented, losing the lamellar nanostructure of the virgin graphite. Geometrically speaking, such cross-linked BSUs form nanopores that could be considered as potential sites for radionuclides trapping.

The decrease of L_a, the coherent domain (BSU) diameter was also confirmed after ion beam irradiation by the measurement of the rotation moirés fringes in the 11DF dark field images, which was in perfect correlation with Raman results.
As we expected, the nanometer scale examination appeared extremely important to explore as it was planed at the beginning within the framework of Carbowaste program, based on our knowledge in carbon materials.

Irradiated graphite studies have recently begun on G2 samples issued from the nuclear reactor of Marcoule, France. The nuclear graphite was irradiated at a temperature close to 300°C. Compared to virgin graphite characterized by a weak defect band, Raman spectrum of irradiated graphite shows a slight increase of this later. This aspect has been confirmed by TEM observations with the 002 LF mode, for which the polyaromatic layers were slightly distorted. We attributed this relatively weak

structural degradation of this irradiated graphite (about 4dpa) to the irradiation temperature.

presently, our experiments are in progress to study other irradiated graphite depending on their location in the UNGG reactor (which were submitted to other irradiation degrees and/or temperatures), and from other types of reactors. For this, a HRTEM image analysis will be used to acquire more quantitative structural data.

2 Summary

Very good progress on the characterisation of structural changes in virgin and irradiated graphite before treatment has been undertaken in the first 19 months of the CARBOWASTE project. This work package task had focused on the changes in graphite structure by irradiation and before treatment. Techniques such as Raman microspectrometry, Transmission Electron Microscopy, Scanning Electron Microscopy, confocal scanning microscopy and X-ray Diffraction have been cross-linked not only with work carried out from individual partners but through the comparison of data between partners within WP3. These techniques have enabled the WP3 members to study graphite from the atomic scale to the microscale and will assist in determine the graphite final waste form behaviour.

Additional experiments are now initiated by combined Raman mapping, scanning electron microscopy and optical microscopy in order to distinguish between the binder and the filler in the nuclear graphite. The process which provided a great advance in the study of the ion-implanted graphite was the use of thin sections prepared by the

Focused Ion Beam (FIB) technique. By using thin sections prepared by FIB technique, it was possible to image directly, for the first time, the structural modification due to implantation at the nanometre scale; this can be considered as a great improvement in the characterization of the ion-implanted graphite.

Finally Raman spectroscopy studies between WP3 members shows a clear difference is observed between highly ordered polycrystalline graphite, virgin and irradiated graphite, thus Raman is an effective tool in analysing damage caused to the microstructure by neutron irradiation before treatment.

Publications resulting from this work:

- Ammar, M.R., et al., Characterization of graphite implanted with chlorine ions using combined Raman microspectrometry and transmission electron microscopy on thin sections prepared by focused ion beam. Carbon, 2009. 48(4): p. 1244-1251.
- Vaudey, C.E., et al., Thermal behaviour of chlorine in nuclear graphite at a microscopic scale. Journal of Nuclear Materials, 2009. 395(1-3): p. 62-68.
- Jones, A.N., et al., *Microstructural characterisation of nuclear grade graphite.* Journal of Nuclear Materials, 2008. **381**(1-2): p. 152-157.
- Jones A N, McDermott L, Marsden B J and Wickham A J. Characterisation of Irradiated Graphite Waste in Reactor Decommissioning, Carbon2009. June 2009 (conference paper)

- Marsden B J., Hall G N, Jones A N, Marrow T J. The Life Cycle of Nuclear Graphite in Generation Iv High Temperature Reactors ESIA10. Manchester UK, May 2009(conference paper)

- Jones A N, McDermott L, Marsden B J, Marrow T J. "Characterisation of Irradiated Nuclear Graphite Waste". 7th EPRI International Decommissioning and Radioactive Waste Workshop (in collaboration with EDT-CIDEN), Lyon. October 2008 (conference paper)
- Jones, A.N., et al, The Study of Irradiation Damage in Reactor graphite using High Resolution Transmission Electron Microscopy and RAMAN Spectroscopy (*In preparation for publication)*

3 References

1. Nightingale, R.E., *Nuclear Graphite*. 1962, New York: Academic Press.
2. Solin, S.A. and R.J. Nemanich, *First and Second order Raman scattering from finite-size crystals of graphite.* Physics Review, 1979. **B20**: p. 392.
3. Cancado, L.G., et al., *General equation for the determination of the crystallite size L[sub a] of nanographite by Raman spectroscopy.* Applied Physics Letters, 2006. **88**(16): p. 163106.
4. Ferrari, A.C., *Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects.* Solid State Communications, 2007. **143**(1-2): p. 47-57.

5. Ferrari, A.C. and J. Robertson, *Interpretation of Raman spectra of disordered and amorphous carbon.* Journal of Physics Review B, 2000. **61**: p. 14095-14107.
6. Lee, Y.-J., *The second order Raman spectroscopy in carbon crystallinity.* Journal of Nuclear Materials, 2004. **325**(2-3): p. 174-179.
7. Matthews, M.J., *Origin of dispersive effects of the Raman D band in carbon materials.* Physical Review B - Condensed Matter and Materials Physics, 1999. **59**(10).
8. Nemanich, R.J. and S.A. Solin, *Observation of an anomolously sharp feature in the 2nd order Raman spectrum of graphite.* Solid State Communications, 1977. **23**(7): p. 417-420.
9. Thomsen, C. and S. Reich, *Double Resonant Raman Scattering in Graphite.* Physical Review Letters, 2000. **85**(24): p. 5214.
10. Tuinstra, F. and J.K. Koeing, *Raman Spectrum of Graphite.* The Journal of Chemical Physics, 1970. **53**(3): p. 1126-1130.
11. Knight, D.S. and W.B. White, *Characterization of diamond films by Raman spectroscopy.* journal of Materials Research, 1989. **4**(2): p. 385 - 392.
12. Ammar, M.R., et al., *Characterization of graphite implanted with chlorine ions using combined Raman microspectrometry and transmission electron microscopy on thin sections prepared by focused ion beam.* Carbon, 2009. **48**(4): p. 1244-1251.
13. Vaudey, C.E., et al., *Thermal behaviour of chlorine in nuclear graphite at a microscopic scale.* Journal of Nuclear Materials, 2009. **395**(1-3): p. 62-68.