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Thermal and Structural Properties of Irradiated Graphite from the ASTRA Research Reactor - Implications for Disposal

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ABSTRACT

The release of Wigner energy from ASTRA research reactor graphite has been studied by simultaneous differential scanning calorimetry / synchrotron powder x-ray diffraction between 25 ^{o}C and 525 ^{o}C at a heating rate of 10 ^{o}C.min^{-1}. With decreasing distance from the reactor core, samples from the inner thermal column exhibited Wigner energies from 50 to 600 J.g^{-1} and an increasing degree of crystal structure swelling. The crystal structure of the two closest-to-core samples was fully amorphous. Treatment of irradiated graphite in order to remove the Wigner energy (or significant portions of it) prior to interim storage should be considered.

INTRODUCTION

Storage of energy in form of lattice defects, known as Wigner energy, in graphite irradiated by fast neutrons at low temperatures is a well-known phenomenon[1]. Uncontrolled release of Wigner energy can, under certain conditions, lead to the ignition of the material. This has in fact occurred at the Windscale Pile 1 reactor in 1957[2]. The ASTRA reactor – a 10 MW light water moderated and cooled pool type research reactor in operation in Seibersdorf, Austria, between 1960 and 1999 – is undergoing decommissioning[3]. The entire reactor block will be dismantled. The resulting material is to be either free released (cleared), *e.g.*,

concrete from the top section of the reactor block where activation and/or contamination is not expected, or handled as radioactive waste, conditioned, and placed in interim storage on site. (Incidentally, following decontamination, the reactor building will be used as an interim radioactive waste storage facility.) The material that will have to be conditioned and stored includes approximately 10 tons of reactor grade graphite from the inner and outer thermal columns of the reactor. Over the 40 years of reactor operation, the graphite has been exposed to an estimated integrated fast-neutron flux of 2 x 10^{21} n.cm^{-2}. Since the temperature of the graphite never exceeded 100 ^{o}C, annealing of lattice defects did not occur and the accumulation of significant amounts of Wigner energy is to be expected. The activity of the main slow-neutron activation product, ^{14}C, in the graphite from the inner thermal column, based on measurements of graphite from the outer thermal column, is no lower than 1000 Bq/g, with other radionuclides, e.g., ^{60}Co and ^{152}Eu, present in trace amounts.

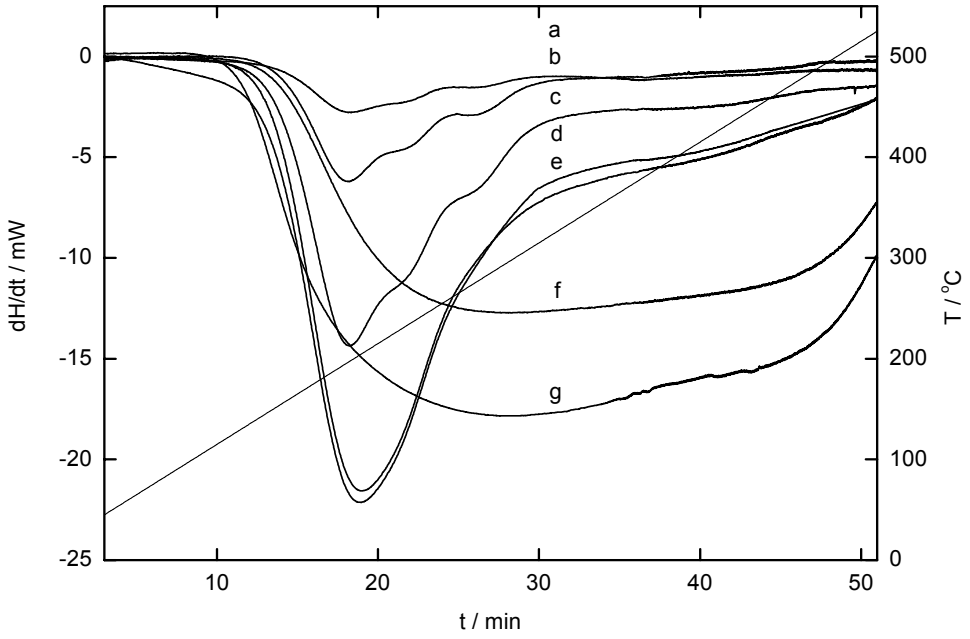
To support the conditioning, interim storage, and final disposal of nuclear graphite, it is necessary to quantify the Wigner energy content of the material and to understand the release of Wigner energy in a variety of relevant scenarios, such as slow, low-temperature cycles driven by the exothermic curing of the grout encountered in storage or faster, high-temperature ramps emulating the thermal conditioning of the material. In addition to addressing these practical concerns, there is the possibility of gaining deeper insight into the Wigner energy phenomenon *per se*. This is due, in particular, to the availability of integrated neutron flux data for any position within the graphite thermal columns. Because of the gradual decay of the neutron flux with distance from the reactor core, samples of graphite exhibiting a wide range of irradiation histories are available. Hence, the amount of Wigner energy, its release kinetics, and associated crystal structure changes can be studied as a function of integrated neutron flux (fluence).

EXPERIMENTAL

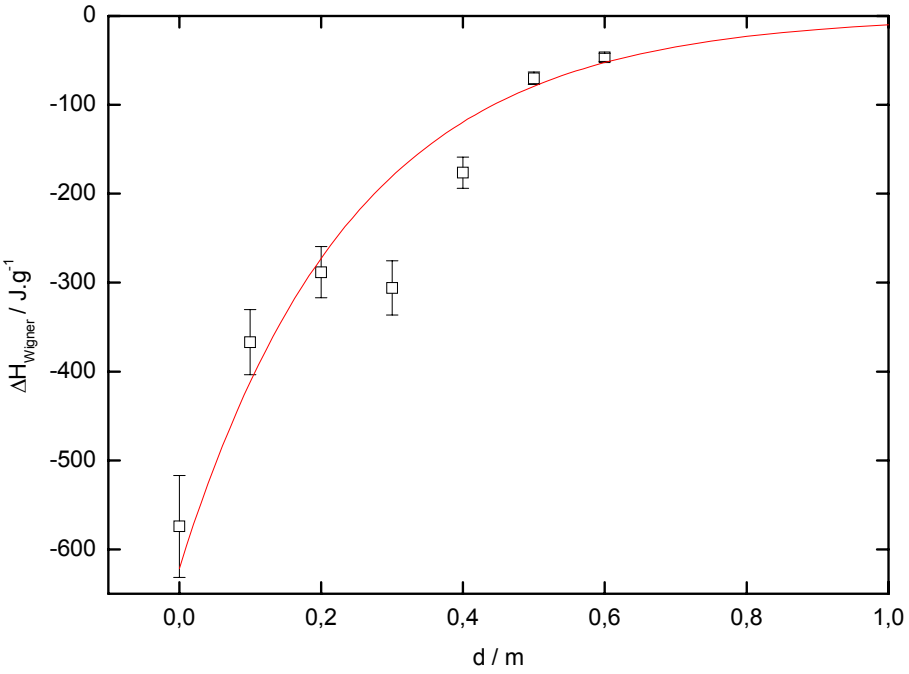
DSC is a standard thermal analysis method widely applied to study processes in materials accompanied by heat evolution or absorption. The sample is typically subjected to (repeated) heating or cooling at a predetermined rate in a controlled atmosphere. DSC can also provide information on the kinetics of processes occurring in the sample. XRD is also a standard technique of structure analysis. Employing a synchrotron instead of a laboratory x-ray source leads to a significant increase in the data acquisition rate and enables the combination with another analytical technique, in this case DSC. DSC/XRD is a novel technique for advanced materials characterization. In particular, extremely accurate correlation of thermal and structural events in the studied material can be achieved, not possible with either method used separately. The DSC/XRD instrument used has been described previously[4-7]. The conical inner thermal column, with the maximum expected accumulation of Wigner energy, has been centrally sampled by core drilling at 7 positions labeled a through g, with distances from the surface near the reactor core ranging from 0.0 (g) to 0.6 (a) m. One sample from each position, machined into a disk 5.0 mm in diameter and 1.0 mm thick[6], weighing approximately 60 mg, was measured. Two DSC scans between 25 ^{o}C and 525 ^{o}C at 10 ^{o}C.min^{-1} were performed with each sample, accompanied by a full 2θ XRD scan every 10 ^{o}C at a scan rate of 1 deg/s between 5 deg and 45 deg. The wavelength of the synchrotron x-rays was λ = 0.82650 Å. XRD patterns were evaluated by Rietveld refinement using the GSAS software package[8] with only background, profile coefficients, histogram scale factors, diffractometer zero, absorption correction, and lattice parameters c and a being optimized. The heat flux measured by DSC in the first run is a result of the sample heat capacity and the release of the Wigner energy, while in the second run only heat capacity should contribute to the heat flux, assuming complete Wigner energy release in the first run. Hence, subtraction of the second-run from the first-run data and integration yields the Wigner energy released in the first run. Simultaneous differential scanning calorimetry / synchrotron powder x-ray diffraction (DSC/XRD) was performed at the Advanced Photon Source (APS) of the Argonne National Laboratory (ANL).

RESULTS AND DISCUSSION

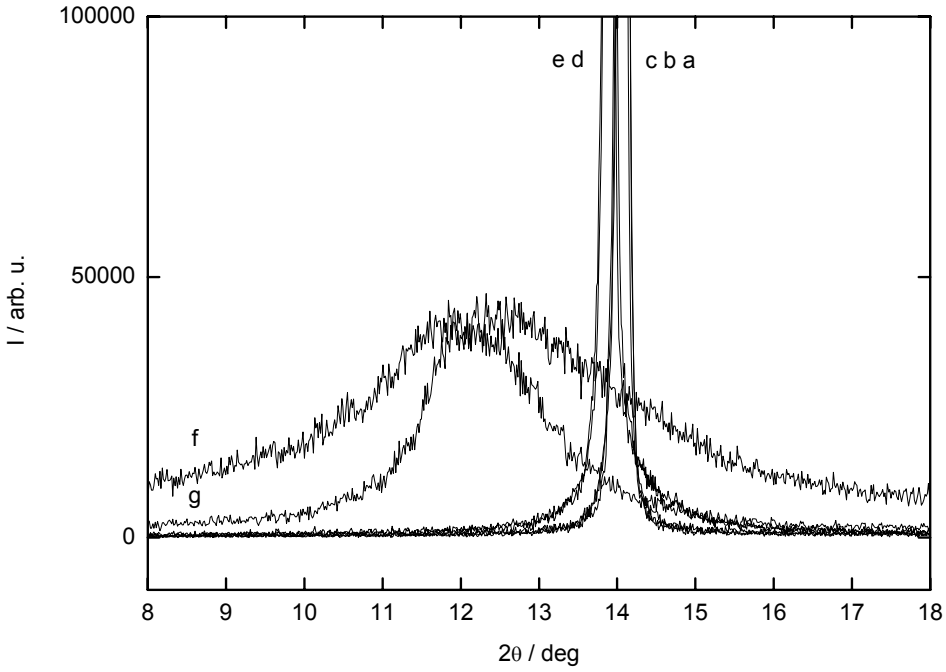
A set of DSC plots obtained for a set of samples a through g is shown in Figure 1. Samples a through e exhibit a maximum rate of heat release around 200 °C and negligible heat release at 525 °C. In addition, samples a through c show a pronounced fine structure observed previously[9]. The character of the DSC plot obtained with samples f and g is entirely different in that no sharp peak and/or fine structure is present and significant heat release continues at 525 °C.



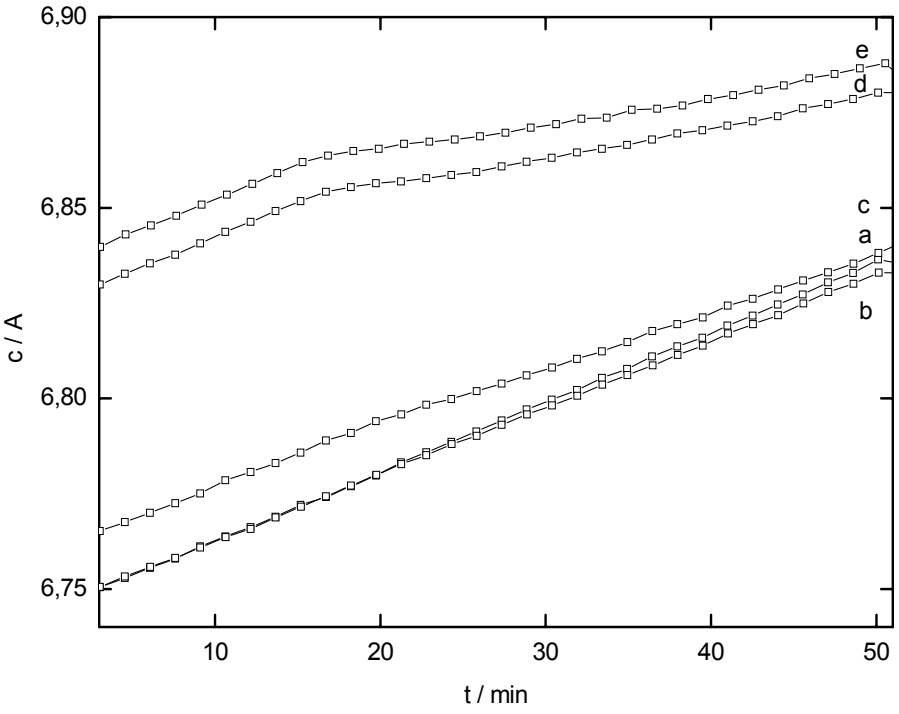
Integration of the DSC plots between 25 °C and 525 °C yields directly the Wigner energy released. The resulting plot of Wigner energy as a function of distance from the surface near the reactor core is shown in Figure 2. It is seen that the Wigner energy ranges from ca. 50 $J.g^{-1}$ for sample a to ca. 600 $J.g^{-1}$ for sample g. Assuming an instantaneous adiabatic release of this energy at a constant graphite heat capacity of 1 $J.g^{-1}.K^{-1}$, this would lead to a temperature increase of between 50 °C and 600 °C. These values confirm that treatment of the ASTRA graphite as well as graphite irradiated under similar conditions in order to remove the Wigner energy prior to interim storage should be considered.



A low-angle section of a set of XRD patterns taken at 25 °C is shown in Figure 3. The 002 graphite diffraction peak at ~14 deg is missing in samples f and g, being replaced by a single amorphous peak at ~12.2 deg (*c* = 7,78 Å). This correlates well with the different DSC plot character in the same samples noted previously.



The changes in the graphite *c* lattice parameter obtained as a result of Rietveld refinement using the XRD patterns from samples a through e between 25 ^{o}C and 525 ^{o}C are shown in Figure 4. (The graphite *a* lattice parameter did not exhibit any measurable changes.) Marked swelling along the *c*-axis (*c* = 6.75 – 6.85 Å, normally 6.72 Å) is seen at 25 ^{o}C. Between 25 ^{o}C and ca. 200 ^{o}C, the samples undergo thermal expansion consistent with a thermal expansion coefficient of ~2.7 x 10^{-5} $^{o}C^{-1}$ – an order of magnitude more than the value of 2.7 x 10^{-6} $^{o}C^{-1}$ reported for the unirradiated material by the manufacturer. The break in the curve at ~ 200 ^{o}C coincides with the maximum in energy release rate noted previously.



CONCLUSIONS

Heating of graphite samples from the inner thermal column of the ASTRA research reactor in a DSC at 10 $^{o}C.min^{-1}$ from 25 ^{o}C to 525 ^{o}C leads to the release of most of the Wigner energy, with a maximum energy release rate at ~200 ^{o}C. The magnitude of the Wigner energy ranges from ~50 J.g-1 (a) to ~600 J.g-1 (g). Treatment of irradiated graphite in order to remove the Wigner energy

prior to interim storage should be considered. (Incineration might still be the most reasonable disposal option. However, questions concerning releases of ^{14}C need to be addressed.) Crystal structure of samples f and g (closest to the reactor core) is destroyed. A single amorphous peak at ~12.2 deg is present in the XRD patterns (c = 7,78 Å). Crystal structure of samples a through e (farther from the reactor core) is intact, with marked swelling along the c-axis. (c = 6.75 – 6.85 Å, normally 6.72 Å). The break in the c *vs.* t curve (XRD, Rietveld refinement) coincides with the maximum in energy release rate (DSC).

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LITERATURE

1. W. Primak, Phys. Rev., 103, 1956, 1681.
2. M. Wise, in Proceedings of a TC Meeting on Nuclear Graphite Waste Management , IAEA, 1999.
3. F. Meyer, Nuclear Technology & Radiation Protection, 2003, 2, 61.
4. D. Lexa, Rev. Sci. Instruments, 70, 1999, 2242.
5. D. Lexa, A. J. Kropf, and L. Leibowitz J. Nuclear Materials, 279, 2000, 57.
6. D. Lexa, Thermochim. Acta, 398, 2003, 241.
7. D. Lexa, Thermochim. Acta, 401, 2003, 239.
8. A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (1994).
9. T. Iwata, J. Nuclear Materials, 133&134, 1985, 361.