

Applications Note

Surface analysis of nuclear graphite

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Overview

In this short study we will explore the differences in surface chemistry between two different graphites used in the nuclear industry. In recent times a wide variety of nanostructured carbon forms have been observed in nuclear graphite which vary the graphitic nature of the material. The nature of these forms can greatly affect the material's ability to act as an effective moderator. Here we will discuss the elemental composition of the graphite surface and the extent of graphitic sp^2 bonding.

Introduction

Graphite is one of the key materials used in the current generation of nuclear reactors in the UK. Since the early days of nuclear fission graphite has been recognised as an excellent neutron moderator and reflector allowing sustainable controlled fission.

Contaminants in moderator rods are a major problem as they can act as neutron absorbers. This causes decreased fission and production of unwanted isotopes – a common cause of radioactive waste. The goal of this application is to understand the surface chemistry of two different graphites: Pile Grade A (PGA) and Gilsocarbon (Gilso). PGA is an early form of nuclear graphite used in many reactors world-wide, particularly in the UK in the Magnox series. It is derived from a petroleum coke (which is a by-product of the oil refining industry). Gilsocarbon was developed later and is used in the Generation II Advanced Gas-Cooled Reactors. The Gilsonite coke is produced from refining the asphalt. Here we will study the two graphites and try to identify differences in surface chemistry and extent of sp^2/sp^3 character.

Experimental

All measurements were acquired using a Kratos AXIS Supra photoelectron spectrometer. The AXIS Supra incorporates several features which make high resolution spectroscopic analysis of these types of challenging samples routine:

- A 500 mm Rowland circle Al X-ray monochromator;
- Coaxial charge neutralisation system;
- Magnetic lens;
- 165 mm hemispherical analyser;
- Delay line detector.

The two graphitic samples were cut from larger rods using a mechanical saw.

Results

After introducing the graphite samples into the spectrometer, survey spectra were acquired to identify the elements present on the surface. Figure 1 shows the spectra after automated elemental peak identification.

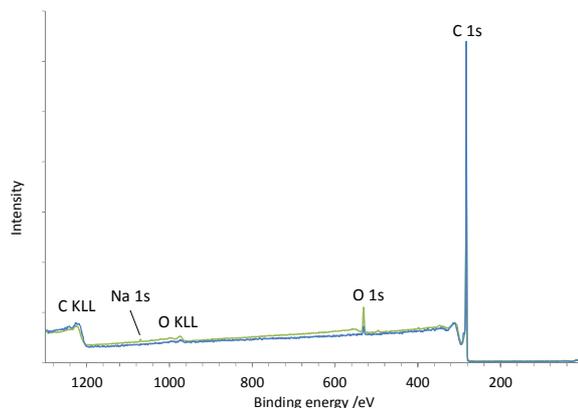


Figure 1: Survey spectra for Gilso (green) and PGA (blue).

Quantification of the survey spectra for the two samples (table 1) showed as expected mainly carbon on the surface with a small amount of surface oxygen. The oxygen can be attributed to a thin film of adventitious carbon which is present on all air-exposed samples. Adventitious carbon is generally comprised of short chain, perhaps polymeric non-graphitic hydrocarbons species with small amounts of both singly and doubly bound oxygen functionality¹. No other elements were detected in the PGA surface however several contaminants of low concentration were identified in the Gilso sample.

Element	C	O	Si	S	Na	N	Cl
PGA	98.70	1.30	-	-	-	-	-
Gilso	93.92	5.16	0.11	0.07	0.19	0.52	0.03

Table 1: Surface quantification for Gilso and PGA graphite surfaces.

High resolution C 1s spectra were acquired to identify the chemical states of the carbon in the surface (figure 2).

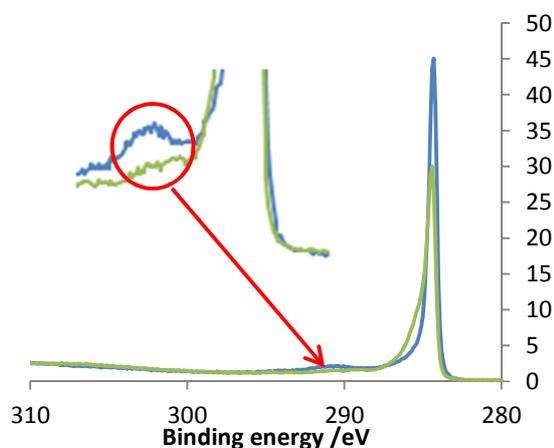


Figure 2: C 1s spectra for Gilso (green) and PGA (blue).

For both graphite samples the C 1s peak appears at 284.4 eV binding energy. The C 1s spectrum for PGA has an asymmetric line shape towards high binding energy. This peak shape is typical of graphitic carbon. There is also a pronounced peak at >290 eV – a shake-up satellite previously attributed to sp^2 bonding. In aromatic systems this structure has been shown to be due to $\pi \rightarrow \pi^*$ transitions involving the two highest filled orbital and the lowest unfilled orbital. In general, the more pronounced the loss peak the greater degree of sp^2 bonding. The Gilso C 1s spectrum differs greatly from PGA. There is no longer a clearly defined shake-up feature and a shoulder is clear on the high binding energy side of the primary peak ~285-286 eV. This shoulder is most probably increased sp^3 character and some C-O chemistry.

To gain further information regarding the bonding states of the two different graphite samples, carbon KLL Auger electron lines were also acquired. Following ionization by photoelectron emission an outer shell electron can fill the created vacancy and the energy released can result in the emission of an Auger electron. Analysis of the X-ray induced C KLL Auger peak can help distinguish the bonding states in a semi-quantitative manner for non-functionalized samples. Scaglione *et al.* proposed a simple method of quantifying the relative amount of sp^2/sp^3 character in a carbon material using this first derivative². The energy difference between the spectrum maximum and minimum is known as the d-parameter and is linearly related to the concentration of sp^2 character. Figure 3 shows the first derivative spectra for the two graphite samples.

Here there is a clear distinction in energy difference between the peak maximum and minimum for the two graphites. PGA shows ~74% sp^2 character compared to ~20% sp^2 character of Gilso. The correlation of results obtained from the high resolution C 1s and C KLL spectra indicate that the PGA sample's surface contains a higher concentration of graphitic carbon.

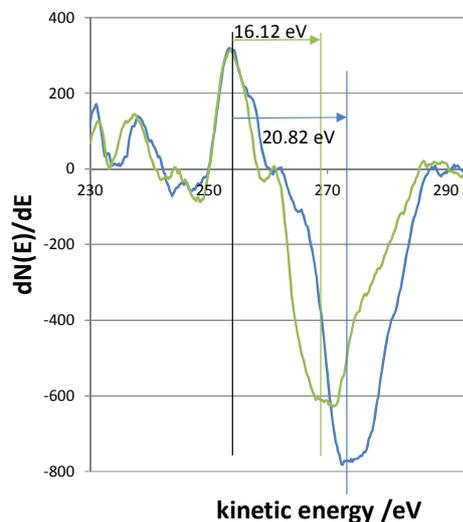


Figure 3. First derivative C KLL Auger spectra.

Conclusions

Two graphite samples were analysed using XPS to determine carbon chemistry at the surface. Small concentrations of contaminants were seen on the surface of the Gilsocarbon surface and the high-resolution C 1s spectrum showed less sp^2 character than for the PGA sample. Further analysis of the Auger parameter allowed the degree of surface $sp^2: sp^3$ to be quantified. This study highlights the use of the AXIS Supra photoelectron spectrometer in detecting low concentration contaminants and in determining bonding arrangements in carbon materials

Acknowledgements

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References

- [1] T.L. Barr, S. Seal, J. Vac. Sci. Technol. A 13(3) (1995) 1239.
- [2] Scaglione *et al.* Appl. Surf. Sci., 47 (1991) 17-21.