Nuclear Instruments and Methods in Physics Research A 780 (2015) 27–32

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research A

journal homepage: www.elsevier.com/locate/nima

Model for neutron total cross-section at low energies for nuclear grade graphite

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ARTICLE INFO

Article history:
Received 19 September 2014
Received in revised form
28 November 2014
Accepted 15 January 2015
Available online 23 January 2015

Keywords:
Small Angle Neutron Scattering
Small Angle X-ray Scattering
Porosity
Graphite

ABSTRACT

At subthermal neutron energies, polycrystalline graphite shows a large total cross-section due to small angle scattering processes. In this work, a new methodology to determine pore size distributions through the neutron transmission technique at subthermal energies is proposed and its sensitivity is compared with standard techniques. A simple model based on the form factor for spherical particles, normally used in the Small Angle Neutron Scattering technique, is employed to calculate the contribution of small angle effect to the total scattering cross-section, with the width and center of the radii distributions as free parameters in the model. Small Angle X-ray Scattering experiments were performed to compare results as a means to validate the method. The good agreement reached reveals that the neutron transmission technique is a useful tool to explore small angle scattering effects. This fact can be exploited in situations where large samples must be scanned and it is difficult to investigate them with conventional methods. It also opens the possibility to apply this method in energy-resolved neutron imaging. Also, since subthermal neutron transmission experiments are perfectly feasible in small neutron sources, the present findings open new possibilities to the work done in such kind of facilities.

1. Introduction

Advanced materials have nowadays a wide variety of applications in rapid development, like in the storage of information in magnetic disks, or in improvements in the mechanical properties of steel, high-impact plastics and super alloys and the current carrying in superconductors. The properties of these materials are critically determined by their structure at nanometric scale. Supported by this technological interest, a method to explore the bulk structure in a fast way which gained relevance in recent times is the thermal neutron transmission technique [1]. With the same rationale, the subthermal neutron transmission has been employed to study nanometric structures, as recently tested for the first time in graphite [2] (a material of great interest in nuclear industry), as an alternative to the well-known Small Angle Neutron Scattering technique. The total cross-section of subthermal neutrons in graphite had been repeatedly measured by different research teams in the last few decades, revealing that for neutrons of energies below 0.0018 eV (i.e. slightly less than that of the first Bragg edge) the experimental value varies from 4 to 8 barns, depending on the porosity level. In contrast, calculations using standard theoretical models that compute the crystal structure, but not the structure at nanometric scale (as employed in the nuclear data processing code NJOY [3]), produce a value of 0.2 barns. Recent experimental studies [2] have shown that this difference in the total cross-section is due to neutrons scattered at small angles, i.e. refractions and reflections in the great number of existent solid/air interfaces due to the graphite porosity, not taken into account by NJOY.

Graphite is widely used in nuclear installations, due to its ability to moderate fast neutrons and reflect slow neutrons. Examples are the proposed nuclear fuel made of graphite balls containing uranium oxycarbide or uranium dioxide employed in Very High-Temperature Gas reactors (one of the reactor concepts for the next generation of nuclear power plants), or the cylindrical graphite bricks that form the core of the Advanced Gas Reactors (widely employed in the United Kingdom), serving both as neutron moderator and structural components. In the latter case, years of neutron irradiation caused profound microscopic changes in the material that resulted in shrinking of the graphite bricks. But because the neutron bombardment does not spread evenly through the brick material, the rates of recession are also irregular. This causes tension and eventually cracking, affecting the safe operation of the power plants. Thus, a good characterization of the

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http://dx.doi.org/10.1016/j.nima.2015.01.055
0168-9002/

porosity of materials is particularly significant in graphites employed in the nuclear industry. Nuclear grade graphites are those with a density greater than 1.7 g/cm^3 (the theoretical value being 2.2 g/cm^3), which defines an upper bound on its porosity, that is an important parameter in reactor calculations.

Most of the methods to characterize the porosity of materials are based on adsorption properties [4]. Widely employed techniques are the mercury porosimetry, vapor–liquid equilibrium method [5], and liquid–solid thermoporometry [6]. The most popular method, known as the Brunauer–Emmett–Teller (BET) method [7], is based on gas adsorption. As this method is based on the area that is occupied by gas molecules, it is inaccurate either when the surface is too rough, or when the pores are too small or completely closed. Avnir et al. [8,9] found that the surfaces of most materials are fractals at the molecular size range. A consequence of this is that the routine analyses that employ the BET technique overestimate the effective area, since they consider an extra adsorption caused by the surface roughness. As an example, in the study of Kaneko et al. [10] BET measurements of the specific area in microporous carbons showed an overestimation of 40% due to capillary condensation. Besides the mentioned problem, the extra pressure applied to the gas can lead to pore deformation. On the other hand, microscopy techniques, besides not being representative of the whole volume, cannot be applied to microporous materials (pore sizes less than 2 nm).

The usual tools to explore the structure of solids and liquids in the nanometric scale are small angle X-ray and neutron scattering techniques (SAXS and SANS, respectively). While SAXS requires high-flux radiation facilities and good properties of longitudinal coherence (as provided by synchrotron radiation sources) and is sensitive to inhomogeneities in the electronic density of the sample, the SANS technique explores inhomogeneities in scattering length density and requires neutron facilities (e.g. reactors) to produce a monochromatic beam of cold neutrons. Both techniques explore the scale range from 1 to 100 nm and are applicable to both amorphous and crystalline materials. Some typical applications of SAXS and SANS include the determination of the pore size distribution and the estimation of the specific area in nanoparticulated systems.

As commented above, subthermal neutron transmission proved recently to be a tool to explore SANS effects. The interest in developing techniques based on neutron transmission is twofold. On the one hand it reinforces the role of small neutron facilities where this technique can be adequately implemented [11,2], while at high-flux sources high speed experiments can be performed, thus allowing real time studies during transformations. On the other hand, it can be adequately employed in neutron imaging data analysis. Energy- resolved neutron imaging has gained considerable interest over the last decade as a non-destructive tool to visualize distributions of different physical properties in macroscopic objects [12–18]. From the instrumental side this has been made possible due to advances in detector technology [19,20], the advent of more intense pulsed neutron sources and the development of dedicated monochromating devices at neutron imaging instruments of stationary neutron sources [21,22]. These advances in instrumentation have been accompanied by the development of basic physical models to interpret and analyze the energy-resolved neutron transmission of different material systems, in order to extract the information of interest from the transmitted neutron spectra. For polycrystalline materials it is possible to quantify crystallographic phases [23] and elastic deformation [24–26] and applied stresses [27], and to less extent texture and plastic deformation [16,28]. For single crystal materials, it is possible to determine the crystal orientation, mosaicity and elastic strain [29]. Neutron imaging techniques combined with grating interferometers have also been used to visualize the spatial distribution and quantify the signal due to ultrasmall-angle scattering within the sample [30].

In this paper we present a theoretical model to analyze the energy resolved neutron transmission signal that appears as a result of small-angle scattering within a sample. The proposed model allows the quantification of the spatial distributions in the nanometric range that exist within a sample. The model comprises a description of the pore sizes via a Log-Normal distribution and a form factor of spherical pores, and a standard description of the bulk solid. The contributions to the cross-section caused by the crystalline lattice (elastic coherent term) as well as the vibrational modes of the lattice (inelastic term) are considered through the NJOY code, and the contribution by 1-phonon coherent scattering is estimated according to the results of Al-Qasir [31]. We apply this model to characterize the pore distribution in nuclear graphite produced by different manufacturing techniques from energy resolved neutron transmission experiments. The experimental neutron work has been presented in a previous report [2], so it will be only briefly described in this paper. In order to assess the results of the procedure presented in this paper, we performed SAXS measurements at the LNLS (Campinas, Brazil) on the same systems. We compare the results from both methods.

2. Experimental

2.1. Samples

Three different types of graphite were examined in this work, needle-coke, pitch coke and isostatic-pressed graphite, which differ in the way they were manufactured:

- Needle coke graphite is the most porous species [32]. Samples were cut from a 24 cm cube provided by the RA-6 Nuclear Reactor, of the Centro Atómico Bariloche, Argentina. The density of the material is 1.681 ± 0.008 g/cm^3. Elemental composition determined by EXAFS is C 99.815%, S 0.102%, Ca 0.047%, Si 0.026%, Al 0.009%, and K 0.001%. Pores of around 1 mm are visible to the naked eye.
- Pitch-coke graphite is a byproduct of pitch produced by heat treatment, leading to more isometric particles than needle-coke graphite. The resulting material is more dense 1.725 ± 0.004 g/cm^3 than the needle coke graphite. Although the sample has a smoother surface than pitch coke graphite, pores are still visible to the naked eye. Spherical samples were machined out from a rod.
- Isostatic-pressed graphite is manufactured from finer coke particles, and has very uniform and isotropic properties, that makes it suitable to be used as neutron moderator. Spherical samples were molded by isostatic pressing. These samples presented the largest density (1.740 ± 0.004 g/cm^{-3}).

2.2. Experimental techniques

SAXS experiments, performed in transmission mode, were done in the SAXS1 beamline at the Laboratorio Nacional de Luz Sincrotron (LNLS) in Campinas, Brazil. The beamline works with a fixed energy of 8 keV and a beam size of 1.5 mm (horizontal) $\times$ 0.5 mm (vertical). The X-ray detection was performed with a solid state detector PILATUS 300 K with a resolution of $0.1(\delta E/E)$. To increase the statistics, the detection threshold was set at 7 keV. Two ranges of q were measured, $0.11\ \mathrm{nm}^{-1} < q < 4\ \mathrm{nm}^{-1}$ and $0.03\ \mathrm{nm}^{-1} < q < 1.5\ \mathrm{nm}^{-1}$, to cover the highest possible range of momentum transferred. Seven graphite samples were employed, four corresponding to needle-coke and three to pitch-coke.