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Near-surface structure and residual stress in as-machined synthetic graphite

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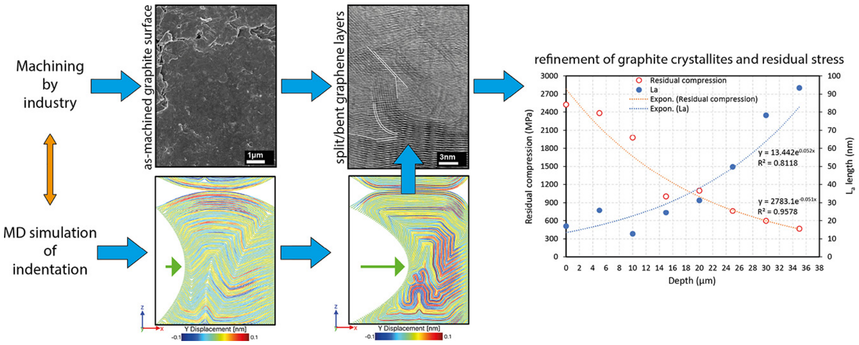
HIGHLIGHTS

- Typical machining of highly graphitised iso-graphite leads to a plastically deformed surface with refined crystallites.
- The plastic deformation in graphite is evidenced by HRTEM images showing split and/or bent graphene layers.
- The C-C σ bonds in the plastic/elastic deformation region are highly stressed with a maximum net compression >2.5 GPa.
- MD modelling of plastic deformation in graphite by means of indentation shows splitting and bending of graphene layers.

GRAPHICAL ABSTRACT



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ABSTRACT

We have used optical and electron microscopy and Raman spectroscopy to study the structural changes and residual stress induced by typical industrial machining and laboratory polishing of a synthetic graphite. An abrasion layer of up to 35 nm in thickness formed on both machined and polished surfaces, giving the same I_D/I_G ratios evidencing graphite crystal refinement from an L_a of ~110 nm down to an average of 21 nm, but with different residual compression levels. For the as-polished sample, structural change was limited to the near surface region. Underneath the as-machined surface, large pores were filled with crushed material; graphite crystals were split into multi-layered graphene units that were rearranged through kinking. Graphite crystal refinement in the subsurface region, measured by L_a, showed an exponential relationship with depth (z) to a depth of 35–40 μm. The positive shift of the G band in the Raman spectrum indicates a residual compression accompanied by refinement with the highest average of ~2.5 GPa on top, followed by an exponential decay inside the refined region; beyond that depth, the compression decreased linearly down to a depth of ~200 μm. Mechanisms for the refinement and residual compression are discussed with the support of atomistic modelling.

1. Introduction

Carbon materials are used in many applications such as core components of a nuclear reactor, electrodes in sensors and batteries, contact parts for friction and wear reduction and many components for bearing thermal, electrical and/or mechanical load. In some of

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these applications, it is the carbon surface that likely plays a key role in dictating its performance. However, many carbon materials are specified in terms of characteristics of their bulk, instead of their surfaces, hence leading to difficulties to establish correlations between performance and structure of a carbon material. Whilst, in the literature world, there is little information and understanding on the structure of an as-finished surface of a carbon material, we can see its importance through the following two case studies: (a) *nuclear graphite qualification test*; (b) *carbon electrodes regeneration*.

In GEN IV nuclear reactor development, graphite continues to be used in some high temperature reactors (HTR) for multiple objectives: moderating and reflecting neutrons for heat capture, exchanging heat with coolant through its good thermal conductivity, facilitating intricate geometric features to boost heat exchange and sustaining the core structure for as long a period of time as possible for both safety and economic reasons. Hence, graphite manufacturers keep developing new grades with better properties in order to fulfil the desired objectives for a modern reactor [1–5]. Whilst nuclear graphite has been developed for this purpose for more than half a century, there is not yet enough understanding of the possible correlations between the microstructure of a virgin graphite grade and the variation of physical properties with increasing neutron irradiation at different temperatures. This understanding is required to guide the design and use of nuclear graphite. Therefore, materials engineering and reactor designers still rely on an expensive and time-consuming qualification programme to obtain all necessary physical properties for manufacturing and designing graphite reactor components. Such an experimental testing is realised through accelerated neutron irradiation in a materials testing reactor (MTR) with high neutron flux. To ensure the neutron flux is as high as possible, only limited space is available in an MTR, making it impossible to have large testing specimens irradiated reaching a sufficiently high neutron dosage in a relative short period of time. Because of that, a trade-off is usually made to ensure efficiency by significantly scaling down the sizes of testing specimens to a level where it is still representative of the graphite microstructure.

Modern nuclear graphite grades, including those in development, tend to use much smaller coke fillers to achieve the following advantages: isotropy, high tensile and compressive strength, and higher density. Typical coke filler sizes are 10 to 20 μm, but some grades, such as those developed for molten salt reactors, can have a filler size as small as 5 μm. Hence, specimens used for neutron irradiation can be as small as 2.4 mm × 2.8 mm × 24 mm, as used by Oak Ridge National Laboratory (ORNL) [6]. To apply defined neutron doses to the specimens, they are usually put into an aluminium capsule (called a ‘rabbit’) which is shuttled into a nuclear reactor core [7]. The specimens need to be machined mechanically to the necessary size. This will inevitably create an outer layer of deformed material, which we propose, does not represent general bulk properties. The amount of damage i.e. the thickness of the deformation layer may lead to different conclusions with respect to the irradiation behaviour. If the fraction of the damaged volume is high i.e. if the dimension of a test specimen is very small this layer will become more significant.

The importance of surface preparation of a carbon electrode has been highlighted by many researchers. The preparation includes mechanical polishing, laser and electrochemical pre-treatment, vacuum heat treatment, etc., as reviewed in the literature [8]. Mechanically polishing has a long history of practice and remains the most common preparation practice for carbon electrodes used in electrochemistry. Typically, a carbon electrode is polished with silicon carbide paper followed by a series of alumina slurries, with successively smaller grit sizes down to 50 nm sized particles. It is generally believed that a coarse polish results in a relatively rough but reactive surface and that an increase in the oxygen to carbon (O/C) ratio is responsible for performance improvement. If the change in the O/C ratio on the surface is associated with structure or residual strain, it is not yet supported by any evidence.

Raman spectroscopy is a popular technique, since it is a non-destructive testing method and is widely used for the understanding of structural changes in graphite [9–15]. Due to the low transparency of graphite, acquired Raman photons likely carry contributions of the surface structure only, in particular if a confocal Raman microscope is used [16]. However, many published papers in the literature have not clarified the surface finishing conditions, implying the question if the measurements obtained, are representative of the investigated specimen. The aim of this study is to show the degree of surface effects upon the measurements.

We have assessed the effect of different surface finishes of a synthetic polygranular graphite grade on the microstructure. This was done by optical microscopy, scanning electron microscopy (SEM), Raman spectroscopy and transmission electron microscopy (TEM). To support the understanding of the experimental observations and to underpin the possible mechanisms behind them, we perform indentation simulations upon a single crystal of graphite, using molecular dynamics (MD), in the Discussion section.

2. Experimental procedures

2.1. Materials and sample preparation

The investigated graphite grade SNG623 was moulded by isostatic pressing (isographite) at Sinosteel Advanced Materials Co. Ltd. (China). This is one of the grades that have been subjected to neutron irradiation qualification in Oak Ridge National Laboratory. Details of the manufacture and structure of the as-manufactured graphite, have recently been reported by März et al. [17,18], and are briefly outlined here. The average diameter of coke fillers used for this grade is about 20 μm, and these were mixed with the pitch binder before isostatic pressing in a mould. The as-moulded green body was impregnated by pitch, followed by baking and graphitisation at a temperature >2800 °C. The representative properties are: density 1.81 g/cm^3, porosity 17%, and Young's modulus 11 GPa, as reported by Yang et al. [19]. It comprises of coke fillers, binding carbon as well as pores and nano-/micro-cracks. Besides these features, carbon in rosette and chaotic structures were also found, as has been widely observed by other researchers in other nuclear graphite grades such as IG110, NBG18 and Gilsocarbon [20–26], stemming from quinoline insolubles [27,28], sometime called QI particles.

The surface finishing conditions investigated in the present study are described below. The as-machined surfaces investigated were the planar ones of disc samples that were supplied by the manufacturer. These disc samples have a diameter of 10 mm and a thickness of 0.5 mm. Samples were trimmed to the desired dimensions by cutting, followed by machining, a standard method used by the manufacturer to finish testing samples, including those used for neutron irradiation testing in an MTR.

The as-polished surface sample was prepared by cutting and mounting into conductive epoxy resin, followed by metallographic cross-sectioning through applying the following steps. The cut surface was ground using P320 SiC paper till it became flat, then 9 μm diamond suspension was used to remove surface material for 5 min, followed by 3 μm diamond suspension polishing for 4 min and finally 40 nm OP-S colloidal silica suspension polishing for 2 min. Polishing is expected to result in a ‘less damaged’ surface, compared to machining.

The as-fractured surface sample was prepared by manually breaking the sample to expose a fracture surface. In contrast to a surface prepared by cutting or polishing where “damage” is evidenced by a strong D band in a Raman spectrum [29], an as-fractured surface can expose pre-existing cracks originating from manufacturing processes, but little damage is expected [29].

Cross-sectional thin foils for TEM analysis were prepared by focussed ion beam microscopy (FIB) using a FEI Nova 600 Nanolab™ DualBeam™ system (Thermo Fisher Scientific, Oregon, USA). The