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Residual stress measurements in polycrystalline graphite with micro-Raman spectroscopy

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HIGHLIGHTS

- Micro-Raman spectroscopy can measure significantly small residual stresses.
- Gilsocarbon, NBG-18 and PGA graphite were evaluated for residual stresses.
- Residual stresses in the constituents of graphite were evaluated.
- Binder and filler particles are often found under compressive and tensile stresses.

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ABSTRACT

Micro-Raman microscopy technique is applied to evaluate unevenly distributed residual stresses in the various constituents of polygranular reactor grades graphite. The wavenumber based Raman shift (cm^{-1}) corresponds to the local residual stress and measurements of stress dependent first order Raman spectra in graphite have enabled localized residual stress values to be determined. The bulk polygranular graphite of reactor grades – Gilsocarbon, NBG-18 and PGA – are examined to illustrate the residual stress variations in their constituents. Binder phase and filler particles have shown to be under compressive and tensile stresses, respectively. Among the studied graphite grades, the binder phase in Gilsocarbon has the highest residual stress and NBG-18 has the lowest value. Filler particles in Gilsocarbon have the highest residual stress and PGA showed the lowest, this is most likely due to the morphology of the coke particles used in the manufacturing and applied processing techniques for fabrications. Stresses have also been evaluated along the peripheral of pores and at the tips of the cracks. Cracks in filler and binder phases have shown mixed behaviour, compressive as well as tensile, whereas pores in binder and filler particles have shown compressive behaviour. The stresses in these graphitic constituents are of the order of MPa. Non-destructive analyses presented in this study make the current state-of-the-art technique a powerful method for the study of stress variations near the graphite surface and are expected to increase its use further in property determination analysis of low to highly fluence irradiated graphite samples from the material test reactors.

1. Introduction

Graphite has a long and rich tradition of research and has widespread application as a neutron moderator and is used as a structural component in nuclear reactors (Fermi, 1952; Nightingale, 1962). In recent years, with interest in Gen-IV reactor design, graphite has attracted considerable attention as a potential material, since it can be employed as a fast neutron moderator/reflector structural component in Very High Temperature and Gas-cooled reactors (Bonal et al., 2009; Marsden and Hall, 2012).

There are a variety of artificially produced polycrystalline graphite grades commercially available as reactor graphite and they are characterised by their: forming processes (extrusion, pressing, vibration and isostatic moulding, etc.), utilized source coke for manufacturing, their grain size, type of binder and filler particles, their randomly distributed multi-scaled porosities and nano-scale 'Mrozowski' cracks. Nuclear graphite grades are specifically manufactured for use within the nuclear reactors core to a specification

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that is aimed at retaining its moderating, physical, and mechanical properties under nuclear radiation environment even at high temperatures (Simmons, 1965). However, reactor core graphite is subject to a hostile environment of fast neutrons and hot coolant gas in which it experiences irradiation-induced hardening and in some cases radiolytic oxidation during the exposure life. These irradiation-induced effects lead to progressive changes in the physical, mechanical properties and in particular, build-up of significant stresses and deformation in the graphite components (Marsden and Hall, 2012; Tsang and Marsden, 2006, 2007). During graphite manufacture, which involves several high temperature heating cycles (Marsden and Hall, 2012), internal stresses (Kuroda et al., 2005; Rand, 2012) are generated at the micro-scale in the constituent phases of graphite grades. The manufacturing stresses retained in bulk graphite billets as internal (residual) stresses and may cause cracking (Hodgkins et al., 2006; Kelly, 2000; Kuroda et al., 2005). In addition, such unintended residual stresses in artificially manufactured graphite grades may limit their service life depending up on the neutron irradiation temperature and doses. Therefore, it is important to characterise all grades of graphite to evaluate the irradiation material properties to understand the evolution of these properties and, hence predict component behaviour under the intended irradiation environment. Important reactor graphite grades are Gilsocarbon, Nuclear Block Graphite-18 (NBG-18) and Pile Grade-A (PGA) considered in the present study. These graphite grades are polycrystalline and heterogeneous; comprised of various carbonaceous phases such as coke filler particles, pitch binder phase, quinoline insoluble particles and graphitic and turbostratic graphite phases. The issues related with the build-up stresses in the constituent phases are significant. Internal stresses may possibly actuate the initiation and propagation of dislocations and nucleation of new cracks and voids. Stresses may also trigger swelling behaviour and dimensional change in graphite at low temperature under irradiation condition as observed in NBG-10 graphite (Burchell and Snead, 2007) and grade TSX graphite (Kennedy and Woodruff, 1989). Therefore, internal/residual stresses may play a significant role in explaining the failure of components. There are techniques available for measuring the distribution of internal strains/stresses in materials; however they are invasive, semi-invasive, require complex computer simulated modelling or may be applied to only a restricted class of materials. A few techniques such as X-ray diffraction, deep-hole-drilling (DHD), finite element simulations, micro-indentation and ultrasonic wave methods have been investigated for application in graphite (Nakhodchi et al., 2011; Shibata et al., 2008). In this paper, the internal (lock-in) stresses in various constituents of polycrystalline reactor grades graphite such as filler, binder, and along the peripheral of pores and at the tips of the cracks, have been evaluated using micro-Raman spectroscopy, a non-invasive analytic method for stress evaluation in near-surface submicrometer regions of reactor graphite. The applicability of this method to both non-irradiated and irradiated graphite is a promising method to access information on residual stresses effectively and non-invasively.

Micro-Raman spectroscopy is a non-destructive technique and provides information on the microscopic state of stresses in the constituents of materials with up to a micrometre of lateral and depth spatial resolutions (Anastassakis et al., 1970; Wolf and Maes, 1998). The lateral and depth spatial resolution is along the *XY* and *Z* directions, respectively and the *Z* spatial resolution depends on the confocality of the spectroscope used. In particular, a spatial resolution in the order of 1 μm is effective for the local stress measurement and a better spatial resolution can be achieved with 'polished' samples (Wolf, 1996). An inelastic interaction of laser source with crystal lattice vibrations is employed for stress measurements with high lateral resolution and thus, the crystalline material can be probed non-destructively without the need for complex and time-consuming sample preparations (Wolf, 1996).

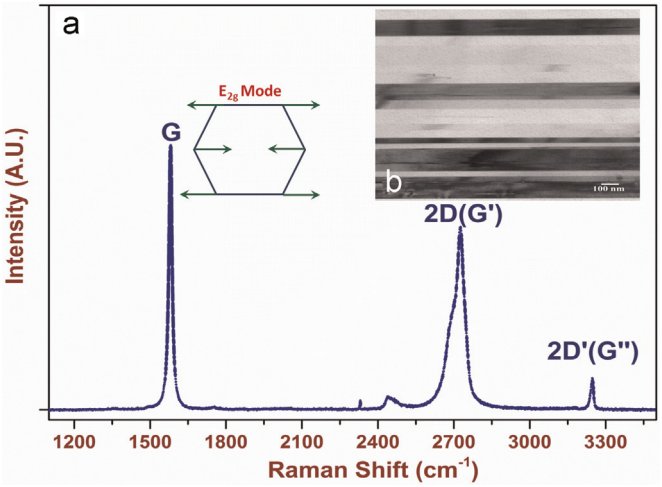

Fig. 1. (a) Raman spectrum from HOPG taken with 532 nm laser excitation wavelength. The spectrum shows the presence of G-peak at 1580 cm^{-1} (E_{2g} symmetry) and absence of D-peak. (b) A bright field TEM micrograph of HOPG shows layered structures of 20–200 nm thickness and a strong orientation [0002] along the stacking direction.

The first-order stokes-Raman spectrum of Highly Ordered Pyrolytic Graphite (HOPG), with relatively near perfect graphite crystallographic geometry, exhibits a single G-peak, which corresponds to the $k \approx 0$ vibrations of the doubly degenerate optical phonons (E_{2g} symmetry) and the Raman G line represents almost negligible residual stresses (Ferrari, 2007). The Raman spectrum and bright field transmission electron (TEM) micrograph of HOPG are shown in Fig. 1. However, in artificially manufactured graphite, the constituent phases remain under residual stresses developed during fabrication process, which causes polarization dependent shifts which are observed to be dependent on the internal stress values (Mohr et al., 2010; Sakata et al., 1988). Thus, the Raman G line (optical phonons) in artificially manufactured graphite shifts due to the presence of internal stresses and the magnitude of this stress is directly proportional to the Raman line shift. A candid way to relate measured Raman shift to stress magnitude is the use of a stress model illustrating the stress state in the constituents or in the bulk sample within crystallites of arbitrary orientation. A linear relationship between Raman line-shift and stress has been previously applied to estimate the stress values in graphite fibre (Sakata et al., 1988), graphene based mechanical systems (Mohiuddin et al., 2009), quartz (Harker et al., 1970), polycrystalline Mn–Zn ferrite (Yamashita and Ikeda, 2004), polycrystalline silicon (Becker et al., 2007; Wolf and Maes, 1998) etc.

It is well-known that compressive stress shifts the Raman line to a higher frequency, while tensile stress shifts it to a lower frequency, as shown in Fig. 2 (Wolf, 1996). The splitting of doubly degenerated E_{2g} optical mode (G-band) into two components G^+ and G^- is due to the effect of anisotropic (deviatoric) stress that possibly changes the crystallographic symmetry and lifts the two-fold degeneracy completely or partially (Mohiuddin et al., 2009; Sakata et al., 1988). However, hydrostatic stress within the constituents of graphite only produces a shift and the original symmetry remains intact (Frank et al., 2011; Ganesan et al., 1970; Tuinstra and Koenig, 1970). Therefore, in the present example, the graphene hexagonal symmetry – 2D building block of the graphite structure – remains preserved.

The Raman line-shift is conditional on the material's property – phonon deformation potential – and corresponds to a change in