Laser Ultrasonic Assessment of the Effects of Porosity and Microcracking on the Elastic Moduli of Nuclear Graphites

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Abstract

Laser ultrasonic methods have been used to measure the elastic moduli of various nuclear graphites. Measurements were made to assess wavespeeds for longitudinal and shear waves in different propagation directions and these were used along with density measurements to compute the longitudinal and shear moduli as well as Young's modulus. All moduli decreased with increasing graphite porosity and these variations could be interpreted using models describing the effect of porosity on material stiffness. Extrapolations for these models to zero porosity were used to infer the moduli for theoretically dense graphite; the results were far below predicted values reported in the literature for fully dense, polycrystalline, isotropic graphite. Differences can be attributed to microcracking in the graphite microstructure. Using models for the effects of microcracking on modulus, estimates for microcrack populations indicate that the number of cracks per unit volume must be much greater than the number of pores per unit volume. Experimental results reported in the literature for irradiated graphites as well as for the stress dependence of graphite modulus are consistent with the influence of microcracking on elastic behavior and could be interpreted using concepts developed here. Results in this work for graphite structure-property relationships should allow for more sophisticated characterization of nuclear graphites using ultrasonic methods.

Keywords: laser ultrasonics, nuclear graphite, porosity, microcracking

1. Introduction

Bulk nuclear graphites are multifunctional materials that play critical roles in various reactor designs. They can serve as neutron moderators, reflectors and structural components in reactor cores. As a class of materials, nuclear graphites display a range of complicated microstructures even though they have high chemical purity [1]. These microstructures relate directly to the precursors used to synthesize graphite as well as the processing steps used to form these materials into billets for the manufacture of reactor components [2]. While the properties of single crystal graphite are well known [3], the properties of bulk graphites depend heavily, if not predominantly, on microstructure [4]. Microstructural elements include crystalline graphite, amorphous carbon, porosity, microcracking as well as others and each influences various behaviors depending on its presence in the overall microstructure [2,5]. The extent to which these microstructural elements appear in any given type of graphite depends on the methods used for production. In the nuclear environment, these components of the microstructure affect overall performance, influence the rates at which damage accumulates and, ultimately, govern the degradation of material performance [2,6-8]. In particular, graphite strength and stiffness are among the properties that are important for material performance in nuclear applications.

When used in the reactor core, graphite is exposed to high temperatures and neutron irradiation as well as oxidative species with the precise conditions being dictated by the type of reactor under consideration. Operational temperatures can cause changes in stiffness and strength and creep can occur when graphite is subjected to fast neutron irradiation under mechanical loading [9-11]. Graphite oxidation has the effect of increasing material porosity and this can impact material stiffness and strength [6,12,13]. Also, neutron irradiation initially increases stiffness and strength, but beyond some dose, both decrease [14]. All of these effects have been studied in various graphites and models have been developed to predict how these properties will vary during reactor operation with the goal of identifying service lifetimes [15]. However, even if models are used to predict the material behavior, there is a need to perform inspection of critical components to verify material integrity and to update models with information regarding the state of the material. Since material stiffness appears to correlate with strength in these materials, some type of measurement of the elastic moduli could prove valuable in assessing the state of the material and could be used to infer changes of the microstructure.

In this work, the moduli in a selection of nuclear graphites have been measured using laser ultrasonic methods. Ultrasonic measurements of longitudinal and shear waves have been made in different propagation directions in each of these graphites and were converted to corresponding moduli using determinations of sample density and wavespeed. With these moduli, Young's modulus could be determined as well. Trends between modulus and porosity volume fraction were identified and, in combination with models describing the stiffness of porous materials, were used to assess the influence of microcracking on the modulus in these materials. Models for the relationship between microcracking and modulus have been used to estimate the crack populations necessary to account for the behavior of the graphites in this study.

2. Background on Nuclear Graphite Modulus and Related Models

2.1. Nuclear Graphites

As a structural material, graphite exhibits interesting behaviors under conditions that exist in reactor cores. As has been noted, neutron irradiation can initially produce significant increases in graphite stiffness and strength [14] – these can be advantageous for the structural performance. The microstructural mechanism responsible for these changes is related to primary knock-on atoms (PKAs) inserted between (0001) planes in the graphite structure. Nucleation and growth of interplanar PKA regions produces swelling or expansion along the c-axis (or [0001] direction) of graphite crystallites. This swelling interacts with other microstructural features such as adjacent pores and microcracks (including Mrozowski cracks) and can affect the bulk mechanical properties by altering these features [16]. In particular, induced compressive stresses that close microcracks can lead to increased stiffness

and strength. Continued neutron exposure ultimately reduces strength when swelling can no longer be accommodated by the graphite microstructure – induced internal stresses reach levels that facilitate material failure. Since reductions in modulus accompany this loss of strength, measurements of modulus could provide valuable insight into the structural integrity of graphite.

In this study, the moduli of 13 different nuclear graphites have been measured to provide baseline information on the as-produced state of these materials. Some of these are currently produced by graphite manufacturers for possible use in reactors while others are legacy graphites that were either used in previous reactor designs or were developed for adoption in the past. Nuclear graphites display a range of crystallinity, porosity, grain sizes, pore size distributions, grain size distributions and grain orientation distributions that relate to the precursor materials and processes used during graphite production. Details regarding production methods and microstructures for some of the graphites used in this study are provided by Burchell *et al.* [17] and by Karthik *et al.* [18]. Generally, graphites are synthesized from petroleum- or pitch-based cokes through a sequence of processing steps that include calcination, grinding and blending, mixing with binders, forming, baking and impregnation, and graphitization [2]. Additional processing to purify the graphite can be performed – this is important for nuclear graphites to ensure predictable behavior in the reactor environment. Even though these processing steps are nominally the same for most graphites, differences in the starting coke, the grinding operations, the forming processes as well as the impregnations can yield materials with widely varying microstructures that exhibit different densities, grain sizes and anisotropy. Figure 1 shows scanning electron micrographs of three different graphites studied in this work – IG-110, NBG-18 and HLM. These images illustrate microstructural differences among these materials that might influence various properties including their elastic responses. While these micrographs primarily illustrate micrometer scale porosity, other important microstructural differences exist that could be identified by examining these graphites using higher resolution microscopy. Despite these differences, nuclear graphites are highly crystalline. This unifying characteristic not only has important implications for the overall mechanical properties of these materials but also permits a generalized investigation of structure-property relationships.

2.2. Models for Effects of Microstructure on Modulus

2.2.1. Moduli of Porous Media

Porosity plays a significant role in determining the stiffness of nuclear graphites, and its presence can be quantified using a range of techniques. For example, open porosity can be measured using mercury porosimetry while closed porosity can be inferred from measurements of open porosity and evaluation of total porosity (using X-ray or small angle neutron scattering or determinations of sample mass and volume). The elastic responses of materials, including those associated with ultrasonic measurement, are generally assumed to depend on total porosity and there are many models in the

literature that have been used to interpret the variation of elastic modulus with porosity. In early work on a type of isotropic graphite (POCO graphite), Cost *et al.* measured Young's modulus and the shear modulus as a function of porosity over the approximate range 0.13 to 0.32 for the porosity volume fraction [19]. They considered using a linear fit for their results but instead used an exponential fit to model trends. This approach was chosen owing to the experimental findings at that time, but was not justified on a theoretical basis. Later work by Shibata *et al.* examined the variation in the longitudinal wave velocity in two different isotropic graphites (IG-110 and IG-430) as a function of porosity [13] and found that their results could be interpreted using models put forth by Takatsubo and Yamamoto [20]. These models predict a nearly linear variation of Young's modulus with porosity volume fraction (for low porosities) and include dependence on pore shape. The work presented here will use models proposed by Hashin and Shtrikman for the bounds on the moduli of two phase materials [21,22]. If the primary phase is assumed to be graphite and the secondary phase is composed of porosity, then expressions for the upper bound on Young's modulus, E' , and shear modulus, G' , as a function of porosity, φ , can be written using their results as follows:

$$E' / E = e(\lambda, G, \varphi) \frac{1 + \lambda/G}{1/3 + (2/3 + \lambda/G)e(\lambda, G, \varphi)/g(\lambda, G, \varphi)} \quad (1)$$

and

$$G' / G = g(\lambda, G, \varphi) \quad (2)$$

where E and G are the Young's modulus and shear modulus, respectively, for the porosity-free case,

$$e(\lambda, G, \varphi) = 1 - 3\varphi(\lambda + 2G)[4G + \varphi(3\lambda + 2G)]^{-1} \quad (3)$$

and

$$g(\lambda, G, \varphi) = 1 - 15\varphi(\lambda + 2G)[9\lambda + 14G + 2\varphi(3\lambda + 8G)]^{-1} \quad (4)$$

with $\lambda = G(E - 2G)/(3G - E)$ being a Lamé constant related to the porosity-free moduli. The exact expression for E' / E in Eq. (1) can be approximated by $E' / E \approx e(\lambda, G, \varphi)$ and differs from the exact result only by a few percent for conditions to be considered in this work. Using estimates for the stiffness of porosity-free, nuclear graphites, the expressions given in Eqs. (1) and (2) can be evaluated as a function of porosity yielding the results presented in Fig. 2. For the porosities considered, Young's modulus and the shear modulus vary in nearly the same manner (the two plots overlap over most of the range) and appear to have a dependence on porosity that is almost linear.

2.2.2. Moduli of Microcracked Media

Microcracking likely contributes, perhaps equally, to the overall moduli of graphite [18]. In this work, microcracking refers to all crack-like structures with characteristic dimensions much smaller than

the ultrasonic wavelengths being used for measurements. Bulk measurements in graphite typically employ ultrasonic frequencies below 10 MHz and these would yield ultrasonic wavelengths greater than approximately 160 μm (based on a shear modulus of 4.5 GPa and a density of 1.81 g/cm^3). Material structures, such as cracks, tend to scatter ultrasound when their dimensions exceed the ultrasonic wavelength. However, structures much smaller than the ultrasonic wavelength do not scatter strongly but their presence does affect various material properties (in an effective medium approximation). For the purposes of this work, it is assumed that all micro- and sub-micrometer cracks primarily affect ultrasonic propagation by modifying the elastic moduli being measured. Among these are Mrozowski cracks that readily form in graphites during processing as a result of differential thermal stresses and occur between parallel graphite layers in crystallites as well as along basal planes at filler/matrix interfaces. These cracks can be seen in high magnification micrographs [23], but quantification of the characteristics of these structures is relatively difficult compared to determination of total porosity. Even though cracks could be considered to be extremely high aspect ratio pores (a limiting form), they do not contribute to determinations of total porosity using measurements of sample mass and volume, and their effect on modulus must be taken into account separately. There are a variety of models in the literature describing the influence of microcracks (also called strong discontinuities) on modulus [24-37]. Even though the literature describing acoustic interactions with microcracks and related discontinuities is considerable, no experimental studies have been performed to assess the validity of these models. In the absence of a preferred approach to modeling the moduli of microcracked materials, the development presented by Zheng will be used [38].

This model can be related to the energy states of materials containing cracks – especially microcracks that have dimensions much less than the acoustic/ultrasonic wavelengths of interest since these are weak scatterers and do not re-direct the propagating elastic wave. Microcracks affect stress state energies in the material and can be described using established fracture mechanics approaches based on the J -integral. Since microcracks contribute to the total elastic energy state of the material, they affect the effective material stiffness. This type of effective medium approach can be used to quantify the expected variation of elastic stiffness with crack density. According to Zheng [38], the strain energy per unit crack surface area as expressed by the J -integral, J , can be written as follows:

$$J = (K_I^2(1 - \nu_0) + K_{II}^2(1 - \nu_0) + K_{III}^2)(1 + \nu_0) / E_0 \quad (5)$$

where E_0 is the Young's modulus and ν_0 is the Poisson ratio of the uncracked material while K_I , K_{II} , K_{III} are the stress intensity factors corresponding to crack opening under mode I, II and III loading by ultrasonic waves. For oriented, non-interacting, long-narrow-rectangular cracks, wave propagation

perpendicular to the crack surfaces yields the following results for the microcrack-modified Young's modulus (E_3) and shear moduli (G_2, G_1) [38]:

$$E_3 / E_0 = (1 - 2\nu_0 + 2\nu_0^2\chi)[(1 - 2\nu_0 + 2(1 - \nu_0)^2\chi)(1 - 2\nu_0^2\chi)]^{-1} \quad (6)$$

$$G_2 / G_0 = [(1 - \nu_0)\chi + 1]^{-1} \quad \text{and} \quad G_1 / G_0 = [\chi + 1]^{-1} \quad (7)$$

where E_3 is Young's modulus for material displacement perpendicular to the crack surface, G_2 is the shear modulus for displacement perpendicular to crack length (long side), G_1 is the shear modulus for displacement along the crack length and G_0 is the modulus of the uncracked material. The critical parameter in these formulae is χ which Zheng refers to as the effective crack density (crack surface area per unit volume multiplied by the crack width). However, it is more correctly identified as the ratio of the internal energy density associated with cracks to the elastic energy density of the intact material – a crack energy density coefficient – and can be written as follows:

$$\chi = \pi n_c w^2 l \quad (8)$$

where n_c is the number of cracks per unit volume, w is the width (short side) of the crack face and l is its length (long side). In all of these expressions, the effective stiffness of the material decreases as crack density increases. This is shown in Fig. 3 where the elastic moduli E_3 / E_0 and G_1 / G_0 (as expressed in Eqs. (6) and (7)) are shown as a function of the crack energy density coefficient. Since the crack geometry assumed here does not accurately reflect the microcracking that is likely present in the graphites in this work, other crack geometries should be examined and used to model more complicated crack distributions, but these types of studies are beyond the scope of this work. Even so, the model here is instructive and should provide an indication of the general influence of microcracking on stiffness in nuclear graphites.

2.2.3. Moduli of Porous Media Containing Microcracks

These models should provide insight into the roles that porosity and microcracks play in determining the overall stiffness of graphite. However, it should be noted that the complicated microstructural elements in graphites interact in ways that are not fully captured by these simple models. Even so, for the purposes of this work, graphite will be considered to be composed of a secondary phase (pores) imbedded in a primary phase (graphite) containing microcracks, and each of these phases will be modeled using the ideas developed in the previous sections. With this description in place, the porosity-free values for modulus from Eqs. (1) and (2) (E and G) assume the roles of the moduli for the microcracked material in Eqs. (6) and (7) (E_3 and G_2 and/or G_1). In other words, if Young's modulus is

considered and Eqs. (1) and (6) are expressed as $E' = f(\varphi)E$ and $E_3 = h(\chi)E_0$, then $E' = f(\varphi)h(\chi)E_0$ – this assumes that the effects of porosity and microcracking are separable. This approach implies that the modulus of a porous material with microcracking can be estimated if porosity, effective crack density and the modulus of the intact material are known. Alternatively, this overall description can be used to estimate the effective crack density – a quantity that is difficult to measure or determine otherwise. Again, consider Young's modulus. Equation (6) can be re-written to show effective crack density as a function of the normalized modulus for the microcracked material – $\chi = H(E_3 / E_0)$ (where the function H is the inverse of h so that $\chi = H(h(\chi))$). Using the previous definition for $f(\varphi)$ yields $\chi = H(E' / (f(\varphi)E_0))$. This means that effective crack densities can be estimated once porosity and modulus are known and permits an interesting comparison between crack and pore number densities.

The pore number density, n_p , can be expressed as $n_p = 3\varphi / (4\pi R^3)$ where R is the radius corresponding to an average pore volume, $v_p = 4\pi R^3 / 3$. Also, the effective crack density can be used to obtain the crack number density using previous definitions: $n_c = \chi / (\pi w^2 l)$. The number of microcracks per pore is simply the ratio of these number densities:

$$\frac{n_c}{n_p} = \left(\frac{\chi}{\varphi}\right) \frac{4R^3}{3w^2 l}. \quad (9)$$

The ultimate value in this overall approach for the current work is that it links ultrasonic measurements of modulus to important microstructural features of graphite and shows how alterations related to porosity or microcracking brought about by the service environment of the graphite might influence modulus.

2.3. Experimental Determination of Graphite Moduli

2.3.1. Graphite Ultrasonic Samples

Ultrasonic test samples were prepared from graphite blocks (or billet sections) obtained from Oak Ridge National Laboratory as well as from various manufacturers. Sample dimensions were approximately 50 mm x 50 mm x 6 mm (length x width x thickness) with ultrasonic propagation occurring through the thickness of each sample. At least two samples of each graphite type were tested and these were taken from different locations in the graphite blocks that were received. The orientation of each sample was perpendicular to others for a particular graphite grade. Additional samples for various grades were included to gather information on the variability of properties when the graphites were from different production runs or to assess effects of anisotropy in more detail. Even so, this overall approach to sample selection (in which a single sample of a given orientation was used to represent the behavior of the overall material in that direction) likely affects the generality of the results presented in this work. In some cases, the thickness directions could be related back to important directions characteristic of

forming operations that occurred during graphite manufacture (such as an extrusion direction), but in other cases the relationship between sample and billet orientation could not be determined. Similarly, the general location of some billet sections in the original billets were known, but in most cases they were not. Since graphite properties vary with position in billets, this uncertainty and restricted sampling necessarily affect the generality and interpretation of results in this work. To minimize variability related to sample surface preparation, surfaces subjected to pulsed laser irradiation were finished using silicon carbide grinding paper while those used for ultrasonic detection were polished using 1 μm diamond paste. All samples were ultrasonically cleaned in a deionized water bath and were allowed to dry before ultrasonic measurements were made.

2.3.2. Ultrasonic Measurements

There are a variety of ultrasonic methods that can be used to determine modulus and each has characteristics that recommend its use. Depending on the methods used as well as the conditions under which measurements are made, modulus values can vary and, consequently, comparison of results must be made with attention to the measurement protocol. For this study, a standard transmit-and-receive, through-thickness measurement geometry was used in which an ultrasonic transmitter was located directly opposite the receiver on the graphite sample surface. In this configuration, transit times for ultrasonic waves can be measured and can be used to compute the modulus of the material using the following relationship:

$$c_k = \rho(T / \Delta t_k)^2 = \rho v_k^2 \quad (10)$$

where c_k is the modulus being measured ($k = L$ for longitudinal waves and $k = S$ for shear waves), ρ is the sample density, T is the sample thickness, Δt_k is the transit time for the ultrasound through the sample and v_k is the wavespeed. If the variation of modulus with porosity is needed, then measurements of density and wavespeed can be used to compute modulus while the bulk porosity can be obtained from density using values for theoretical density. The relationship between density and porosity, φ , is given by the following:

$$\varphi = (1 - \rho / \rho_0) \quad (11)$$

where ρ_0 is the density for material with no porosity (theoretically dense material). Using this relationship, Eq. (10) can be re-written as follows:

$$c_k = \rho_0(1 - \varphi)v_k^2. \quad (12)$$

This expression indicates that two factors contribute to the dependence of modulus on porosity – porosity itself as well as the measured variations of wavespeed with porosity.

2.3.3. *Laser Ultrasonics*

Conceptually, laser ultrasonic methods should provide the same information as other ultrasonic measurement techniques when modulus measurements are made. However, unlike contacting, piezoelectric-based transducers, laser ultrasonic methods do not require the use of liquid/gel couplants that can permeate the material and bias measurements. Also, since these types of couplants are not used, laser-based ultrasonic sensors can potentially be used in inspection systems to assess the state of nuclear graphites in service environments. Some preliminary understanding of the use of laser ultrasonic methods for ultrasonic assessment of graphites is needed in order to develop these types of systems – the results presented in this work demonstrate, in a broad fashion, the use of these methods.

Laser ultrasonic measurements were completed using the system shown schematically in Fig. 4. A pulsed, Nd:YAG laser producing 8-10 ns pulses at 1064 nm with energies in excess of 300 mJ served as the source for the ultrasonic transmitter. These pulses were attenuated and focused on the sample surface so that material ablation was not observed after initial surface conditioning. The resulting ultrasonic transmitter produced ultrasound characteristic of a thermoelastic source with amplitudes that permitted detection at various locations on a given sample. Laser ultrasonic sources of this type excite multiple ultrasonic modes (longitudinal, shear, surface and lateral waves) each having broad frequency content. Representative waveforms corresponding to the graphites highlighted in Fig. 1 are shown in Fig. 5 to illustrate the nature of the signals recorded using this type of instrumentation. Fourier transforms of recorded ultrasonic transients show that signals contain significant energy from quasi-static frequencies up to ten(s) of megahertz – the upper limit being related primarily to characteristics of the material under study.

All measurements were performed in an epicentral geometry – the transmitter being located directly opposite the receiver on different sides of the sample. The receiver was a Michelson-type, path stabilized interferometer (shown schematically in Fig. 4) with a diode-pumped, frequency-doubled Nd:YAG laser (532 nm). The effective operating bandwidth of this instrument was approximately 20 kHz to 50 MHz – more than sufficient to capture the ultrasonic transients at the reception location. When used for ultrasonic measurements in graphite, this type of system might appear to have various shortcomings. First, even though graphite is black and is strongly absorptive at the wavelengths used for excitation, the ultrasonic transients launched by a thermoelastic source might not be large enough to detect owing to the low thermal expansion coefficient for graphite. Fortunately, all graphites examined in this work proved to be quite good ultrasonic transmitters owing to the interaction between the source laser beam and the graphite (specific details regarding optical absorption, photothermal energy conversion and the character of the resulting ultrasonic source will not be considered here). Next, since graphite is black and absorbs quite well in the visible portion of the spectrum, optical reception using the interferometer

might appear to be a poor choice. However, when polished to an optical finish, the front surface reflection from graphite can be quite strong and provides more than enough optical return for interferometric detection of ultrasound.

The ultrasonic measurements reported in this work were used to determine the longitudinal and shear moduli of various graphite samples (with Young's modulus being derived using standard relations for isotropic materials). These moduli were computed using measured times-of-flight from laser ultrasonic waveforms along with measurements of sample thickness and density. Density measurements were performed using simple measurements of sample dimensions (to compute volume) along with sample mass determinations. It was found that this approach to density measurement yielded more consistent results than those obtained using water displacement methods. The principal uncertainty in making modulus measurements using this approach is determination of the times-of-flight for the various ultrasonic arrivals since the waveforms are complicated and must be correctly interpreted. Modeling can assist the interpretation process but cannot completely reproduce all aspects of recorded signals. Consequently, times-of-flight measurements have been made on ultrasonic arrivals that relate to single transits through the sample. When possible, revivals (corresponding to multiple transits through the thickness) have also been used to refine measurements since these permit pulse-echo overlap estimates for times-of-flight.

3. Ultrasonics Results and Analysis of Modulus Variation with Porosity and Microcracking

3.1. Ultrasonics Results

Results of laser ultrasonic measurements are summarized in Table 1 and in Fig. 6 where the longitudinal and shear moduli for all samples are presented as a function of material mass density. The designations for the various graphites are commonly used in the literature and details regarding each can be found in various reports [9,39]. The graphical presentation in Fig. 6 has been chosen since it illustrates a clear trend for graphite stiffness as a function of material density even though the only commonalities among the graphites are, presumably, their chemical purity and the general processes used during material synthesis. This is true except for BAN which has processing steps that differ significantly from other nuclear graphites resulting in altered properties of this graphite relative to others [40]. Linear trend lines fit to the data (excluding values for BAN) are also shown since they approximate the overall variations of graphite stiffness with density. Scatter of the data about the trend lines has several sources that can be readily identified. Variations in density for a given graphite include actual variations that occur during production – some samples were taken from non-adjacent regions in billet sections – and also reflect measurement uncertainties. Variations in stiffness result from inhomogeneity in the graphite and also include effects related to graphite anisotropy (stiffness in different directions varies). The effects of inhomogeneity (microstructural variations) and measurement uncertainty can be estimated by comparing

modulus values in graphites that are known to be relatively isotropic such as IG-110. Using values in Table 1, the longitudinal and shear modulus measurements for the two samples included in this study differ by approximately 5%. The effects of anisotropy on reported modulus values can be estimated by examining results for an anisotropic graphite such as PCEA which is extruded and should exhibit transversely isotropic behavior. Three different samples of PCEA were used in this study with samples being fabricated with surface normals for corresponding faces that were orthogonal to one another. With these sample orientations, two of the longitudinal moduli listed in Table 1 should have the same value – two values differ by approximately 3% while the third differs from the other two by approximately 6-9%. Interpretation of the shear modulus values obtained for the three PCEA samples is more problematic since the measurement results reported were not obtained using linearly polarized shear waves – laser ultrasonic shear waves from the sources used in this work were essentially radially polarized and this necessarily results in mixed shear modes in the received waveforms for two of the PCEA measurements. Even so, owing to symmetry considerations, two of the shear modulus measurements should be equal and the third should differ just as was the case for the longitudinal wave. For PCEA, two of the shear modulus values differ by approximately 7% while the third differs from the other two by 13-19%. These observations indicate that uncertainty related to microstructural variations (not related to anisotropy) combined with measurement uncertainty leads to several percent variation in the longitudinal modulus and approximately 7% variation in the shear modulus. Anisotropy accounts for an additional 3-6% variation for the longitudinal modulus and 6-12% for the shear modulus. For the purposes of this presentation, this anisotropy will not be considered in detail since the measurements in different directions will simply provide additional scatter to the data. Presumably, the trend lines simply provide an indication of the average modulus that might be realized for any given density (or similarly the average density for any given modulus) if an exhaustive sampling of microstructures were available for characterization. Since the sampling of microstructures is necessarily incomplete, the functional forms for trend lines must be assumed to be correct in order to analyze the data successfully.

3.2. Variation of Modulus with Bulk Porosity

As the graphite micrographs in Fig. 1 illustrate, nuclear graphites are porous and it is well known that porosity plays a significant role in affecting the moduli of these materials. For purposes of comparing the current results to related work in the literature, the longitudinal and shear moduli have been used to compute Young's modulus and density has been converted to porosity volume fraction (using a theoretical density of 2.26 g/cm³). This allows Young's modulus and the shear modulus to be shown as a function of porosity – results are presented in Fig. 7. In Fig. 7a, the effect of grain type (based on ASTM D7219-08) on this relationship is shown by noting which graphites are fine grain (filled symbols) and which are medium grain (open symbols). The results do not show any discernable trend

that indicates grain type affects material stiffness for a given density. In Fig. 7b, the effect of coke source (pitch – filled symbols, petroleum – open symbols) is shown. Generally, graphites processed with pitch-derived coke appear to have lower porosities (on average), but coke source does not appear to influence modulus for a given density. Finally, in Fig. 7c the effect of the forming method is shown. For the graphites studied in this work, most were formed by one of the following processes: extrusion (filled symbols), isostatic molding (open symbols) or vibromolding (crossed symbols). While it appears that vibromolding produces materials with the lowest porosity, no clear trend between the forming method and modulus emerges for graphites of a particular density. The absence of clear and identifiable effects of grain type, coke source or forming method on modulus as a function of density (for this sample set) indicates that the primary factor affecting material stiffness is porosity. In Fig. 8, all modulus data are presented without additional identification and will be analyzed as a single data set representing a statistical sampling of graphite modulus as a function of porosity.

Results are shown with linear and exponential trend lines that are fit to the data. The functional form for the linear fit is suggested by the model developed by Hashin and Shtrikman and is supported by previous studies of particular graphites that have shown modulus values that vary nearly linearly with porosity [13,19,41] while the exponential fit is suggested by work presented by Cost *et al.* [19]. Again, the porosity derived here is related to measurements of sample masses and volumes and does not include contributions to porosity that might be measured using other techniques such as BET surface area measurements that would involve all accessible surfaces – including those associated with open microcracks. Given the richness of graphite microstructure, it is interesting that overall trends exist for the data gathered across the range of graphites in this study even though porosity was not intentionally varied. In contrast, the results presented by Cost *et al.* [19] and by Shibata *et al.* [41] were for particular graphites in which porosity was intentionally varied to assess related effects on graphite stiffness. By focusing on particular graphite types, these studies yielded stiffness values that included far less scatter than is the case for the results presented here.

It should be noted that the correlation coefficients for the various fits shown in Fig. 8 are quite poor, but this should be expected since the approach taken here is based on a statistical interpretation of the data. The trends are based on models for the relationship between porosity and modulus and the random scatter of points about the trend line represents the variations in microstructure (for a given porosity) that can give rise to different values for modulus. The results here suggest that there exist general relationships between graphite porosity and moduli that might be used to obtain further insight into the structure-property relationships in these materials. This statement is particularly applicable for a given graphite since the underlying microstructure will not display the variability of the sample set contained in this work.

3.3. Modulus of “Theoretically Dense” Nuclear Graphite

Using the models for modulus variation with porosity, the results in Fig. 8 permit estimates for the moduli of theoretically dense nuclear graphite by noting the intercepts with the modulus axis. This general procedure was used by Cost *et al.* who inferred that a fully dense version of the graphite they studied would have a Young’s modulus of 25.5 GPa and a shear modulus of 9.7 GPa. Employing their use of an exponential fit with the measured results here yields values of 24.4 GPa and 10.1 GPa for the respective moduli. Using the linear fit, the moduli would be 18.8 GPa and 7.6 GPa. These experimentally-based estimates provide some indication of the expected moduli for a generalized, polycrystalline, theoretically dense graphite that contains microcracks. As was outlined previously, estimates for the effective crack density can be made by using these values along with the models for the moduli of materials containing microcracks. To complete this analysis, Eqs. (6) and (7) require values for the moduli of theoretically dense, uncracked, polycrystalline graphite, but these are unknown presumably owing to the inability to produce materials with these characteristics. Values for these moduli will be taken from models that use well-known values for the single crystal stiffness tensor to compute the corresponding moduli of polycrystalline materials with randomly-oriented grains.

Unfortunately, theoretical estimates for the moduli of polycrystalline graphite are particularly difficult to obtain owing to the extremely high elastic anisotropy displayed by single crystal graphite. The difference between the upper bound (based on Voigt averaging) and the lower bound (based on Reuss averaging) for Young’s modulus is nearly 500 GPa [42]. The corresponding difference for the shear modulus is approximately 210 GPa [42]. Clearly, these differences suggest some care must be taken in selecting the model that is used to estimate the theoretical stiffness of fully dense, crack-free, polycrystalline graphite. Among the models that could be used – Reuss, Hashin-Shtrikman, Kröner, Kiewel-Bunge-Frische, Voigt [42] – the Reuss and Voigt models rarely yield accurate modulus values for materials having microstructural elements that are randomly oriented in three dimensions and this suggests that one of the other models should be used. For subsequent analysis in this work, we will use the lower bound estimate based on the generalized approach developed by Hashin and Shtrikman since it provides the lowest values that might accurately predict the moduli for materials with complicated, three-dimensional microstructures [22]. The lower limit values for Young’s modulus and the shear modulus in graphite are 39.9 GPa and 14.9 GPa respectively for this model [42]. These values represent the moduli for uncracked material (E_0 and G_0 in Eqs. (6) and (7)) and can be used to estimate effective crack densities. Using the experimentally-based estimate for Young’s modulus in a theoretically dense, microcracked material (18.8 to 24.4 GPa) along with the value from the corresponding crack-free material (39.9 GPa), Eq. (6) can be used to compute an effective crack density of $0.35 \leq \chi_E \leq 0.67$ where the subscript indicates that this estimate is based on Young’s modulus. The corresponding estimate based on

the shear modulus (7.6 to 10.1 GPa for microcracked versus 14.9 GPa for uncracked material) yields $0.48 \leq \chi_G \leq 0.95$ – the subscript indicates that this estimate relates to the shear modulus. These estimates for the effective crack density provide some indication of the degree of microcracking in the microstructure of a generalized, nuclear graphite material.

3.4. Estimation of Microcrack Number Density

The interpretation of the effective crack density (crack energy density coefficient) is problematic since it involves parameters related to the crack size as well as the crack population number density. However, it should be noted that the quantity associated with crack geometry ($\rho w^2 l$) can be computed using measurements of microcrack dimensions so that the corresponding population number densities can be estimated. These dimensions appear to be related to the various components of the graphite microstructure including the binder phase and filler particles and range from tens of nanometers to several micrometers [43-46] and can be roughly equal to pore diameters in various graphites (such as IG-110). This relationship permits an interesting comparison between pore and crack population densities. If microcrack dimensions are $l = 10w$ with $l = \pi R / 4$ then Eq. (9) indicates that there are roughly $275 \times (\chi / \phi)$ cracks per pore. If the effective crack density is taken to be in the range $0.48 \leq \chi \leq 0.67$ (based on the overlap of the ranges obtained previously) and porosity is taken to be $\phi \approx 0.2$ (the average for the graphites included in this study), then there should be approximately 660 to 920 microcracks per pore. This estimate for microcrack density (for the assumed crack size) represents a lower bound and would be higher if the theoretical modulus for graphite were to exceed the lower bound predicted using the Hashin-Shtrikman model. The overall conclusion from this analysis is that there are many more cracks per unit volume in graphite than there are pores. This result is partly supported by SEM micrographs presented by Wen *et al.* [23,45] and Zheng *et al.* [46] as well as by TEM results given by Chi and Kim [43,44] that show many cracks per pore. Clearly, if the estimate for microcrack density were 10^{-2} per pore or 10^6 per pore, then the overall analysis suggested here would be suspect – it is remarkable that a physically meaningful result is obtained with a minimum of information.

4. Discussion

There are various points developed in this work that deserve additional consideration. Among them is the method used to identify moduli for fully dense graphite. The choice to use linear and exponential fits to the modulus versus porosity plots was based on inspection of various models presented in the literature as well as on previous analysis by other researchers who experimentally examined the relationship in more detail. Whether the functional variation was assumed to be linear or exponential, the primary result to be extracted from the analysis was the modulus at zero porosity – no physical

significance was assigned to the derivatives of the curves. However, the model developed by Hashin and Shtrikman, given in Eqs. (1) and (2), provides a more detailed description that was not used to evaluate the data, but could be used in a more robust analysis since the shape of the modulus versus porosity curve depends on the modulus at zero porosity – the derivatives of the curve are linked to the intercept – and, as a result, *two moduli can be extracted as fitting parameters from a single curve of modulus versus porosity*. As appealing as this might be, neither the least-squares fit of Eq. (1) to data for Young’s modulus nor the least-squares fit of Eq. (2) to the shear modulus data was acceptable since both yielded non-physical results for the Lamé constant λ – the reason for this is a subject for additional investigation.

Moving from porosity to microcracking, a major assumption in the analysis involved choices for the moduli of nonporous and crack-free, polycrystalline graphite (E_0 and G_0). In the analysis, the lower bound moduli suggested by Hashin and Shtrikman were used. Measurements of graphite modulus as a function of neutron dosage or as a function of applied pressure can add support to these choices since both can close microcracks (decreasing their contribution to the overall elastic energy state) and increase the measured stiffness of graphite. While these types of experiments have not been performed on the samples used in this study, related work has shown that Young’s modulus increases considerably when irradiated with neutrons. Work by Bradford and Steer on neutron-irradiated Gilsocarbon graphites indicated that “structure” related changes to Young’s modulus caused the stiffness of these materials to rise from 15-20 GPa to a maximum of 35-45 GPa [16]. Within the context of this discussion, the increase in modulus (~ 20 GPa) might be attributed to the closing of microcracks in the material. This type of closing has been observed by Wen *et al.* for Mrozowski cracks in nuclear graphites irradiated with electrons [23] and the increase in modulus measured by Bradford and Steer is very close to the difference between the microcrack-free modulus and the zero-porosity modulus assumed for the graphites included in the current study (roughly 15-20 GPa). Work by Ishiyama *et al.* on IG-110 showed that Young’s modulus increased by a factor of approximately 2.5 as a result of neutron irradiation [14]. Given an initial value of 10.2 GPa, the maximum would be approximately 25 GPa yielding a 15 GPa increase that could be attributed to closing of microcracks – again, in the range of assumptions made here. In addition, the work by Bradford and Steer as well as that by Ishiyama *et al.* showed that tensile strength reached maximum values at neutron dosages that also produced maximum values for Young’s modulus. This type of behavior in brittle materials is consistent with crack closing/elimination since stress intensity factors and modulus both depend directly on crack size [47,48].

In order to estimate the effective crack density for a particular graphite grade (or sample) using the procedure outlined in this work, some method for altering porosity would be needed to obtain values for the modulus at zero porosity. Porosity can be increased through oxidation processing, but this affects

graphite microstructure in more ways than simply increasing pore size and/or number density since filler and binder phases oxidize at different rates [7]. This preferential processing of the microstructure ultimately affects the size and distribution of pores and likely affects the number density of microcracks, but this has not been verified. A more direct route to estimating microcrack populations is to assess changes in modulus brought about by crack opening or closure. This can be accomplished by imposing known stresses on the material, measuring changes in modulus and interpreting these changes with models that effectively represent microcrack characteristics in that graphite grade. The most effective stress state to accomplish this type of measurement would involve hydrostatic loading since this could be used to close all cracks regardless of crack orientation. Unfortunately, there do not appear to be studies that have measured the modulus of graphites under hydrostatic pressure, but studies have been performed that report variations in stiffness that have been brought about by uniaxial loading. Yoda *et al.* performed measurements of modulus on IG-11 using longitudinal ultrasonic waves propagating along the direction of loading [49]. Whether loading was tensile or compressive, modulus decreased with material strain, but since strains were large ($> 0.1\%$ compressive strain, $>0.03\%$ tensile strain) permanent changes to the elastic modulus occurred – this is consistent with crack initiation/growth that would increase the crack volume fraction. The measurements made by Yoda *et al.* during compression are particularly interesting since they show reduction in modulus as well as some recovery of modulus (perhaps 5-10%) during sample unloading. While the absolute reductions can be related to increased crack volume fraction, recovery indicates that some type of reversible (elastic) change to the microstructure occurred during loading/unloading. Within the context of microcracking, this change can be related to crack closure processes that effectively change the crack volume fraction sensed by ultrasound. More recently, Bodel has performed measurements of modulus on nuclear graphites using longitudinal ultrasonic waves propagating along as well as transverse to the direction of loading [50]. All measurements were made using compressive loads (< 70 MPa). In Gilsocarbon, Bodel found that modulus decreased with increasing load and irreversible changes to modulus occurred during initial loading. Subsequent loading/unloading cycles primarily showed reversible changes to modulus with higher compressive loads yielding lower modulus values. These results as well as others presented by Bodel are consistent with the influence of microcracks on modulus in graphite materials. When taken together, the studies by Yoda *et al.* and Bodel along with the results of this work show that microcracking effects on modulus in graphite can potentially be isolated from other factors. While quantitative models have not been developed or verified to interpret these types of measurements, directions for future work are indicated by the results presented here.

5. Conclusions

In this work, laser ultrasonic methods have been used to measure the stiffness in a selection of nuclear graphites. Measurements were made to assess wavespeeds for longitudinal and shear waves in different propagation directions in the graphite samples and these were converted to effective longitudinal and shear moduli using determinations of sample density. Using these moduli, Young's modulus was computed. Overall trends for these moduli indicated that they increased with graphite density or, put another way, decreased with graphite porosity. These trends could be interpreted using linear and exponential fits to the data and this is consistent with various models in the literature that have been used to model variations of modulus with porosity at low porosity volume fractions. Extrapolations of these fits to zero porosity were used to infer the moduli for theoretically dense graphite. These values were far below those expected based on various models that have been developed in the literature to predict the moduli of fully dense, polycrystalline, isotropic graphite. This discrepancy could be interpreted as being related to microcracking in the graphite microstructure. Models have been used to estimate the microcrack number densities that would be necessary to account for the behavior of the graphites in this study and results indicate that hundreds of microcracks per pore would be needed to reduce graphite stiffness from predicted values to those inferred from measurements. This is reasonable given the microstructures observed in various graphites. Furthermore, results reported in the literature are consistent with the influence of microcracking on elastic stiffness and could be interpreted using concepts developed here. Additional experiments are needed to quantify the relationship between modulus and microcrack densities and these should be developed using more accurate models that include microcrack orientation distributions. Having these types of structure-property relationships should allow for more sophisticated characterization of nuclear graphites using ultrasonics methods.

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Table 1: Grade, Density and Elastic Moduli of Nuclear Graphite Samples

Graphite	Density (g/cm ³)	Longitudinal Modulus (GPa)	Shear Modulus (GPa)	Young's Modulus (GPa)	Grain Type*	Coke Type	Forming Method	Source
HLM	1.76	10.84	3.44	8.72	medium grain	Petroleum	Extruded	SGL Carbon / USA
HLM	1.74	9.93	2.85	7.40				
H-451	1.73	11.98	3.81	9.66	medium grain	Petroleum	Extruded	SGL Carbon / USA
H-451	1.72	11.40	3.56	9.06				
H-451	1.67	11.38	4.41	10.44				
IG-110	1.71	8.81	2.71	6.94	fine grain	Petroleum	Isostatically Molded	Toyo Tanso / Japan
IG-110	1.71	9.28	2.87	7.32				
IG-430	1.83	10.86	4.23	9.99	fine grain	Pitch	Isostatically Molded	Toyo Tanso / Japan
IG-430	1.83	12.32	4.68	11.18				
NBG-10	1.79	13.53	5.93	13.16	medium grain	Pitch	Extruded	SGL Carbon / France
NBG-10	1.79	14.12	5.53	13.03				
NBG-10	1.81	15.05	5.64	13.54				
NBG-17	1.88	14.18	4.44	11.29	medium grain	Pitch	Vibromolded	SGL Carbon, Germany / France
NBG-17	1.87	15.94	4.63	12.00				
NBG-18	1.88	12.91	4.78	11.53	medium grain	Pitch	Vibromolded	SGL Carbon, Germany / France
NBG-18	1.88	13.00	4.04	10.29				
NBG-18	1.87	13.63	5.15	12.33				
NBG-18	1.84	13.41	4.56	11.34	fine grain	Petroleum	Isostatically Molded	SGL Carbon, Germany / France
NBG-25	1.85	13.36	4.67	11.50				
NBG-25	1.85	13.76	4.87	11.95				
PCEA	1.75	10.33	3.91	9.34	medium grain	Petroleum	Extruded	GrafTech Intl. / USA
PCEA	1.75	9.42	3.41	8.30				
PCEA	1.80	10.03	4.19	9.56				
PCIB	1.86	13.62	4.77	11.74	fine grain	Petroleum	Isostatically Molded	GrafTech Intl. / USA
PCIB	1.88	13.70	4.71	11.66				
PGX	1.77	9.92	3.38	8.39	medium grain	Petroleum	Molded	GrafTech Intl. / USA
PGX	1.78	10.10	4.28	9.70				
S 2020	1.77	13.20	5.06	12.03	fine grain	Petroleum	Isostatically Molded	Carbone of America / USA
S 2020	1.77	13.23	5.19	12.22				
BAN	1.96	9.40	4.24	9.23	medium grain	Petroleum Other	Extruded	GrafTech Intl. / USA
BAN	1.96	10.55	3.60	8.93				

* Grain type designation based on ASTM D7219-08, "Standard specification for isotropic and near-isotropic nuclear graphites", ASTM International, West Conshohocken, PA 19428-2959, USA.

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Figure 1: Scanning electron micrographs of three different graphites used in this study: a. IG-110, b. NBG-18, c. HLM. These images highlight microstructural differences, especially porosity, among these materials.

Figure 2: Computed variation of elastic modulus with porosity volume fraction based on models developed by Hashin and Shtrikman. The moduli are normalized by values obtained at zero porosity.

Figure 3: Computed variation of elastic modulus with the microcrack energy density coefficient based on models presented by Zheng. This coefficient depends on crack number density, n , as well as on crack geometry.

Figure 4: Schematic illustration of the laser ultrasonic apparatus used to measure ultrasonic wave times-of-flight in nuclear graphite. The transmitter source was a pulsed Nd:YAG laser and the receiver was a path-stabilized, Michelson-type interferometer.

Figure 5: Laser ultrasonic waveforms for three different graphites showing the directly transmitted longitudinal and shear wave arrivals. The trigger noise early in early in each waveform is related to the pulsing of the source laser. a. Waveform obtained for IG-110. The arrival at approximately 7.5 μs is the reflected longitudinal wave (3 transits through the sample thickness). b. Waveform for NBG-18. c. Waveform for HLM.

a.

b.

Figure 6: a. Longitudinal stiffness of various nuclear graphites as a function of material density. b. Shear stiffness as a function of density. The solid lines in each plot represent the best fit lines to the data (omitting values measured for BAN – see text for discussion).

Figure 7: Young's modulus and shear modulus (from Table 1) for nuclear graphite as a function of porosity volume fraction highlighting effects of a. grain type, b. coke source and c. forming method.

Figure 8: Young's modulus and shear modulus for nuclear graphites as a function of porosity volume fraction. The solid lines represent linear and exponential best-fit curves to the respective data sets. The fits have been extended to zero porosity volume fraction to estimate the corresponding moduli for fully dense graphite containing microcracks.