Laser Ultrasonic Sensing of Oxidation-Induced Microstructural Changes in Nuclear Graphites

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Abstract— **Serving both as a structural and as a functional material, nuclear graphites have a range of useful mechanical, chemical and radiation-related behaviors that are important for nuclear applications. The raw materials used as feedstock along with the manufacturing processes used for production of these materials results in a complicated microstructure composed of graphite filler, graphitized pitch binder, and voids/defects that include porosity and microcracks. These heavily influence the overall elastic moduli of nuclear graphites and must be taken into account when interpreting ultrasonic measurements. Indeed, the measured elastic moduli are generally close to the Reuss limits – the theoretical, lower bounds for the moduli – but no attempts have been made to explain these results within the broader context of elasticity in porous materials containing microcracks. In this work, we report ultrasonic measurements of elastic moduli for nuclear graphites as a function of the bulk porosity and interpret them using relatively simple, physics-based models that describe the effects of porosity and microcracking on modulus. Modifications to these models are explored to account for microstructure-related effects on modulus such as those that are associated with oxidation-induced porosity. These models can be used to interpret a broad range of ultrasonic measurements reported previously for nuclear graphites, and the insight gained into the elastic responses of these materials can be used to guide the use of ultrasonic methods to assess the structural integrity of nuclear graphites.**

Keywords—laser ultrasonics characterization, material property, elastic modulus, porosity

I. INTRODUCTION

In this work, we report ultrasonic measurements of elastic moduli for nuclear graphites as a function of the bulk porosity and interpret them using physics-based models that describe the effects of porosity and microcracking on modulus. In particular, oxidation-induced changes to porosity are considered along with its effect on the moduli of polycrystalline graphites. The presentation will include the following areas to develop descriptions of the elastic moduli of these materials: (1) effective medium theories for porous materials, (2) elastic moduli for polycrystalline materials, (3) porosity development and selective oxidation, (4) discussion of results, and (5) conclusions.

II. EFFECTIVE MEDIUM THEORY FOR POROUS MATERIALS

Effective medium theories assume that property measurements are insensitive to the length scales associated with microstructural phases present in a material. Consequently, the measured properties are the same as those that would obtained for a homogeneous material that represents the essential behavior of the multiphase material. The principal challenge for these theories is the development of expressions that relate the properties of the effective medium to those of the constituent components of the actual material. Many theories have been developed to address this challenge, but among those that could be used, the one presented by Hill [1] and by Budiansky [2] is particularly useful for this work since it leads to results that effectively represent the linear elastic response of nuclear graphites.

This theory was used by Hsu and Wu to interpret modulus measurements in a two-phase polymer composite [3]. Focusing on the variation of Young's modulus with volume fraction, they accurately modeled this variation including aspects of percolation that appeared in their system. Fortunately, the results of this theory can be described in a few equations. Following Hsu and Wu, the bulk modulus (K) and the shear modulus (G) of the effective medium can be related to the moduli of the constituent components (K_1, K_2 and G_1, G_2) and their respective volume fractions (f_1, f_2) using two, coupled equations. These equations are as follows:

$$f_1(1 - K_1 / K)/(3K_1 + 4G) + f_2(1 - K_2 / K)/(3K_2 + 4G) = 0 \quad (1)$$

$$f_1(1 - G_1 / G)/(aG_1 + G) + f_2(1 - G_2 / G)/(aG_2 + G) = 0 \quad (2)$$

with

$$a = (8 - 10v)/(7 - 5v) \quad (3)$$

and

$$v = (3K - 2G)/(6K + 2G). \quad (4)$$

where v is the Poisson Ratio of the effective medium. Using the definition of volume fraction, it can be shown that $f_2 = 1 - f_1$.

For this work, polycrystalline graphite will serve the role of first component of the composite and air will be the second. The shear modulus for air is zero and the bulk modulus should be small compared to that for graphite. Eliminating the bulk

modulus, K, from Eqs. (1)-(4) and letting $G_2 = 0$ results in a cubic equation for G [4]:

$$\alpha G^3 + \beta G^2 + \gamma G + \delta = 0 \qquad (5)$$

where $\beta = 24(K_1 + K_2) + 12(f_1 K_1 + f_2 K_2) + 16 G_1(5 f_2 - 2)$, $\gamma = 27 K_1 K_2 + 12 G_1[(5 f_2 - 2)(K_1 + K_2) - (f_1 K_1 + f_2 K_2)]$, $\delta = 9 K_1 K_2 G_1(5 f_2 - 3)$ and $\alpha = 32$. A central, essential assumption that this model makes is that the properties of the two phases are not functions of volume fraction. This is true for air, but the moduli of the solid phase could vary with porosity as a result of processes that produce incommensurate changes to the microstructure. Since the solid components in graphite are composed of a multiscale microstructure with crystallites (~10^2 nm) joined in graphite grains (20 to 800 μm) that are incorporated into a three-dimensional solid matrix derived from a binder phase, it is difficult to conceive of any process that would change porosity while preserving the relative representation of each component in the microstructure. This idea will be explored when the moduli of oxidized graphite are considered.

III. MODULI FROM THE THEORY FOR POLYCRYSTALLINE MATERIALS

Even though the actual microstructural constitutions of nuclear graphites are complicated, the solid phase containing filler particles and graphitized binder will be represented by an idealized, fully-dense, polycrystalline assembly of randomly-oriented, graphite crystallites. For a polycrystalline aggregate that behaves isotropically, two independent elastic moduli can be used to describe the elastic response, but these must relate to the five single crystal moduli of the constituent crystallites. The relationships between the aggregate moduli and those for single crystal graphite depend on the microstructural composition of the material which dictates how stresses and strains are shared throughout.

Among the many schemes that have been developed to model distribution of stresses and strains, those by Voigt and Reuss are the simplest. While these two schemes are typically illustrated using highly idealized material microstructures, they emerge from more general treatments describing the moduli of multicomponent systems [5]. These treatments assume that certain microstructures can be realized in which the stresses (strains) in different components of the microstructure are proportional to the average, overall stress (strain) in the material – the proportionality being different for each of the components.

If the stresses (strains) are the same in these components, then the averaging scheme yields the Reuss (Voigt) result. The reason that polycrystalline graphites have moduli that tend towards the Reuss description is that microcracks and porosity in the microstructure accommodate wide variations in strain such that the isostrain condition essentially cannot be realized – the material behavior deviates considerably from the central assumption of Voigt averaging. Unfortunately, this does not indicate how closely the assumption for Reuss averaging is followed. Regardless, these schemes can be implemented relatively easily and provide useful upper (Voigt) and lower (Reuss) bounds for the isotropic moduli.

The isotropic, elastic moduli of interest for ultrasonics results are C_{11} and C_{44} (using two-index notation) and these are related to the single crystal elastic constants (c_{ij}) as follows for Voigt averaging [6]:

$$C_{11}^V = (8 c_{11} + 3 c_{33} + 4 c_{13} + 8 c_{44}) / 15 \qquad (6)$$

and

$$C_{44}^V = (7 c_{11} - 5 c_{12} + 2 c_{33} - 4 c_{13} + 12 c_{44}) / 30 \qquad (7)$$

where the superscript indicates that these moduli correspond to the Voigt limit. Using the Reuss averaging scheme, the elastic moduli can be expressed conveniently using the single crystal elastic compliances (s_{ij}). The results for this scheme are as follows [6]:

$$C_{11}^R = (S_{11} + S_{12}) / [(S_{11} - S_{12})(S_{11} + 2 S_{12})] \qquad (8)$$

and

$$C_{44}^R = 1 / S_{44} \qquad (9)$$

where the superscript indicates that these are for Reuss averaging, and

$$S_{11} = (8 s_{11} + 3 s_{33} + 4 s_{13} + 2 s_{44}) / 15 \qquad (10)$$

$$S_{12} = (s_{11} + 5 s_{12} + s_{33} + 8 s_{13} - s_{44}) / 15 \qquad (11)$$

$$S_{44} = 2(7 s_{11} - 5 s_{12} + 2 s_{33} - 4 s_{13} + 3 s_{44}) / 15 . \qquad (12)$$

For many materials, the Voigt and Reuss limits can be close to the measured moduli, but this does not happen for polycrystalline graphite since single crystal graphite is highly anisotropic. Hill suggested that a simple arithmetic average of the shear moduli obtained using the Voigt and Reuss schemes provided values that were close to those measured for certain materials [1]. Hill's suggestion (which yields the Hill average) has been extended by others to estimate other moduli of polycrystalline materials [6]. However, for polycrystalline graphite, the Hill averages for the moduli exceed experimental estimates and are not useful for modeling purposes. Researchers examining the elastic behavior of graphite have suggested that microcracking in polycrystalline graphite is responsible for observed differences [7,8]. Among the cracks that form in graphite, those that occur along basal planes (known as Mrozowski cracks) have the effect of reducing the single crystal moduli. Using modified values for these moduli [9], revised estimates for the Reuss and Voigt limits can be obtained.

Even with these revisions, the Hill averages still provide estimates for the elastic moduli that are too high. In previous work, we proposed a modification to the Hill averaging scheme that used a weighted average of the Reuss and Voigt limits to arrive at modulus values. This modification is essentially a re-application of a simple theory for the moduli of composite materials [5] since it considers the graphite to be composed of two components of differing moduli – one relatively stiff (Voigt limit) and the other compliant (Reuss limit) – such that the overall modulus can be obtained simply by taking a weighted average of the moduli of the two components. This approach is outlined briefly using scalar notation to support subsequent

analysis. The overall strain ($\overline{\varepsilon}$) in the polycrystalline aggregate can be expressed as an average based on volume fractions (v_R, v_V) and the strains in the two contributing components ($\varepsilon^R, \varepsilon^V$):

$$\overline{\varepsilon} = v_R \varepsilon^R + v_V \varepsilon^V . \qquad (13)$$

If it is assumed that the strains in the individual components are proportional to the overall strain such that $\varepsilon^R = a^R \overline{\varepsilon}$ and $\varepsilon^V = a^V \overline{\varepsilon}$, then Eq. (13) yields:

$$1 = a^R v_R + a^V v_V \rightarrow a^V = (1 - a^R v_R)/(1 - v_R) \qquad (14)$$

where $v_V = 1 - v_R$ has been used. For the aggregate, $\overline{\sigma} = \overline{C}\overline{\varepsilon}$ where $\overline{\sigma}$ is the overall stress and $\overline{C}$ is the material modulus. If $\overline{\sigma} = v_R \sigma^R + v_V \sigma^V = v_R C^R \varepsilon^R + v_V C^V \varepsilon^V$, then the following result is obtained when the previous relationships are used:

$$\overline{C} = C^V + a^R v_R (C^R - C^V) = a^R v_R C^R + (1 - a^R v_R) C^V . \ (15)$$

When $a^R v_R = 1/2$, Eq. (15) simply yields the Hill average, but this equation represents a more general result that can be applied to graphites and used to interpret previous reports in the literature. For example, Cost et al. noted that estimated values for the moduli of fully dense, polycrystalline graphite are close to but higher than the Reuss limits [10] – subsequent studies have agreed with this observation [11]. Based on Eq. (15), this suggests that the product $a^R v_R$ tends towards unity. This could happen if the volume fraction of graphite that behaves in a Reuss-like fashion approaches unity while, at the same time, the connectivity of the overall microstructure (indicated by a^R) takes on a similar value. As a first approximation, this relatively simple view is useful since it does account for the variations in bonding that occur in graphites. For example, filler particles are not coherently bonded with the graphitized binder phase (interfacial atomic-level structures are not maintained between the filler and the binder), but within the binder phase, crystallites can form a continuous random network. This type of microstructure should be expected to behave in ways that can be represented as a collection of regions that satisfy Reuss-like conditions connected by regions that display Voigt-like behavior. In previous work [12], the result in Eq. (15) was represented using a simpler form:

$$\overline{C}_{ij} = r C_{ij}^R + (1 - r) C_{ij}^V \qquad (16)$$

where $r = a^R v_R$ and $0 \le r \le 1$. The expression in Eq. (16) is a generalized form for the Hill average.

IV. POROSITY AND SELECTIVE OXIDATION

The outline provided in the previous sections can be used to construct a physics-based model describing the moduli of porous, isotropic, polycrystalline graphite. This model can be used to assess the variation of modulus that should occur in nuclear graphites when porosity is altered. Measured porosities

for a variety of nuclear graphites fall in the range $0.16 < f_2 < 0.27$ and, with appropriate application of the model, the variation of the measured moduli with porosity can be successfully interpreted. In particular, when porosity is changed by graphite oxidation, the model can be used to interpret modulus values obtained using ultrasonic measurements. Since oxidation of graphite occurs preferentially along the edges of basal planes, this will incommensurately affect the microstructure [13-15]. Since transfer of elastic deformation between adjoining crystallites along basal planes essentially establishes the Voigt limit, this suggests the contribution of the Voigt limit to the overall modulus of oxidized graphites will diminish as oxidation progresses and could be linked to changes in porosity. This implies that the weighting parameter, r, somehow increases with porosity.

Unfortunately, it is not clear what the relationship between r and f_2 should be. The simplest form that likely reflects some aspect of the physical processes taking place during oxidation would be a linear relationship: $r = r_i + b f_2$ where r_i and b serve as fitting parameters for interpretation of experimental measurements. This form has been used previously and, when combined with other parts of the development here, can be used to accurately represent the variation of elastic moduli with oxidation-induced changes to graphite porosity [12]. However, additional insight can be gained from concepts associated with Eq. (15) and can be used to model modulus variations. Since $r = a^R v_R$, the freedom exists to attribute changes in r to variations in a^R and/or v_R. Since v_R describes the volume fraction of the material that behaves in a Reuss-like fashion and a^R relates to the connectivity of the various regions (determining the relative contributions of each to the overall moduli), either could vary with porosity thereby affecting the dependence of r on f_2. If it is assumed that both a^R and v_R depend linearly on porosity, then the following result is obtained:

$$\begin{aligned} r = a^R v_R &= (a^{R_i} + \alpha f_2) \times (v_{R_i} + \beta f_2) \\ &\approx r_i + (\alpha v_{R_i} + \beta a^{R_i}) f_2 \end{aligned} \qquad (17)$$

where $r_i = a^{R_i} v_{R_i}$. The quadratic term has been omitted in the final expression since it is small for most conditions of interest ($f_2 < 0.5$). The result in Eq. (17) contains parameters that are perhaps experimentally inaccessible, but they can be linked broadly to the material microstructure and can be used to interpret oxidation-induced modulus changes in nuclear graphites.

To demonstrate the use of this approach to fit experimental data, moduli measured in oxidized samples of IG-110 and NBG-18 using laser ultrasonic methods will be considered. The use of these methods for measurements in nuclear graphites has been described in detail previously [8]. These data along with modeled fits are shown in Fig. 1. Note, if the condition

$r_i + (\alpha v_{R_i} + \beta a^{R_i}) f_2 > 1$ occurs, then it is assumed $r = 1$ with the understanding that all of the remaining microstructure is Reuss-like in its behavior.
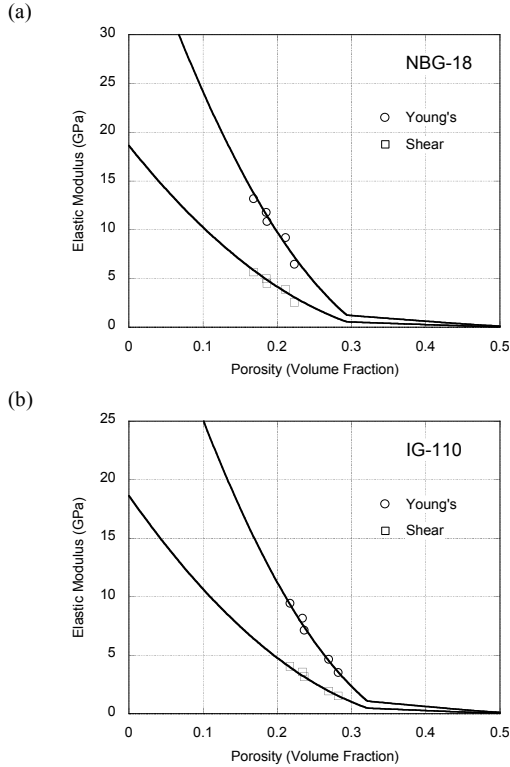
(a)

(b)

Fig. 1. Young's and shear moduli for two different oxidized graphite grades shown as a function of porosity: (a) NBG-18 and (b) IG-110. Symbols represent experimental measurements. Solid curves are modeled fits to the measurements.

V. Discussion

To arrive at a satisfactory description for the moduli of nuclear graphite, assumptions regarding the connectivity of the material microstructures of these materials must be made, and these lead to results expressed in Eq. (16). To achieve the modeled fits to modulus measurements of oxidized IG-110 and NBG-18, the same values for the microcrack-modified, single crystal elastic moduli were used [12] along with the same values for the initial fractional content of Reuss-like microstructure ($r_i = 0.92$). The only parameter that differs for the modeled curves is the value for $b = (\alpha v_{R_i} + \beta a^{R_i})$ indicating that the fractional Reuss-like behavior of the microstructures of these materials varied at different rates as oxidation proceeded and porosity increased. For NBG-18, the value used for the fit shown in Fig. 1 is 0.27 while the value for IG-110 is 0.24: b is 9% higher in NBG-18. Since the grain size (filler particle size) is larger for NBG-18 (0.3 mm average, 1.6 mm maximum) than for IG-110 (20-25 μm average), the interfacial area between grains and graphitized binder is lower in NBG-18 than in IG-110 on a volume basis. This lower interfacial area allows for more rapid reductions in grain-binder connectivity for a given change in porosity and this should yield larger values for b –

the result obtained experimentally. It is known that oxidation proceeds preferentially in the binder-derived graphite phase [16,17] and this indicates that differences in b are likely related to porosity-related changes to a^R that are quantified by α. Detailed studies of oxidized microstructures would need to be performed to confirm this assignment.

VI. Conclusions

This work shows that ultrasonic assessment of the elastic responses of nuclear graphites can provide insight into the structure-property relationships in these materials when appropriate models are used to interpret experimental results. The physics-based models for porous, microcracked materials developed here can be used to assess how various graphite microstructural components affect the moduli of these materials. While the effective medium approach used in this work does not take into account specific aspects of graphite microstructure, the overall elastic behaviors of polycrystalline graphite can be related to microstructure using effective medium models and can be used to refine interpretation of elastic modulus measurements reported for nuclear graphites.

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