Mode I Fracture Toughness Prediction for Multiwalled-Carbon-Nanotube Reinforced Ceramics

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Abstract

Eshelby-Mori-Tanaka models with a continuum damage mechanics approach are developed to predict the elastic damage and fracture toughness of multiwalled-carbon-nanotube (MWCNT) reinforced ceramics as a function of MWCNT fraction. This damage model is introduced in a modified boundary layer modeling approach to predict damage accumulation leading to crack propagation from a pre-existing crack tip in a process window where damage and fracture are captured under plane-strain Mode I loading. The model is validated against experimental fracture toughness data for a MWCNT 3-mol% yttria-stabilized zirconia composite and successfully predicts the observed saturation in fracture toughness at about 25% volume fraction MWCNTs.

Keywords:

Carbon nanotubes; Damage model; Fracture toughness; Modeling and simulation; Ceramic composites

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1. Introduction and Background

Ceramics are candidate materials for high-temperature applications, but unreinforced ceramics typically exhibit brittle behavior and are vulnerable to cracking and crack growth processes leading to catastrophic failure. Therefore, without fiber or other reinforcements, ceramics are not easily used for structural applications. The science of toughening ceramics to improve fracture toughness, strength, and reliability has progressed over the past decades [1-2] so that high toughness ceramic composites reinforced with strong, continuous fibers can be fabricated with toughness values greater than $20 \text{ MPa}\sqrt{\text{m}}$ and substantial crack resistance behavior (R-curves). Ceramics can also be reinforced with ductile phases, whiskers, chopped fibers, controlled debonding layers, and can be made self-reinforcing or transformation toughened [2]. Each of these toughening methods can be controlled and tailored but toughness increases appear to be greatest for continuous fiber composites when the fiber/matrix interphase is designed for the proper amount of debonding during crack growth and the fibers exhibit high strength. Otherwise, toughness increases are limited [2].

With regard to toughening ceramics, there is interest in incorporating multiwalled carbon nanotubes (MWCNTs), or more simply CNTs, into ceramics to produce composites with improved mechanical properties for structural applications since MWCNTs possess extraordinary mechanical properties that largely exceed those of conventional ceramic or carbon fibers [3-4]. CNTs have been added to a wide range of materials, including polymers, metals, and ceramics [4-6] and have demonstrated increases in fracture toughness and strength in certain materials, mainly in polymers and brittle oxides. In brittle ceramic materials, such as zirconia [3, 6-8], alumina [9], silicon carbide [10], and silicon nitride [11] the increases are somewhat less since synthesis of CNT-ceramic composites presents formidable challenges and enhancements in

mechanical properties were not always achieved as illustrated by this summary of work in yttria stabilized zirconia (YSZ), or also referred to as yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) [12]. The reasons for these unremarkable changes in fracture toughness were reportedly due to (i) a poor dispersion of CNTs in the matrix, (ii) degradation of CNTs during processing, (ii) CNT clustering at the ceramic grain boundaries, (iii) weak bonding between the CNTs and the ceramic matrix, and (iv) a lower density compared to the monolithic ceramic, i.e., an increased flaw population [12]. Spark plasma sintering and careful nanotube arrangements have been shown to improve toughening, at least in YSZ materials, by reducing nanotube damage by sintering at lower temperatures and achieving improved densification. Nanotube alignment appears to play a large role relative to 3D random arrangements [13], but these arrangements are difficult to achieve, and many research groups focus instead on improving dispersions of 3D CNTs to avoid agglomeration and clusters of nanotubes on grain boundaries. These effects are also generally observed in other material systems as noted above for SiC, Si₃N₄, and Al₂O₃ matrices reinforced with CNTs.

Recently, Mazaheri et al. [7, 8] have processed CNT reinforced 3%-yttria stabilized zirconia (3YSZ) composites by spark plasma sintering (SPS) and have shown that reinforcing 3YSZ with CNTs results in significant increases in stiffness and fracture toughness as long as the CNT contents can be homogenously distributed in the ceramic matrix. The latest results from this group demonstrate excellent CNT dispersion in a 3Y-TZP matrix consolidated by SPS and a measured fracture toughness K_I^c above 15 MPa $\sqrt{m}$ using indentation methods, which, however, often give higher values compared to bulk tests. It is also not clear from this work if the toughening is due to the fine grain size, from improved transformation toughening, or from CNT

toughening. In any event, these CNT composites are gradually improving but many issues remain to be resolved [12].

In the meantime, predictive models for mechanical properties (i.e., elastic properties, strength and fracture toughness) of CNT ceramic composites are lacking and such models can guide processing of these materials. As mentioned earlier, polymers, ceramics and metals have all been used as the matrix material for producing composites with CNT reinforcements, however CNT/polymer composites have been the most studied system due to the high ultimate tensile strain of polymers and the ease of processing, functionalization, tailoring, and fabrication of polymer composites [14]. Mechanical property prediction models have been developed for CNT/polymer composites, but an equivalent body of models is absent in the literature for CNT/ceramic composites. In this section, we will review the key models developed for CNT/polymer and CNT/metal composites, in particular, with a focus on the Eshelby-Mori-Tanaka (EMT) based models [15-17] as these models have been proved to be sufficiently accurate and efficient to justify the development of an Eshelby-Mori-Tanka approach (EMTA) to CNT/ceramic composites developed and described in the following sections. The research and challenges in modeling CNT composites have been discussed in [18].

Reinforcing a matrix material with CNTs can produce a composite with higher stiffness, strength, and toughness than the unreinforced material. Such increased mechanical properties are not solely the result of the excellent mechanical properties of CNTs but also due to an adequate dispersion of CNTs in the matrix and a strong interfacial adhesion between the CNTs and matrix material, which can be obtained through chemical functionalization of the CNT surface in contact with the matrix material. Without this functionalization CNTs interact with the surrounding matrix mainly through the Van der Waals force, which do not provide for efficient

load transfer across the CNT/matrix interface [19]. Conceptually, the chemical functionalization represents the CNT/matrix “*interphase*”. Predictive models should capture this nanoscale feature in order to accurately predict the increase in mechanical properties of well-processed CNT composites.

Odegard et al. [20] were among the pioneering authors who developed a multiscale modeling approach to predict the elastic properties of single-walled (SW) CNT/polymer composites linking molecular dynamics (MD) to continuum modeling in conjunction with an EMT method. These authors first used MD analyses to establish a model for the molecular structure of the nanotube and the adjacent polymer chains [20]. Next, their equivalent-continuum model [21] was applied to build the effective or equivalent fiber representing the nanotube and local polymer, and finally, the EMT micromechanics combined with fiber orientation averaging were applied to compute the elastic properties of the CNT/polymer composite. Their results show substantial increase in longitudinal elastic modulus with nanotube alignment and volume fraction [20]. MD analyses were also used by Frankland et al. [22], but without combining with an EMT model, to determine the stress/strain behavior of CNT/polymer composites. The effects of nanotube waviness on the elastic modulus of CNT/polymer composites were studied by Fisher et al. [23] and Bradsaw et al. [24]. These authors used finite element analyses in conjunction with an EMT model and found significantly lower modulus for wavy nanotube composites than the values for straight nanotube composites. Shi et al. [25] also applied an EMT model to compute the elastic properties of wavy CNT/polymer composites. In their model, a wavy CNT was modeled as a helical spring, and nanotube agglomeration was treated. It was found that both nanotube waviness and agglomeration significantly reduce the stiffening effect of CNTs. More recently, Shao et al. [26] replaced curved CNTs and those with partial debonding by equivalent straight

short fibers embedded in a matrix material, and then applied a Mori-Tanaka scheme to compute the effective moduli of the resulting composite. They found that both debonding and waviness reduce the elastic stiffness significantly. The effect of nanotube waviness and random orientation on the nanotube elastic properties and stress/strain response were also investigated by Li and Chou [27] using a micromechanical model combined with finite element analyses. In their model, a two-dimensional description of the CNT/polymer composite is achieved by discretizing in finite elements a representative domain containing either aligned CNTs, or wavy CNTs, or random curved CNTs. Fracture inside the domain was predicted by the maximum stress criterion, and their results showed that relative to straight nanotubes, CNT waviness reduces the composite elastic modulus but increases its ultimate strain while randomly oriented wavy CNTs reduce both the composite elastic modulus and tensile strength.

Seidel and Lagoudas [28] explored EMT, self-consistent, and composite cylinder micromechanics to predict the elastic properties of CNT composites. Clustering of CNTs in a polymer matrix was treated using a tessellation procedure. In addition to clustering, these authors also investigated the effects of CNT/matrix interphase regions (due to functionalization and polymer wrapping) on the composite elastic properties using a multi-layer composite cylinder approach that extended the Hashin and Rosen [29] model. Their model also predicted the increases in both longitudinal and transverse elastic moduli for the composite as the number of nanotube walls increases [28]. It was also found that randomly oriented CNT composite results obtained by the EMT method compared well the experimental data [30].

There has been little modeling work on CNT/metal matrix composites. The most remarkable work seems to be performed by Barai and Weng [31] who developed a two-scale micromechanical model to study the plasticity of CNT metal matrix composites. The EMT

approach was adopted to treat both large-scale and small-scale problems. The effects of CNT agglomeration and interface condition on plastic strength of the composites were investigated, and Barai and Weng's study showed that CNTs are a very effective agent but CNT agglomeration and poor interface condition can severely reduce the composite stiffness and elastoplastic strength. More recently, Dong et al. [32] developed a dislocation density based model combined with EMT micromechanics to study size dependent strengthening mechanisms in CNT/metal matrix composites. It was found that refinement of matrix grains does not only enhance the strength of the matrix, but also weakens the thermal expansion mismatch strengthening induced by the reinforcement.

The literature survey shows that a significant number of studies have been conducted using the EMT approach to predict the elastic properties of CNT composites, in particular CNT/polymer composites, but little work was done to address the nonlinear composite behavior due to damage or plasticity of the matrix material. Multiscale models accounting for progressive damage are needed to predict the composite stress/strain response up to failure to predict composite fracture strengths. In addition, such models combined with finite element analyses are needed to predict fracture toughness of CNT composite as a function of governing microstructural parameters.

This paper describes the development of a multiscale modeling approach to predict fracture toughness of CNT-reinforced ceramic composites to provide guidance for processing these materials for structural applications. Straight nanotubes are assumed, and thus the current work does not account for nanotube waviness. It includes (i) prediction of elastic properties using an Eshelby-Mori-Tanka approach (EMTA) [15-17], (ii) development of a mechanistic damage model accounting for matrix cracking to predict the composite nonlinear stress/strain response to

tensile loading to failure, and (iii) application of this damage model in a modified boundary layer (MBL) analysis [33-35] using the ABAQUS[®] finite element package to predict fracture toughness and crack resistance behavior (R-curves) for ceramic materials containing CNTs at various volume fractions.

The modeling work provides insight and guidance to processing these materials for composite microstructures to achieve optimal mechanical properties for structural applications. The predictions illustrated in the following sections show that homogeneously dispersed CNTs in a ceramic matrix significantly increase the resulting composite stiffness, strength, and fracture toughness. However, the fracture toughness increases may not attain the levels needed for the applications of these materials as structural materials, especially in nuclear reactors. In addition, even assuming well-distributed CNTs, the tensile strength and fracture toughness values saturate at moderate CNT volume fractions and tend to decrease at relatively high CNT volume fractions. In this paper, predictions of fracture toughness as a function of CNT volume fraction have been validated against the experimental data for a MWCNT nanostructured zirconia composite system determined by Mazaheri et al. [8]. The results of this article are valuable guidance to the experimental processing of CNT composites and suggest that the development of additional toughening mechanisms needs to be explored in order to achieve the goals of adequate fracture toughness for structural applications.

2. Prediction of Elastic Properties

2.1 Computational Method

It has been reported that distributing nanoparticles including CNTs in a matrix material (i.e., polymer or ceramic) at contents for which the particles can be well-dispersed leads to substantial increases in elastic moduli for the reinforced material [4, 7, 8]. However, applications of

established micromechanical models do not provide accurate predictions of elastic properties if the functionalization interphase formed between the nanotube and the matrix material is ignored. This interphase is a nano-effect responsible for important increase in stiffness [20, 28] for the as-formed composite compared to unreinforced ceramics or ceramics reinforced with conventional fibers. Figure 1 shows a schematic of the computational procedure to compute the elastic properties of a CNT composite from the properties and features of the constituents. In this work, the Eshelby-Mori-Tanaka approach (EMTA) is used at each stage of the computation illustrated in Figs 1a to 1c. The stiffness of a UD composite based on EMTA is given by [15-17]:

$$\mathbf{H} = \mathbf{H}_m + f (\mathbf{H}_f - \mathbf{H}_m) \mathbf{A} \quad (1)$$

where $\mathbf{H}_f$ and $\mathbf{H}_m$ are the stiffness tensors of the inclusion and the matrix material, respectively; f is the inclusion volume fraction, and $\mathbf{A}$ is the inclusion strain concentration tensor given by

$$\mathbf{A} = \mathbf{T}[(1-f)\mathbf{I} + f\mathbf{T}]^{-1} \quad (2)$$

$$\text{with} \quad \mathbf{T} = [\mathbf{I} + \mathbf{S} \mathbf{H}_m^{-1} (\mathbf{H}_f - \mathbf{H}_m)]^{-1} \quad (3)$$

where $\mathbf{I}$ is the identity tensor, and $\mathbf{S}$ the Eshelby tensor that depends on the inclusion aspect ratio and the matrix elastic properties. Mura [36] gives expressions of $\mathbf{S}$ for different inclusion shapes. The stiffness tensor of a composite with a fiber orientation distribution (Fig. 1c) is determined from the solution of the UD composite (Eq. 1) that is averaged over all possible fiber orientations using the Advani-Tucker model [37]:

$$\begin{aligned} \bar{H}_{ijkl} = & B_1 \tilde{a}_{ijkl} + B_2 (a_{ij} \delta_{kl} + a_{kl} \delta_{ij}) + B_3 (a_{ik} \delta_{jl} + a_{il} \delta_{jk} + a_{jl} \delta_{ik} + a_{jk} \delta_{il}) \\ & + B_4 \delta_{ij} \delta_{kl} + B_5 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \end{aligned} \quad (4)$$

where the coefficients B_i ($i = 1, 5$) are the invariants of the stiffness tensor of the UD transversely isotropic composite (Eq. 1) given in [37]. Tensors a_{ij} and $\tilde{a}_{ijkl}$ are the second and fourth-order

orientation tensors, respectively, and δ_{ij} is the identity tensor. Tensor a_{ij} is either predicted by a process model or measured, and then a closure approximation is used to estimate the fourth-order tensor $\tilde{a}_{ijkl}$ from a_{ij} . Wetzel's closure approximation [38] is used in this work.

Fig. 1. Schematic of the EMTA homogenization procedure.

The elastic properties of a CNT composite are computed based on the procedure depicted in Fig. 1. The computation considers the UD composite containing aligned CNTs (Fig. 1a) from which the first EMTA homogenizations are performed to obtain the homogenized stiffness of the CNT/hollow space and of the CNT/interphase system (Fig. 1b). If the number of walls increases, the hollow area is reduced accordingly. Next, the second round of EMTA homogenization is carried out to determine the stiffness of the UD composite containing aligned equivalent fibers embedded in a matrix material (Fig. 1c). Finally, the fiber orientation averaging technique [37] (Eq. 4) is applied to compute the stiffness of the as-formed composite. In this paper, CNTs are assumed to be well dispersed and randomly oriented in a ceramic matrix, and as a consequence, the components of a_{ij} are: $a_{11} = a_{22} = a_{33} = 1/3$ and $a_{ij} = 0$ with $i \neq j$.

For an illustration of the computational method to estimate the elastic properties of MWCNTs, the EMTA calculation considers nanotubes having a 12.5 nm-external radius and 0.34 nm-thick individual walls [28]. Figure 2 presents the predictions for the MWCNT elastic

moduli as a function of the number of walls. It shows that both longitudinal and transverse moduli increase with increasing number of walls, and for large numbers of walls, the moduli achieve the elastic modulus of graphene (≈ 915 GPa). Using MWCNTs instead of SWCNTs reduces the hollow space inside the tubes and consequently increases the CNT elastic moduli accordingly and renders the tube behavior isotropic with the transverse elastic modulus approaching the longitudinal modulus (Fig. 2) for a large number of walls. These findings agree with the results reported by Seidel and Lagoudas [28] using the composite cylinder/self-consistent method. In this paper, MWCNTs are assumed to have a large number of walls so that they achieve the elastic modulus of graphene for both the longitudinal and transverse directions.

Fig. 2. EMTA Prediction of for the equivalent (homogenized) CNT elastic moduli as a function of the number of walls.

2.2 Prediction of Elastic Properties for MWCNT/3YSZ

This section applies the EMTA method to predict the elastic properties of a MWCNT/3YSZ composite processed and studied by Mazaheri et al. [8]. The MWCNTs are about 20 μm long and have a diameter about 10 - 20 nm. The transmission electron microscopy (TEM) images by these authors [8] for a 5-wt%-MWCNT/3YSZ show a homogenous grain size distribution and fairly homogeneous distributions of CNTs in the nanostructured zirconia ceramic. Also, clean interfaces between CNTs and zirconia grains were reported. However, no information about the thickness and elastic properties of the functionalized interphase was available, as this information was not obtained experimentally. In this paper, an EMTA reverse engineering method is used to identify the elastic properties of the MWCNT/3YSZ interphase. As the thickness and elastic properties of the interphase are not known, the *reverse engineering* procedure assumes a value for the interphase thickness (equal to half of the MWCNT radius) to solve for the elastic properties using EMTA. The procedure starts using the elastic properties of MWCNTs determined in the previous section and the measured elastic properties of the 3YSZ matrix [7-8], and an initial guess values for the elastic modulus and Poisson's ratio of the interphase. The selected values should be lie between the elastic properties of MWCNTs and those of the 3YSZ matrix. The Poisson ratio for MWCNTs was determined previously from the computation of the elastic properties of MWCNTs and is 0.26. 3YSZ's Poisson ratio used in the computation is 0.27 computed from the Young's and shear moduli reported in [7-8]. If the EMTA prediction for the elastic modulus of the as-formed composite is compared with the measured value within the 2% relative error, the iterative procedure stops, and the values of the interphase elastic properties are identified. If not, adjustments of the interphase elastic properties

are conducted, and the EMTA computation continues with the updated values for the interphase elastic properties until the 2% accuracy agreement is reached.

Fig. 3. Predicted shear modulus compared to measured data [7-8] for a MWCNT/3YSZ system as a function of MWCNT volume fraction.

The shear moduli of sintered MWCNT/3YSZ composites with MWCNT weight fractions from 0 to 5% were experimentally determined [8]. In this paper, the measured shear modulus for 1.5 wt% MWCNTs (= 92 GPa) is used by EMTA reverse engineering to determine the elastic properties of the interphase between MWCNTs and the zirconia matrix. The as-identified elastic properties are then used by EMTA to compute the elastic properties for *all the MWCNT/3YSZ composites with different MWCNT contents*, and the shear moduli results are reported in Fig. 3. The agreement between the predicted and measured elastic moduli for a given range of MWCNT volume fractions validates the EMTA reverse engineering approach to identify the interphase elastic properties. Fig. 3 also presents Mazaheri et al.'s experimental data [8] and EMTA

predictions without accounting for the functionalization interphase. It shows that the solution accounting for the interphase agrees well with the experimental results while the standard application of EMTA underestimates the composite shear modulus. However, we also observe that the agreement between EMTA results accounting for interphase and the measured data are better at low CNT volume fractions while these predictions tend to deviate from the data at higher volume fractions. It is believed that the difficulty to completely disperse CNTs at high concentrations in a matrix limits the enhancement of elastic modulus that could be achieved in practice. In addition, increasing the volume fraction of CNTs to some extent would increase their waviness and thus decrease the composite elastic modulus.

3. Damage Modeling

To predict the composite fracture toughness and crack resistance behavior, it is necessary to model the damage development that affects the composite stiffness in order to compute the composite stress/strain response up to failure. It has been reported that CNT ceramic composites subjected to loadings undergo matrix cracking [39]. For composites that are well processed, the functionalization interphases between CNTs and the ceramic matrix possess a strong bond that prevents the debonding of nanotubes in the way that is observed for conventional fiber composites. If debonding occurs, this mechanism happens inside the matrix [39]. Based on these experimental observations, this paper describes matrix cracking as the key progressive mechanism responsible for damage leading to failure of CNT-reinforced ceramic composites.

3.1 Model Formulation

A mechanistic damage model to describe matrix cracking in CNT ceramic composites is derived from a model for glass-ceramics developed by Nguyen et al. [35] that is termed

“mechanistic” since its formulation uses both micromechanics and continuum damage mechanics. It assumes elastic CNTs completely randomly dispersed in a ceramic matrix whose cracking behavior is described by a continuum damage description. An incremental EMTA method combined with fiber orientation averaging is used to incrementally determine the composite response.

Using a scalar damage variable, D , for matrix cracking, the elastic deformation energy density chosen as the thermodynamic potential is expressed in terms of matrix strains, ε_{ij}^m and D :

$$\Phi(\varepsilon_{ij}^m, D) = \frac{1}{2} H_{ijkl}^m(D) \varepsilon_{ij}^m \varepsilon_{kl}^m \quad (5)$$

where $H_{ijkl}^m(D)$ denotes the stiffness tensor of the matrix material affected by damage characterized by D . From Eq. 5, the matrix constitutive response and thermodynamic force associated with D are obtained as [40]:

$$\sigma_{ij}^m = \frac{\partial \Phi}{\partial \varepsilon_{ij}^m} = H_{ijkl}^m(D) \varepsilon_{kl}^m \quad (6)$$

and

$$F = \frac{\partial \Phi}{\partial D} = \frac{1}{2} \frac{\partial H_{ijkl}^m(D)}{\partial D} \varepsilon_{ij}^m \varepsilon_{kl}^m \quad (7)$$

The Clausius-Duhem inequality, which is the dissipation criterion, reads:

$$\begin{aligned} -F \dot{D} &\geq 0 \\ \text{If } F < 0 \rightarrow \dot{D} > 0 &: \text{damage progresses} \\ \text{If } F \geq 0 \rightarrow \dot{D} = 0 &: \text{damage is stable} \end{aligned} \quad (8)$$

Next, in order to define a damage criterion, we utilize the concept of *damage threshold function* similar to that used by Renard et al. [41] for polymer composites:

$$f(D) = F_c(D) - F \quad (9)$$

where $F_c(D)$ is the damage threshold function of D . $F_c(D)$ can be computed numerically using Eq. 7 and the matrix stress-strain response identified from the composite stress-strain data by a reverse engineering method.

Finally, the damage evolution law for the matrix material is obtained using the damage criterion (Eq. 9) and the consistency conditions, $f = 0$ and $df = 0$:

$$dD = \frac{-\frac{\partial H_{ijkl}^m(D)}{\partial D} \varepsilon_{ij}^m d\varepsilon_{kl}^m}{\frac{1}{2} \frac{\partial^2 H_{ijkl}^m(D)}{\partial D} \varepsilon_{ij}^m \varepsilon_{kl}^m - \frac{\partial F_c(D)}{\partial D}} \quad (10)$$

In this paper, a linear reduction of the matrix elastic modulus with the damage variable is used [35, 42]:

$$E_m(D) = E_m^0 (1 - D) \quad (11)$$

where E_m^0 is the initial elastic modulus in the undamaged state. Introducing Eq. 11 in Eq. 10, the matrix damage evolution law becomes:

$$dD = \frac{\frac{\partial H_{ijkl}^m(D)}{\partial D} \varepsilon_{ij}^m d\varepsilon_{kl}^m}{\frac{\partial F_c(D)}{\partial D}} \quad (12)$$

Eq. 12 determines the damage variable increment caused by an increment of the matrix strain $d\varepsilon_{ij}^m$ due to composite deformation.

The composite stress-strain response is nonlinear due to matrix cracking and is given by:

$$\sigma_{ij} = \bar{H}_{ijkl}(D) \varepsilon_{kl} \quad (13)$$

324 where the composite stiffness matrix $\bar{H}_{ijkl}(D)$ is affected by matrix damage given by Eq. 4 and
 325 computed using Eq. 11 in the EMTA computation procedure.

326 The matrix strain increment is computed from the composite strain increment as:

$$327 \quad d\epsilon_m = \mathbf{A}_m d\epsilon \quad (14)$$

328 with $\mathbf{A}_m$ being the matrix strain concentration tensor that is defined in terms of the averaged
 329 ‘fiber’ strain concentration tensor $\bar{\mathbf{A}}$ as:

$$330 \quad (1-f)\mathbf{A}_m + f\bar{\mathbf{A}} = \mathbf{I} \quad (15)$$

331 where $\mathbf{I}$ is the identity tensor, and $\bar{\mathbf{A}}$ is obtained by application of the fiber orientation
 332 averaging method [37] to the strain concentration tensor $\mathbf{A}$ (Eq. 2).

333 As the composite damage response is nonlinear, the computation is carried out incrementally.
 334 The calculation of the matrix strain increment (Eq. 14) allows computation of the damage
 335 variable increment according to the damage evolution law to update the damage variable. The
 336 matrix elastic modulus is then updated using Eq. 11 to compute the stiffness tensor for the
 337 composite by application of EMTA and fiber orientation averaging. Damage by matrix cracking
 338 can evolve according to Eqs. 8 and 12 until a critical or saturation state at which $D = D_{cr}$ (the
 339 saturation value of D), and the composite can no longer carry load and will fail. Failure of the
 340 composite leading to fiber pullout, initiation and propagation of a macroscopic crack is captured
 341 by the Nguyen et al.’s failure model [35] associated with a vanishing finite element method
 342 [35,43]. It is noted that fiber pullout was not modeled discretely in this work, but this damage
 343 mechanism that corresponds to the final stage of damage was captured by the failure model [35]
 344 and vanishing element method [35, 43] that numerically reduces the stresses and stiffness at the
 345 material failure location to zero in a number of load steps.

3.2 Prediction of Stress-Strain Response for MWCNT/3YSZ

The damage model has been introduced in EMTA-NLA (Eshelby-Mori-Tanaka Approach to Non-Linear Analysis), a Pacific Northwest National Laboratory's capability that is implemented in the ABAQUS[®] finite element package via user subroutines for nonlinear structural analyses. This section illustrates an application of the damage model to predict the stress/strain response of the MWCNT/3YSZ composite as a function of the MWCNT volume fraction. This composite system was examined by Mazaheri et al. [8] and is modeled in Section II of this paper for elastic properties. As the experimental stress/strain data including strength are not available for these composites and the 3YSZ matrix, literature data and adequate assumptions must be adopted regarding the 3YSZ matrix stress-strain behavior to be used in the model to predict the response of the MWCNT/3YSZ composite as a function of the MWCNT volume fraction. The modeling work here aims at elucidating the composite behavior to assess the levels of strength and failure strain that can be achieved under ideal conditions of complete dispersion of MWCNTs in the 3YSZ matrix and perfect bonding between the MWCNTs and matrix.

Figure 4 presents the uniaxial stress-strain curve assumed for the 3YSZ matrix. This curve is built considering the following data for 3YSZ: (i) Initial elastic modulus [7], $E_m^0=198.12$ GPa, (ii) 713 MPa strength [44], and (iii) 0.45% failure strain. As a result, the saturation value of the damage variable is $D_{cr} = 1 - E_m(\bar{\epsilon}_m = 0.0045) / E_m^0 = 0.2$. The initial elastic modulus of 3YSZ measured by Mazaheri et al. [7] agrees with the experimental data by Kondoh et al. [44]. Together with the measured shear modulus [8], the 3YSZ Poisson's ratio is determined to be 0.27. The value of the failure strain adopted is justified as follows. If the behavior of the 3YSZ matrix were linear elastic up to rupture (at the failure stress of 713 MPa), the failure strain would be 0.36%. However, as *progressive matrix cracking* develops in the composite under loading, the

matrix stress/strain response is *nonlinear* up to failure, which corresponds to a failure strain greater than 0.36%. The adopted value of failure strain (0.45%) on the 3YSZ stress/strain curve and all the other material parameters will be assessed in the next section where the damage model is used with the MBL analysis to predict fracture toughness of MWCNT/3YSZ composites.

Fig. 4. The uniaxial stress-strain curve established for the 3YSZ matrix.

Using the matrix stress/strain response, the damage threshold function is computed in the following manner. For a current value of the matrix strain, the current matrix stress and elastic modulus are determined from this stress-strain curve (Fig. 4). Next, the current values of the damage variable and thermodynamic force are computed using Eqs. 11 and 7, respectively. The damage threshold function is obtained as: $F_c(D) = F(D)$. In this manner, the damage threshold function is computed numerically for any value of the damage variable in the $[0, D_{cr}]$ interval.

Fig. 5 provides the damage threshold function computed for the 3YSZ matrix material based on the 3YSZ stress-strain curve given in Fig. 4. The as-determined values are well fitted by a polynomial as illustrated on Fig. 4 that uses a second-degree polynomial.

Fig. 5. The damage threshold function computed for the 3YSZ matrix.

The damage threshold function, the critical value of the damage variable, and the elastic properties of the 3YSZ matrix and MWCNTs are introduced as input data to EMTA-NLA for analyses of MWCNT/3YSZ composites subjected to tensile loading to failure. The computed stress-strain response of MWCNT/3YSZ as a function of the MWCNT volume fraction is reported in Fig. 6 and shows a strong effect of the MWCNT content on the composite behavior. Due to the complete fiber dispersion and perfect bonding assumptions, the initial slope of the curve (elastic modulus) increases with increasing MWCNT volume fraction. In the low to moderate MWCNT volume fraction range (less than 12.5%), the composite strength increases significantly with increasing MWCNT volume fraction, and the strain at composite failure is

little affected. However, between 12.5% and 23% volume fractions, the composite behavior becomes more brittle and exhibits a significant reduction of failure strain although the composite strength increases substantially. Beyond 23% but less than 32% volume fraction, the composite strength saturates and computed failure strains continue to decrease, and after 32% both composite strength and failure strain drop substantially. These results show that even at the ideal condition of complete dispersion of MWCNTs, the strength saturates about 23% MWCNT volume fraction, and both strength and failure strain degrade substantially at higher volume fractions. In practice, the difficulty in dispersing MWCNTs in a ceramic matrix material would likely cause the composite strength to saturate at lower levels and at lower MWCNT volume fractions than 23%. We consider this value to be near ideal behavior.

Fig. 6. Stress-strain responses predicted for the MWCNT/3YSZ composite as a function of MWCNT volume fraction.

4. Fracture Toughness Prediction

The damage model developed for MWCNT reinforced ceramics is used in a modified boundary layer (MBL) modeling approach to predict the composite fracture toughness under Mode I loading. The MBL modeling approach was initially proposed by Tvergaard and Hutchinson [33] to investigate crack growth resistance in elastic-plastic solids. Later, it was also used by other authors [34, 35, 45] to study damage and fracture in a small process zone at the tip of an existing crack. The principle of the MBL modeling approach is described in Fig. 7. Considering an initial crack inside a solid subjected to loading at the solid boundaries (Fig. 7a). If one is interested in conditions for the onset of crack propagation and growth, and the governing parameters, an approach to damage and fracture at the microstructural scale is appropriate. This approach is defined as *small-scale* damage and fracture analysis. It relies on the assumption that damage and fracture is only allowed to develop in a process zone containing an initial crack tip. The process zone must be much smaller than all relevant specimen/structure dimensions so that a boundary layer problem can be formulated with the crack-tip fields in an undamaged solid as the remote boundary conditions applied on the outer contour of a circular region containing the process zone (Fig. 7b). The MBL analysis can be efficiently used to characterize the material fracture toughness and crack resistance behavior without modeling the whole structure with the associated boundary conditions.

For the CNT ceramic composites studied in this paper, the CNTs are assumed to be completely randomly distributed in the ceramic matrix; thus, the homogenized behavior is isotropic, and the crack-tip fields for a crack in an elastic isotropic solid are then used as the remote boundary conditions for the MBL analysis. Under plane-strain Mode I loading condition, the crack-tip displacement components in an elastic solid are given by:

$$\begin{aligned}
u_1 &= \frac{K_I}{2\mu} \sqrt{\frac{r}{2\pi}} \cos\left(\frac{\theta}{2}\right) [\kappa - 1 + 2\sin^2\left(\frac{\theta}{2}\right)], \\
u_2 &= \frac{K_I}{2\mu} \sqrt{\frac{r}{2\pi}} \sin\left(\frac{\theta}{2}\right) [\kappa + 1 - 2\cos^2\left(\frac{\theta}{2}\right)]
\end{aligned}
\tag{16}$$

where r and θ are the polar coordinates centered at the crack tip. K_I denotes the Mode I loading stress intensity factor, μ is the shear modulus, and κ is given by $\kappa = 3 - 4\nu$ with ν being Poisson's ratio.

Fig. 7. Principle of the MBL modeling approach: (a) a crack inside a body is subjected to remote loading, and (b) a damage process window containing the crack-tip is surrounded by a circular region where the asymptotic crack-tip fields are prescribed as boundary conditions.

The damage model developed for CNT ceramic composites discussed in the previous section is used to describe the development of damage leading to crack growth in the process zone. The composite behavior away from the process zone remains linear elastic. Under increasing load applied via boundary conditions (Eq. 16), damage evolves at the crack tip until attaining a critical stage characterized by the value of the damage variable reaching D_{cr} . *The critical damage stage represents the onset of crack propagation in the damage process window, and the*

corresponding value of K_I at this stage defines the material Mode I fracture toughness, K_I^c .

Crack propagation in the process window is captured by the vanishing element model [35].

Figure 8 presents the finite element mesh designed for the MBL analysis to predict fracture toughness of the MWCNT/3YSZ composite system studied in this paper. The whole mesh for the MBL problem is given in Fig. 8a while Fig. 8b shows a snapshot of the mesh in the process window. The outer diameter of the circular region must be much greater than the size of the process window so that damage and fracture occurring in the process window do not affect the remote fields. In this work, the dimension of the process window and the outer diameter of the circular region are 0.7 mm and 70 mm, respectively. According to [8], the length of CNTs in the studied composite is about 20 microns. The mesh size of the elements in the process window containing the crack tip is 35 microns. This mesh size design captures the length scale for this composite for continuum modeling: each element in the process window represents the composite representative volume element that is formed by CNTs of the given length randomly and uniformly dispersed in the 3YSZ matrix.

Fig. 8. (a) Finite element (FE) mesh for the MBL analysis and (b) a magnified view of the FE mesh for the damage/fracture process window.

It is noted that the pure Mode-I loading and the uniform material properties considered in the MBL analysis provides the symmetry for the boundary layer problem and suggests that it would be sufficient to analyze a half of the circular region (Fig. 8(a)). However, for the sake of generality, in this paper we have chosen to model the whole circular region. Analyzing the whole region will allow us to later extend the model to incorporate randomness in material parameters and/or irregular mesh sizes and shapes in the process window for which the symmetry of the boundary layer problem is not achieved.

Figure 9 illustrates the contour of the damage variable in the process window at the onset of crack propagation predicted by the damage model for the composite with 3-wt% MWCNTs (0.077 volume fraction). The corresponding value of the stress intensity factor, K_I , inducing this damage distribution is 7.78 MPa $\sqrt{\text{m}}$. Fig. 9 shows that the damage variable has attained the

critical value ($D_{cr} = 0.2$) at the crack tip for this loading level, and the stress intensity factor is then identified as the critical stress intensity factor or fracture toughness ($K_I = K_I^c = 7.78 \text{ MPa}\cdot\sqrt{\text{m}}$).

Fig. 9. Predicted damage distribution at the onset of crack propagation for the 3-wt% MWCNT/3YSZ.

Similar MBL analyses using the damage model are performed for all the MWCNT/3YSZ composites with weight fractions from 0.04% to 10% (volume fractions from 0.1% to 23%) to predict the fracture toughness of this composite system as a function of CNT content. Predicted fracture toughness results are reported in Fig. 10 that shows significant increases in fracture toughness with the increasing CNT volume fraction up to about 15%. The predicted evolution appears to saturate for volume fractions approaching 20%. The predicted fracture toughness for CNT volume fractions up to 12.4% agrees well with Mezaheri et al.'s experimental results [8]

also given in Fig. 10. The agreement between the predicted and experimental results validates the material parameters identified for the damage model in the previous section.

Fig. 10. Predicted and experimental Mode I fracture toughness vs. MWCNT volume fraction for the MWCNT/3YSZ composites. The experimental results were determined by Mazaheri et al. [7-8] via bending tests of single-edge V-notched beam specimens.

Fig. 11. Development of damage at the loading level $K_I^R = 9.11 \text{ MPa}\sqrt{\text{m}}$ for the 3-wt% MWCNT/3YSZ composite.

Damage can progress further in the process window after initiation if loading is increased. Figure 11 shows damage progression at a higher loading level $K_I = 9.11 \text{ MPa}\sqrt{\text{m}}$ for the 3-wt% MWCNT/3YSZ composite. The present MBL analysis is also used to predict the stress intensity factor vs. crack advance (R-curve) as a function of the MWCNT content. Once the damage variable has attained the critical value at a given integration point in a finite element, the vanishing element method reduces the local element stiffness and stresses to zero in a small number of loading steps, and the stresses are redistributed to the adjacent integration points until the element is completely failed, so that the failed elements represent an open crack. Figure 12 illustrates crack propagation in a process window for the 3-wt% MWCNT/3YSZ composite. The

corresponding stress intensity and crack advance (measured from the initial crack tip) are 9.49 $\text{MPa}\sqrt{\text{m}}$ and 0.245 mm, respectively. The symmetries of the loading and of the finite element mesh with respect to the initial crack plane combined with uniform material properties lead to the symmetric crack propagation shown in Fig. 12. If irregular and asymmetric mesh design or statistical distributions of material parameters were used for the process window, an asymmetric crack pattern would have occurred. The crack propagation in that case would represent a lower amount of work and thus a lower stress intensity factor to drive the crack by a specific length. Thus, the symmetric crack propagation shown here is overly conservative.

Fig. 12. Predicted crack propagation for the 3-wt% MWCNT/3YSZ at $K_I = K_I^R = 9.47 \text{ MPa } \sqrt{\text{m}}$.

The R-curves also predicted by the MBL analysis for all other MWCNT/3YSZ composites with weight fractions from 0.04 to 5% and the results are reported in Fig. 13. For the extent of the crack advance predicted, all the predicted R-curves can be fitted quite well by a power-law of the form:

$$K_I^R = kc^\alpha \quad (17)$$

where K_I^R is stress intensity factor after the onset of crack propagation, and c is the crack advance, and k and α are fitting coefficients. Using Eq. 17, there exists an initial value of c ($c = c_0$) for which $K_I^R = kc_0^\alpha = K_I^c$, the fracture toughness. Although the experimental R-curves for the MWCNT/3YSZ composites studied in this paper are not known, the predicted power-law trend (Eq. 17) was also experimentally observed in other ceramic composite systems [46-47]. Table 1 gives the values of k and α obtained from the fitting of the MBL analysis results (Fig. 13) by the power-law in Eq. 17.

Fig. 13. Predicted stress intensity factor vs. crack advance for the MWCNT/3YSZ composites as a function of MWCNT content. As discussed above, these computed R-curves represent symmetric crack advance and would be expected to be somewhat lower for other crack advance assumptions.

Table 1. R-curves power-law coefficients identified for the MWCNT/3YSZ composites studied in this paper.

MWCNT Content	0.05-wt%	1.5-wt%	3-wt%	5-wt%
c_0 (m)	1.5×10^{-5}	1.5×10^{-5}	1.5×10^{-5}	1.5×10^{-5}
k (MPa.m ^{1/2} .m ^{-α})	13.9	14.8	18.1	19.2
α	6.7×10^{-2}	6.6×10^{-2}	7.7×10^{-2}	7.3×10^{-2}

3. Discussion of Results

The developed damage model, when compared to experimental data, appears to accurately predict the observed results and, since the model is quite general in scope, suggests that CNT strength saturation and decline is to be expected for these materials and that an optimum volume fraction of CNTs exists for a given ceramic matrix depending on the manner in which the matrix undergoes elastic damage in the presence of distributed CNTs.

To understand strength saturation, the evolution of the damage variable with applied stress on the composite is plotted as a function of CNT volume fraction in Fig. 14. These curves show that matrix damage increases with applied stress as expected but damage increases are accompanied by increased load carrying capability for CNT volume fractions in the range from 0 to 23%. Increasing CNT volume fraction in this range augments the load carrying capacity of the composite for the same applied stress since stresses are distributed to more CNTs, and as a result, this reduces stress in the matrix leading to lower matrix damage accumulation. However, at higher CNT fractions beyond 23%, for the same applied stress, more stresses redistributed to the matrix cause higher matrix stresses and strains leading to more matrix damage. Fig. 14 shows clearly that at 40% volume fraction, the damage variable rapidly increases with the applied stress

to the critical value ($D_{cr} = 0.2$), which is the same as the unreinforced ceramic matrix but at much lower applied strains, engendering early failure of the composite (see Fig. 6).

Another way to help understand reductions of composite strength and failure strain at high CNT volume fractions is to examine the computed stresses on the ceramic matrix as a function of CNT fraction for given levels of applied strain as shown in Fig. 15, which shows the evolution of the matrix stress σ_{11}^m with CNT fraction for different values of the composite strain ε_{11} . For $\varepsilon_{11} = 0.001$ and CNT volume fractions less than 23%, σ_{11}^m increases little with increasing CNT fraction, but it evolves substantially for volume fractions beyond 23%, and at about 40% CNT volume fraction the matrix stress σ_{11}^m has almost attained the matrix tensile failure stress of 713 MPa (see Fig. 4). Higher composite strain levels induce higher matrix stresses as indicated in Fig. 15, which also shows that composites with CNT fractions less than about 13% can sustain an applied strain four times the value the composite at 40% can support. The applied stress distribution to the ceramic matrix is nonlinear with respect to CNT volume fraction, which cannot be intuited from Eq. 12.

Fig. 14. Damage variable evolution with the applied stress as a function of MWCNT volume fraction.

Figure 16 provides further insight of the load-carrying capacity of the composite in terms of the matrix strain ε_{11}^m as a function of the composite stress σ_{11} (in the loading direction) and CNT volume fraction. In the range of volume fractions less than 23%, increasing the CNT volume fraction reduces the matrix strain for the same composite stress, but for volume fractions higher than 23%, an increase in volume fraction at the same composite stress causes an increase in matrix strain. As the matrix strains govern the damage evolution law (Eq. 12), an increase in the matrix strain produces an increase in the damage variable increment accordingly, and therefore greater damage accumulation. In a practical sense, addition of CNTs to ceramics increases the overall stiffness of the resultant composite at the expense of failure strain and matrix load carrying capability.

Fig. 15. Evolution of the matrix stress σ_{11}^m with MWCNT volume fraction for different levels of composite strain ϵ_{11} .

The composite stress/strain results reported in Fig. 6 present one of the most important findings in this work. They show that even under the ideal conditions of well-dispersed CNTs and perfect bonding, the composite strength reaches a limit beyond which adding more reinforcements will not lead to improved composite strength and failure strain, but rather serve to decrease failure strain beyond a certain limit that is likely governed by the modulus ratio of the MWCNTs to the ceramic matrix. It is significant that such reductions and limits in strength and failure strain with the concentration of nano-reinforcements have been also observed experimentally in MWCNT/epoxy [48] and silica nanoparticle reinforced epoxy composites [49].

Fig. 16. Evolution of the matrix strain ε_{11}^m as a function of the composite stress σ_{11} and MWCNT volume fraction.

Similarly, the fracture toughness calculations show the same trends, and the crack propagation model presented here predicts a modest increase in fracture toughness with increasing CNT fraction, followed by a saturation level and then a decrease. Saturation is predicted to occur at about the same level, 20 to 25%, at which the strength degradation occurs in the damage model (see Figs. 6 and 13). Although the damage model here does not discretely capture fiber pullout, the model does capture the final stage of damage by numerically reducing the stresses and stiffness at the material failure location to zero in a number of load steps. When data for 3YSZ/MWCNT composites is used the model agreement is excellent as shown in Fig. 13. As significant as Fig. 6, the results from Fig. 13 are also significant and suggest that only modest toughness increases can be achieved by dispersed CNT reinforcements, and for the same

reasons, namely that eventually too much stress is distributed to the ceramic matrix by the much stiffer CNT reinforcements.

5. Conclusions

A modeling approach to predict the fracture toughness and crack resistance behavior of CNT-reinforced ceramic composites is developed and described to provide insight and guidance to processing this class of composite materials to determine if it was possible to achieve the levels of fracture toughness required for applications in advanced nuclear reactors, for example. A series of computational steps including computations of the CNT composite elastic properties and nonlinear stress/strain responses due to micromechanical damage was performed prior to the prediction of fracture toughness. Models for elastic properties and damage by matrix cracking are developed and implemented in predictive tools. The damage model associated with a modified boundary layer modeling approach is able to efficiently predict composite toughness and crack resistance behavior. Predictions of elastic properties and fracture toughness agree well with experimental results from MWCNT/3YSZ composites. The modeling results show that homogeneously dispersing low to moderate contents of CNTs in a ceramic matrix leads to significant increases in the mechanical properties of the as-formed composite, which has a 3D CNT orientation distribution. However, the increase in strength and toughness saturates at high CNT contents, which is likely due to the presence of the much stiffer CNT reinforcement. Therefore, it is not possible to achieve the levels of fracture toughness, estimated to be $K_{I}^c \geq 20\text{MPa}\sqrt{\text{m}}$, considered to be needed for nuclear reactor applications using distributed CNTs in typical ceramic matrices. Currently, remedying this limitation is being addressed by studying other composite microstructures and architectures designed to achieve higher Mode I fracture toughness values.

Acknowledgements

This research was funded by the United States Department of Energy (US DOE) Office of Nuclear Energy under the Nuclear Energy Enabling Technology Reactor Materials (NEET-RM) Program. The US DOE Office of Vehicle Technologies funded initial developments of EMTA and EMTA-NLA software tools. PNNL is a multi-program national laboratory operated by Battelle Memorial Institute for the US Department of Energy under DE-AC06-76RLO 1830.

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