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Title: Ceramic composites: A review of toughening mechanisms and demonstration of micro-pillar compression for interface property extraction

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Abstract:

Ceramic fiber ceramic matrix composites (CFMCs) are exciting materials for engineering applications in extreme environments. By integrating ceramic fibers within a ceramic matrix, CFMCs allow an intrinsically brittle material to exhibit sufficient structural toughness for use in gas turbines and nuclear reactors. Chemical stability under high temperature and irradiation coupled with high specific strength make these materials unique and increasingly popular in extreme settings. This paper first offers a review of the importance and growing body of research on fiber-matrix interfaces as a they relate to composite toughening mechanisms. Second, micro-pillar compression is explored experimentally as a high-fidelity method for extracting interface properties compared to traditional fiber push-out testing. Three significant interface properties that govern composite toughening were extracted. For a 50nm pyrolytic carbon (PyC) interface, the following were observed: a fracture energy release rate of ~2.5 J/m^2, an internal friction coefficient of 0.25 ± 0.04, and a debond shear strength of 266 ± 24 MPa. This research supports micro-mechanical evaluations as a unique bridge between theoretical physics models for micro-crack propagation and empirically driven finite element models for bulk CFMCs.

Representative figure: Figure 7.

Keywords: Ceramic Composite, Internal Friction, Neutron irradiation, Chemical Vapor Deposition, Coating, Toughness, Fracture, Nuclear Materials, Nano-indentation.

I. INTRODUCTION

In the early 1970's, emerging ceramic fiber-matrix composite (CFMC) technologies received significant attention due to their unique mechanical characteristics[1]–[5]. The initial work was driven by the need for high performance materials in jet and rocket engines, where high temperature properties, high specific strength, and mechanical reliability and predictability are required. While CFMC research and development for aircraft applications continue today, advancement of these composites also led to new applications in the nuclear industry and for microwave absorption shielding [6]–[11]. These materials show great promise for use in extreme environments, yet challenges remain that require further research and understanding of CFMC failure mechanisms.

The atomic bonding structure of ceramic materials can provide valuable high temperature (>800 °C) properties including strength, creep resistance, and a variety of unique electrical and optical properties. However, due to the same underlying physics, monolithic ceramics exhibit little to no dislocation movement at relatively low temperatures and are therefore inherently brittle. Fracture of ceramics is a function of flaw size and fracture toughness, characteristics that can vary widely depending on manufacturing and micro-structure of the component [12], [13]. Weibull statistics quantify these properties and govern the predictability of bulk failure. Without plastic deformation and therefore strain energy absorption at the crack tip, unstable crack propagation will proceed at characteristically low values of critical stress (and corresponding low critical fracture toughness), resulting in catastrophic failure that is statistically difficult to predict. Traditionally, this has isolated ceramics to niche applications where tensile and bending stresses are avoided. However, CFMCs have opened the doors to variable load-bearing applications through unique toughening mechanisms. On the micro-scale, brittle failure is tied to the intrinsic fracture toughness of the material and unavoidable[14]. However, due to crack deflection toughening mechanisms, strain on the bulk-scale is observed to be non-linear with respect to the applied stress. This behavior is described as *pseudo-ductility* and accounts for the improved predictability and graceful failure of CFMCs.

A wide variety of ceramics have been studied for use in both fiber and matrix form including alumina, lithium-silicate glasses, and non-oxides such as silicon-carbide (SiC). Of these, SiC has emerged as the leading engineering material for extreme environment applications. It has proven particularly useful for high temperature applications where it exhibits

exceptional strength, creep resistance, chemical stability, and low coefficient of thermal expansion [15]–[19]. Studies have also shown that SiC has excellent neutronic properties including low thermal neutron capture cross-section, low tritium permeability, and high radiation tolerance [20]–[22]. As a result, SiC_f/SiC_m composites are being considered for application as accident tolerant fuel cladding [23] as well as structural components for high temperature fission and fusion reactors. This paper describes the physics and toughening mechanisms of CFMCs and how they relate to SiC/SiC composites development in the context of the nuclear industry. Specific attention is paid to the influence of pyrolytic carbon (PyC) interfaces on composite toughening, and to the methods for identifying and extracting the governing interface properties. By reviewing specific material data as well as the testing methods used to extract fundamental properties, gaps in the existing knowledge base will be identified. Although focused on SiC/SiC, this review also provides insight into key parameters and experimental property extraction techniques for all CFMCs, with a range of fiber, interphase, and matrix compositions.

A. Interfaces and Interface design

Many of the fracture characteristics of CFMCs are heavily dependent on the interface between the fiber and matrix. The interface is a thin coating layer (~ 0.05μm to 1μm) deposited on the fiber surface that can be engineered as a single layer or an alternating sequence of coating and matrix. This layer or layering is often referred to as the fiber-matrix interphase. The interphase is commonly deposited via chemical vapor deposition/infiltration (CVD/CVI) to promote matrix crack deflection and fiber pull-out during mechanical loading. Figure 1 shows examples of the varying geometric and material forms of different interface coatings.

Insert FIG. 1. (a)(b) &(c)

An optimal interface exhibits a balance of low toughness, to promote crack deflection, and resistance to sliding, to increase energy absorption during fiber pull-out. Details of deflection criteria and related interface properties are discussed further below. However, it is important to acknowledge the variety of interface designs that have been considered in the past and why pyrolytic carbon is of interest with respect to SiC composites in the nuclear industry. The *design* of an interphase is characterized by the deposited material, and deposition sequencing geometry (i.e., spacing, thickness, density, and layer schedule). Metals, oxides, and materials with low-energy slip plane crystal structures have been proposed to optimize energy absorption and crack

deflection. Fugitive interfaces [24], [25], where a physical gap is created by coating removal after matrix infiltration, have also exhibited reasonable mechanical properties and toughening characteristics. However, this design can allow environmental degradation of the exposed fiber and introduce challenges for components requiring hermeticity, which is important for nuclear fuel cladding. Metallic coatings (figure 1B) have shown promise with crack deflection and energy absorption through unique ductile phenomena. However, manufacturing challenges with matrix densification, and limits on operational temperature have hindered the advances of these designs [24], [26]. Additionally, many metals have neutron interactions such as transmutation and capture that are undesirable in nuclear applications. Oxide interfaces, inherently oxidation resistant, were introduced following observation of environmental degradation of non-oxide interfaces under aerospace engine component conditions [24], [27]–[30]. Some of the proposed oxides, such as phyllosilicate micas and hexaluminates, exhibit layered crystal structures with low energy slip planes, similar to that of aromatic stacking observed in graphite-like carbon and boron-nitride (BN). Other designs exploit isotropic oxides that have inherently weak bonding at the fiber/coating interface such as monazite ($LaPO_4$), where fracture occurs at the interface as opposed to within the coating. With regard to chemical stability, oxide interfaces are generally most compatible with oxide/glass fibers and matrices. However, introducing an oxide coating to non-oxide (SiC) composites may limit application to low temperatures in order to avoid thermodynamically driven oxidation of the fiber. This phenomenon weakens the fiber and increases the fiber /coating interface strength, ultimately reducing toughness [24].

For SiC_f/SiC_m, most interface work has focused on non-oxide graphite-like material; pyrolytic carbon (PyC) and hex-BN. The established deposition processes and extensive bulk and micro-testing makes these coatings more desirable from the view of product maturity and industry implementation [21], [31]–[33]. Characteristic properties including high temperature stability, SiC chemical compatibility, and desirable fracture properties (enhanced by anisotropy), have popularized the fabrication and analysis of these interfaces [21], [34]–[37]. BN has been shown to exhibit worse oxidation resistance at elevated temperatures in aqueous environments [38], [39]. Additionally, boron-10 (20% naturally occurring) has a neutron capture cross section approximately two orders of magnitude larger than carbon-12 (CENDL-3.1 nuclear cross-section database), causing the interface to act as a neutron poison and reduce thermal fission and reactor efficiency. Finally, it's been discussed that boron impurities in SiC can lead to reduced radiation

tolerance and mechanical strength [40]. As a result, PyC has emerged as the premier contender in the nuclear industry.

B. Physics of CFMC toughening

CFMCs are composed of three constituents; the matrix, fiber, and interphase. Each plays a critical role in the composites ability to absorb strain energy and combined serve as a reliable load bearing material. In general, the linear elastic properties of these composites are derived from the corresponding properties of the fiber and matrix. However, at the onset of matrix cracking in a CFMC, non-linear stress strain behavior (*pseudo-ductility)* is observed due to flaw distribution and composite load-sharing characteristics such as fiber volume fraction and elastic debond poperties [14]. Micro-cracks will propagate until they encounter the fiber/matrix interphase. At the crack tip, local strain fields interact with the interphase and fiber, where the elastic and fracture properties of the interface govern the evolution and propagation of the crack [6], [14], [41], [42].

At the instance of crack tip impingement on the interphase zone, the *He-Hutchinson* criterion (HH) is commonly used to describe the fundamental phenomenon governing how the crack tip will progress; either through the fiber (low toughness composite) or along the axis of the fiber at the interface (high toughness composite). This criterion is built on an integral evaluation of the plane strain problem between dissimilar materials as outlined by He [43]. This evaluation considers the fracture energy release rate, Γ (J/m^2), required by the interface and fiber to cause crack deflection, as a function of Dundur's elastic mismatch parameters, α and β [44]; β is frequently assumed to be 0 in an effort to reduce complexity, and α is interpreted as the material mismatch of plane strain tensile modulus (E'):

$$\alpha = \frac{E_1' - E_2'}{E_1' + E_2'} \tag{1}$$

Where $E' = E/(1+\nu^2)$, subscripts 1 and 2 refer to the interfacing fiber and matrix materials, and E and ν are the Young's modulus and Poisson's ratio respectively for each phase. Ultimately, there exists a critical ratio of the mode I fracture energy release rates between the interface and fiber, Γ_i and Γ_f respectively, that determines if the impinging crack will propagate along the fiber or through the fiber. The fracture energy release rate is an intrinsic material property, described by

an energy balance between strain and surface energy at the fracture plane. For brittle materials, this property can be evaluated using a J-integral approach that characterizes the elastic energy released during fracture, per unit surface area created. Experimentally, this property is obtained by dividing the area under a load versus displacement curve by the area of the two generated fracture surfaces. Figure 2A is a graphical interpretation of the HH criterion that generates a threshold curve to denote the crack propagation versus crack deflection regimes, as a function of the elastic (α) and fracture (Γ) properties of the respective materials.

This evaluation has major implications with respect to modeling and interface design. For a composite system with similar elastic properties between the fiber and matrix ($\alpha \rightarrow 0$) such as SiC/SiC, the criterion requires

$$\Gamma_i \leq 0.25\, \Gamma_f \tag{2}$$

to achieve deflection. Typically, ceramic fibers have a fracture energy of $\Gamma_f \sim 20$ J /m^2 suggesting that Γ_i should be smaller than 5 J/m^2 in order to achieve deflection [14]. Additionally, a common take-away from this criterion is that increasing the relative modulus of the fiber will shift the α parameter to positive values, and increase the allowable deflection ratio Γ_i/Γ_f. For composite design, this suggests that implementation of highly stoichiometric and stiff fiber will improve toughness. Together, this formula suggests that a tough composite, one that exhibits significant crack deflection and fiber pull-out, would be achieved through implementation of a stiff fiber matched with a weak, low toughness interface. The criterion discussed here is simplified, while further evaluations have looked at deflection sensitivity to the mismatch parameter β, the phase angle and fracture mode mixity at the impinging crack tip, and interface anisotropy [24], [45]–[49]. These considerations have shown influence on the characteristics of doubly-deflected cracking and allowable HH criterion ratio limits. Continued refinement of these physics models matched with experimental validation of the intrinsic material properties will be key to model development, fidelity, and composite predictability.

Once the crack has deflected, the propagation and debond length along the fiber is governed by intrinsic shear strength properties of the interface under mode II fracture [14], [24], [50]. In the context of thin interfaces, mode II crack propagation is expected to evolve in the form of secondary cracking and/or echelon cracking. Both phenomena are dependent on flaw distribution and the local stress state of the interface [50]–[52]. Details concerning the

application and assumptions associated with mode II failure are outlined clearly by Cedric and Xia [42], [51]. Cedric's analysis derived the following relationship for fracture energy of Mode II as it relates to mode I:

$$\Gamma_{II} = (3.1 \text{ to } 4.2) * \Gamma_{I} \quad (3)$$

This relationship is applied to experimental property extraction for Γ_I and discussed further below.

An important parameter directly related to the mode II shear strength is the effective debond length along the fiber from the impinging microcrack, briefly expressed in figure 2A. This debond length contributes to the macro-scale composite toughness and ultimate strength by defining micro-crack density and frictional pull-out resistance. Adjusting the interface properties to tailor the debond length plays a critical role in composite optimization and performance. Short debond lengths, characteristic of a stronger interface, lead to high strength and high toughness composite via matrix load sharing and increased micro-crack density respectively. However, if too short, the localized stress of the crack tip is not dissipated and the fiber will fracture in plane with the impinging crack, reducing toughness and composite reliability. Long debond lengths, characteristic of a weaker interface, provides enhanced toughening through extended fiber pull-out, but at the expense of reduced fiber/matrix load sharing thereby reducing the proportional limit of the composite. For most applications, it is generally accepted that there is an optimal debond length that allows for evenly distributed load sharing by the fiber and matrix [14], [41]. In this state, energy dissipation parameters such as micro-cracking density and fiber pull-out length are optimized without overcompensation, allowing for balanced macroscopic strength, toughness, and predictability. Figure 2B shows a qualitative interpretation for fiber/matrix load sharing as a function of debond length [41]. An ideal case may occur when the debond length matches the fiber/matrix stress intersection, where the stress is shared equally outside of the debonded region. However, the fiber/matrix stress intersection is expected to shift depending on the elastic property ratios of the fiber versus the matrix, the frictional sliding resistance of the debonded interface, and extrinsic parameters such as residual clamping stress. Thereby, the optimized debond length will vary for different composite compositions and fabrication parameters. Ultimately, increased loading and/or encounter of a defect at the debond length

provides a local stress state large enough to cause fiber fracture. At this point, energy absorption is governed by shear strength properties of the debonded interface during fiber pull-out.

Insert FIG. 2. (a) (b)

As always, optimization is dependent on the application and it is important to understand the intrinsic and extrinsic parameters that influence the interface. These parameters include extrinsic influences such as fiber roughness (fabrication dependent), residual clamping stress (N_R, dependent on constituent thermo-elastic properties and fabrication temperature), and interphase thickness. Increased fiber roughness and residual clamping stress would increase the internal friction coefficient, thereby reducing debond length and making the composite more brittle. Intrinsic properties include anisotropy, fracture energy release rate, debonding shear strength, and internal (bonded) and dynamic (debonded) friction coefficients [14], [41], [49], [53]. Many of these properties and parameters are interdependent. Without fundamental quantification of the intrinsic and extrinsic properties with respect to one another, as well as verification of resulting deflection and propagation length, it becomes difficult to create a comprehensive model that incorporates the appropriate assumptions to predict composite failure at a fundamental level. This discussion on composite toughening mechanisms and the associated physics models as they relate to bulk composites behavior has been extensively analyzed, and more detailed discussion can be found from Hutchinson (1994 [54]), Evans (1994 [14]), Kerans (2002 [24]), Naslain (2010 [37]), Xia (2012 [42]), Lamon (2015 [41]), Yin (2016 [6]), and Braginsky (2016 [46]).

C. Interface properties and property extraction

From the discussion above, it is reasonable to summarize CFMC toughening into three primary stages of interface-dependent mechanisms:

i) Matrix micro-crack evolution and crack deflection at the interphase
ii) Crack propagation along the fiber
iii) Fiber failure and pull-out

Accordingly, the governing interface properties associated with each stage are

i) The mode I fracture energy release rate, Γ_I, as it relates to the HH criterion ratio
ii) The interface debond shear strength (τ_{debond}) and internal friction coefficient (μ_i)

iii) The frictional sliding stress ($\tau_{sliding}$), as a function of the dynamic friction (μ)

Figure 3 is a schematic that illustrates the contributing properties as they relate to the respective toughening mechanisms in a strained composite. Generally, stages i, ii, and iii occur in succession, however this schematic represents all stages in a single frame.

Insert FIG. 3. (a) (b)

Experimental extraction of each property is critically important to the validation of governing physics models, as well as for component simulation via finite element models. Accurately identifying property values that are representative of the interface *as it exists* within the composite has posed significant challenges. The first challenge is simply length scale. Fiber coatings can be on the order of tens to hundreds of nanometers, making even standard small scale testing techniques such as nano-indentation a difficult task. Additionally, complex geometries associated with fiber weave, fiber diameter, and fabrication processes can complicate and influence the repeatability and data analysis required for property extraction. To date, several test methods and data analysis techniques have been developed to probe the interface while attempting to adjust for these challenges. The most common and direct technique is fiber push-out and push-in testing. Other techniques include scaling of bulk monolithic properties, as well as indirect extraction techniques such as cyclic tensile testing and fracture characterization. The latter requires interpretation and deconvolution of loading/unloading hysteresis loops, saturation micro-crack spacing, matrix cracking stress, permanent strain, and residual crack opening [14], [41], [55]. Both push-out testing and indirect extraction techniques exhibit a wide range of complexities.

The intent of this paper is to illuminate some of the complexities associated with fiber push-out testing, and present micro-pillar compression as a way to reduce complexity and increase fidelity in direct property extraction. With regard to SiC/PyC/SiC composites, this paper looks comprehensively at the governing interface properties, methods of extraction, and how small scale mechanical testing (SSMT) may improve our understanding of the contributing phenomena.

Fiber push-out testing

The fiber push-out test is a well-documented testing method across the composite literature, allowing direct measurement of the interfacial strength and sometimes friction between fiber and matrix after debonding [56]. At first guise, the process for property extraction is quite simple. First, prepare a thin sample with fibers moving through the matrix orthogonal to the polished surface, then use a micro/nano indentation instrument to apply force to the end of the fiber and record the load required to debond and slide the fiber. Finally, divide through by the fiber surface area to extract the respective debond and sliding shear stresses.

If a normal stress at the fiber surface is known, then the friction coefficients associated with debond and sliding can be resolved. However, both the experimental execution and physics models for property extraction impose complexities that have led to data scatter and potential for property misrepresentation. During testing, it is observed that steady state debonding occurs along the interface until the applied force causes instantaneous failure across the remaining bonded length. A visual representation of this phenomenon can be found in figure 2 of Rebillat's work [57]. Not only has the prediction of the steady state debond length proven difficult, but there are many factors that affect the debonding phenomena [41], [42], [57]–[59]. The most prominent are the Poisson and roughness effects along the length of the fiber. Rigorous shear lag analyses carried out by Hsueh, Shetty, and Lawrence [56], [58], [59] [Lawrence-60] have laid the foundation for understanding these effects, and have established appropriate elastic models to describe the local stress states. The analyses describe how Poisson and roughness characteristics give rise to variable axial force along the length of the fiber, resulting in large shear and normal stresses near the point of indentation. Relatively complex analytical solutions to the applied elastic model were developed for effective property extraction. Although theoretically sound, simplifying assumptions were indeed placed [58], and experimental data scatter has been consistently observed (see compiled data in the discussion), limiting confidence in the extracted properties.

Beyond the complexities in data deconvolution, experimental execution of push-out testing presents its own set of difficulties and limitations. For example, while large fibers of >100μm diameter may be easily tested using a universal testing machine and a flat punch, the accuracy of alignment needed for the typical fiber diameter of <10μm in SiC/SiC composites is only achievable using micro-mechanical testing methods such as nanoindentation and precise

positioning stages. As noted in the work of Rebillat et al. [60] and Mueller et al. [61] this leads to difficulties in producing and handling very thin sections of composite suitable for push-out testing, where the final thickness must be accurately known and consistently achieved. An additional difficulty is that the physics models assume that fibers are orientated perpendicular to the polished surface without sub-surface deflection. In practice this may be difficult to verify and care must be taken that fibers oriented at oblique angles are not considered. In addition, the presence and variation of defects along the interphase may contribute significantly to the scattering of the results as described in detail below.

A related consideration is that the type of indenter tip used to perform the test can have a significant influence on the obtained results. Berkovich indenter tips (relatively large angle pyramidal tips) are a common type used in indentation experiments [21], but there are several disadvantages to this approach for push-out tests. First, the tip causes deformation and penetrates the fiber before pushing it out which must be accounted for during analysis, adding uncertainty. Second, due to the high stress field under the tip, facture of the fiber can occur before interface debonding and cause wedging effects in the fiber channel, this can be seen in figure 4A. Third, due to the low aspect ratio of such tip geometry only a small push-out depth can be obtained before deformation of the surrounding matrix occurs. Damage to the surrounding matrix after full displacement (figure 4B) will impact push-back tests that aim to extract the debonded frictional properties by pushing the debonded fiber (of the original push-out test) back into the matrix from the back-side of the sample. As such it is generally perceived that a flat punch type indenter is preferable to reduce material impression and potential wedging. However, this comes with its own disadvantages. As seen in the work of Mueller et al. [61] if either the flat punch or sample is not perfectly flat, a true flat contact will not be made and result in similar bedding effects to that of a sharp indenter discussed above. Secondly the calibration required to assure a perfect micro-scope to indenter alignment is more challenging. This can result in inaccurate placement of the indentation as seen in figure 4A, as well as slower throughput and testing yield.

A final consideration when interpreting fiber push-out data is the effect that local microstructure can have on measured results. Meuller et al. [61] found that the number of fibers surrounding the pushed fiber could have a significant effect on the measured interfacial shear stress. Furthermore, because the fiber is fully imbedded in the matrix, characterizing defects such as voids, contamination, and non-uniform interphase deposition is extremely difficult. Figure 4C

is a scanning transmission electron microscope image of a thin foil that contains the interphase of two separate fibers (far left and far right). The fibers, imbedded less that 15μm apart in the matrix, exhibit significantly different levels of contamination as well as axis alignment.

Insert FIG. 4 (a) (b) & (c)

Future work is required to investigate the implications of these characteristics and develop a microstructurally informed model. SSMT is a potential solution to address these challenges associated with experimental execution, interface characterization, and complex shear lag analyses. A variety of SSMT techniques to extract useful material properties have been applied successfully to brittle ceramics and interfaces [62]–[67]. However, only recently have researchers applied SSMT to characterize CFMC interface properties. Shih et al. were the first to apply micro-pillar compression to SiC/PyC/SiC composites in 2013 [68]. This paper as well as Kabel et al. [69] build on Shih's preliminary efforts by advancing the test methods and property analysis. Major refinements include increasing the number of tested pillars, extending the range of interface inclines, and *in situ* SEM compression for improved confidence in test validity. Technology improvements have also made examination of the interface fracture surface significantly easier, allowing the heterogeneity of matrix and interface to be quantified and accounted for. The mechanics and capabilities of interface-containing micro-pillars are described below.

Micro-pillar compression

The micro-pillar structure, shown in figure 5A, contains the fiber, interphase, and matrix. Micro-pillars are on the order of 3μm in diameter (D), allowing for selective probing that reduces complexities associated with interface characterization. The pillars are assumed pristine such that the interface is fully bonded prior to compression testing. As a result, the extracted properties at failure are characteristic of mode II shearing associated with stage ii toughening. Unfortunately, due to the length scale and instrument loading characteristics, it is common for the pillar to be destroyed following instantaneous debond, making the extraction of stage iii interface properties difficult. Because failure is brittle, it is assumed that the applied elastic strain energy is released entirely via the surface area created during fracture of the interface. Thereby the fracture energy

release rate can be obtained via Eq. 3 to provide unique insight into the stage i toughening criterion, where fiber-push-out testing falls short.

In order to understand the governing debond properties of the PyC interface, the *Mohr-Coulomb fracture* criterion (MC) is applied [53], [68], [69]. This criterion states that ultimate shear strength of a brittle ceramic is resisted by two components. The first is the interface debonding shear strength, τ_{debond}, which is characteristic of the chemical bonding of the material at the plane of fracture. The second is an internal friction resistance described by the coefficient, μ_i, which is considered to be fundamentally different than the static friction of classical physics. Here it describes a resistance to debond initiation that is dependent on the tortuosity of the evolving fracture path. The equilibrium relationship between the failure shear strength and the opposing resistances is described by Eq.4, where the critical shear stress, $\tau_{failure}$, is set to equal the unknown τ_{debond}, and the unknown μ_i multiplied by the applied normal stress (N_R):

$$\tau_{failure} = \tau_{debond} + N_R * \mu_i \tag{4}$$

Experimentally, the applied uniaxial stress state can be resolved into the shear and normal stress at the interface plane, as illustrated in figure 1 of Kabel's work [69].

At failure, the resolved stress state is then a function of the applied failure load, P_{fail}, interface incline, θ, and the inclined interface cross-sectional area; $A = \pi D^2/4*\cos(\theta)$. Eq.4 can then be represented in a more useful form for experimental property extraction by Eq.5:

$$\frac{P_{fail}*sin\theta}{A} = \tau_{debond} + \frac{P_{fail}*cos\theta}{A} * \mu_i \tag{5}$$

By adjusting the interface incline, a unique failure stress state is acquired for each micro-pillar. When plotted in Mohr's space (τ vs σ), the linear relationship as described by Eq.4 & 5 evolves to allow for the extraction of τ_{debond} and μ_i as the τ-intercept and slope respectively. Figure 5A shows a schematic and Figure 5B shows a typical ~3μm diameter micro-pillar with PyC/SiC multilayer interphase. The corresponding force balance is overlaid to express the stress state of the loaded structure. A more detailed discussion of the mechanics and assumptions behind the

MC criterion and micro-pillar testing, including the effect of fiber surface curvature can be found in [69].

Insert FIG. 5. (a) (b) & (c)

With regard to stage i property evaluation, the mode II fracture energy release rate of the PyC interface can be directly extracted for each micro-pillar test. This is achieved though application of the *work of fracture* criterion that states for a brittle material, the area under the load versus displacement curve is equivalent to the work energy that was required to overcome the formation of the new fracture surfaces [70]. Applying Cedric's relationship between mode II and mode I fracture energy, as described in Eq.3, allows for extraction of the stage i governing parameter for interface crack deflection, Γ_I of the interface.

II. EXPERIMENTAL

A. Materials

The composites evaluated in this paper were manufactured by Hypertherm with CVI β-SiC matrix, 5-layer alternating PyC/SiC interphase, with Hi-Nicalon Type S (Nippon Carbon Co., Tokyo, Japan, ''HNLS'' hereafter) fibers [71], [72]. These fibers are nuclear-grade generation III SiC fibers that are characterized by near-stoichiometric chemical composition with low oxygen and free-carbon concentrations, as well as high crystallinity. HNLS fibers exhibit grain size (*d*) ~10-50nm and root mean squared surface roughness (r_{RMS}) ~2.33nm [21], [73], [74]. PyC was deposited via chemical vapor infiltration at ~1000C with varying thicknesses (~50nm-1500nm), true interface thickness values varied across different fibers. Bulk properties including the modulus and ultimate strength for the HNLS composites evaluated in this study can be found in Katoh's work [21], [75].

B. Micro Pillar Compression

Two baseline samples, A and B, were evaluated. Data from sample A was originally presented by Kabel et al. and is reproduced here with permission from ref. [69]. Both exhibited five alternating layers of PyC/SiC before full CVI SiC infiltration, however the thickness of the first PyC coating (at the fiber surface) was varied. Additionally, a composite sample from the

same fabrication batch as sample A was irradiated to 0.97dpa at 350°C in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Lab (ORNL)[75]. SEM measurements revealed interface thicknesses for samples A and A_{rad} at ~ 40nm, and sample B at ~1330nm. It can be noted that these samples were prescribed to be manufactured with 50nm and 500nm PyC first layers respectively, suggesting room for refinement in CVI processing. Table I outlines the sample test matrix and related details including the measured interface thickness, incline groupings, and total number of pillars tested for each sample.

Insert Table I – *Test matrix*

The samples were received as 2 x 2 x 1mm^3 blocks. Each was polished such that fibers at the edge of each sample would have different angles with respect to the horizontal plane of the polishing puck, allowing for stress state variability at the micro-pillar interfaces. The irradiated samples were prepared at ORNL. Figure 5C shows a typical five-layer alternating PyC/SiC interphase of sample A. A TEM investigation carried out in the author's previous work [69] revealed that failure occurs at the thick PyC first layer, and it occurs within the PyC. This is significant because it implies that the extracted properties are characteristic of the PyC, as opposed to the PyC/fiber interface. Because propagation occurs within the first layer following deflection, Eq. 3 remains valid for mono and multilayer interfaces.

Micro-mechanical structures were fabricated using the FEI Quanta 3D dual beam focused ion beam (FIB) (ThermoFisher Scientific in Waltham, MA) via standard FIB milling techniques. Rough and finishing cuts were performed at 30keV with 15nA and 0.1nA currents respectively as illustrated in figure 6. Critical measurements including the interface incline and cross-sectional area were acquired at this stage of the experiment. Interface incline calculations assume perfectly cylindrical fibers. However, deformed cylindrical geometries are frequently observed. To address this, deformed fibers were stringently avoided, and multiple pillars were fabricated on pristine fibers of the same incline to allow for improved statistics.

Insert FIG. 6. (a) (b) (c)

Once fabricated, the pillars were tested *in situ* the SEM with the Hysitron PI-85 Pico-Indenter (Bruker Corp. in Bellerica, MA) using a 5μm diamond tip flat punch. Tests were

performed under displacement controlled loading at 10nm/s. Carrying out the pillar compression *in situ* allows acquisition of live testing video to ensure alignment and contact accuracy. This capability is particularly beneficial to the fidelity of this characterization technique and resulting properties. A typical load-displacement curve and corresponding interphase failure for a 45-degree interface incline pillar from sample HNLS_B is displayed in figure 7. Failure was defined as the first instantaneous load drop (P_{fail}). In the case of figure 7, failure was observed at ~ 1.5 mN.

Insert FIG. 7. (a) and (b)

III. RESULTS AND DISCUSSION

P_{fail} was extracted from the load-displacement curve for each micro-pillar test, as shown in figure 7. The values were subsequently used to calculate the resolved normal and resolved shear stress at the plane of fracture in the interface using Eq. 5. Each sample yielded data for its respective incline plane, which were then group averaged and plotted in Mohr's space. However, prior to applying the MC criterion, a preliminary evaluation of the ultimate failure shear strength, $\tau_{failure}$, was carried out for sample A, A_{rad}, and B. This raw data was plotted with respect to the cosine of the incline angle, as shown in figure 8A. In doing so, the data is adjusted such that the slope of the applied linear regression represents a single normalized value for the ultimate shear strength averaged over the range of test inclines. Analysis of figure 8A revealed a fundamental reduction in ultimate shear strength between A and A_{rad} of ~80 MPa, and of ~300 between A and B. This suggests that both irradiation and increased interface thickness results in a weaker interface. Based on irradiation kinetics, it is suggested that a reduction in strength may be due to microstructural damage that is commonly observed in irradiated carbon materials. In the case of increased thickness, it may be expected that extrinsic parameters such as fiber surface roughness contribute less to the fracture path tortuosity within the PyC, potentially reducing the stress required to fail.

To fully understand the observed change in ultimate strength, the MC criterion investigates and separates the contribution of strength from chemical bonding and internal friction resistance. In figure 8B, the resolved shear stress was plotted versus the resolved normal stress at failure for the incline group averages of samples A, A_{rad}, and B.

Insert FIG. 8. (a) and (b)

A linear regression was applied from which the τ-intercept and slope were extracted to identify the contribution of strength from chemical bonding (τ_{debond}) and internal frictional resistance (μ_i) respectively. Table II summarizes the extracted properties. These values are additionally compiled in table III for comparison against push-out and bulk tensile hysteresis loop evaluations of stage ii and iii interface properties.

Insert Table II *– Interphase Property Values*

With respect to irradiation effects, it can be observed that while the chemical debonding strength decreases with irradiation, the friction coefficient appears to increase. As a whole, the interface was weakened, however the relative contribution of chemical and frictional resistance has shifted. This is likely a result of irradiation induced microstructural changes within the turbostatic graphite-like structures [76], [77] . For thought, consider a perfect graphite lattice for which shear failure occurs at the weakly bound basal planes. As irradiation displaces atoms from the hexagonal framework, it could be conceived that there is an effective reduction in basal plane surface area, resulting in reduced strength. In addition, the displacements may result in new stacking and basal plane arrangement, some of which may have less strength than the others. As a result, the fracture path may become more tortuous in an effort to fail along the weakest plane, resulting in larger contribution of frictional resistance to ultimate failure. There has been extensive research into defect evolution and crystallite reconstruction for graphite and graphite-like materials under irradiation [77]–[79]. It has been found that swelling/shrinkage, dissolution and restructuring of nano-crystallites is strongly dependent on the fabrication parameters, as well as the irradiation and irradiation temperature during operation. Most literature data are associated with bulk nuclear grade graphite which exhibits substantially different microstructure compared to the semi-oriented nano-crystallite nature of thin deposited PyC. Therefore, drawing from conclusions and characteristics of historical nuclear graphite may be misleading.

Looking at the MC property extraction for sample B (PyC~1300nm), it was found that both the chemical bonding strength as well as the frictional resistance was reduced compared to

sample A (PyC ~40nm). It has been observed that CVI PyC may exhibit stronger graphite-like ordering as a function of distance from the fiber surface [36]. If consistent, it is hypothesized that the bond strength is reduced as the lattice structure approaches that of highly oriented pyrolytic graphite (HOPG interlayer shear strength has been found on the order of ~140 MPa [80]), where weak basal plane interactions govern the strength. In this case, fracture tortuosity would also be reduced. Additionally, fiber roughness which may significantly impact fracture path tortuosity in sufficiently thin interfaces, may have much less of an effect on such a thick interface. For example, the RMS roughness for HNLS fibers was found ~2nm and resulting peak roughness at ~8nm [21], [73], [74]. This roughness is on the order of 5-10% of the total thickness of sample A, compared to <1% for sample B. It is believed that the property values extracted from sample B are more characteristic of the true intrinsic properties of PyC.

In future work, it will be critically important to evaluate the PyC microstructure as a function of thickness as well as neutron dose, dose rate, and temperature. A careful and detailed TEM investigation of the PyC layers *as they exist* in these composites will be a necessary step forward in fully characterizing the mechanical property relationships observed in this analysis.

Fracture energy release rate

The mode II fracture energy release rate was directly extracted from several load-displacement curves across samples A and B, as shown in figure 7. A point of concern that may influence property extraction is the possible mechanical interaction of the fiber and matrix during compression. This is likely to be a function of interface incline as well as interface thickness. For example, a shallow inclined interface is expected to experience more normal compression before critical shear stress is achieved. If the PyC is compressed, then a thin interface may lead to increased fiber to matrix interaction prior to failure, increasing the work of fracture. Assuming pure mode II fracture with echelon propagation, we can apply Xia and Cedrix's criterion (Eq. 3) to evaluate energy release rate values for the deposited PyC as a function of thickness and incline. This allowed for extraction of the mode I energy release rate associated with the HH criterion that is critical for stage i toughening. Figure 9 is a graphical representation of the mode I energy release rate, Γ_{PyC}, across the range of interface incline (25° to 65°) with a wide range of thicknesses from 30 to 1500nm (represented by the data labels of figure 9, in nanometers).

Insert FIG. 9

From this analysis, two primary observations can be made. The first is that interface thickness appears to have very little influence in the general trend of the curve. This is interesting considering a clear dependence on thickness observed for shear strength and internal friction coefficient of the interface. It is speculated that the fracture energy release rate is less sensitive to an increased surface area from fracture tortuosity compared to its influence on internal friction resistance. The second observation is that as the interface incline decreases, the release rate energy (and data scatter) increases. It is believed that this is a result of increased mechanical influence from the fiber surface roughness due to increased normal stress required to achieve shear failure. Conversely, as the interface incline increases and approaches a stress state of a pure shear (90°), the curve flattens and appears to approach a saturation value at ~2.5 J/m^2, exemplified by the blue circle in figure 9. In an effort to justify the claim that the observed scatter and increased release rate energy was mechanical in nature, a low angle (25°) thin interface (38nm) pillar test that exhibited both initial debond as well as debonded frictional sliding was characterized. During this test it was possible to reset the indenter tip after initial debonding and re-apply the compression to the remaining micro-pillar cap. The associated load-displacement curve and SEM image of the sheared pillar is shown in figure 10. This test allowed evaluation of the difference between fracture energy release rate of the fully bonded interface (area under the curve of the first load drop (blue)) and the energy release rate of the debonded interface (area under the curve of the second load drop (red), adjusted for the reduced interface contact area). Subtracting out the work of frictional sliding initiation, denoted Γ_{mech}, from the original pristine work of fracture, $\Gamma_{chem+mech}$ allows for consideration of the un-diluted chemical bonding value for the fracture release rate energy of PyC. Performing this energy adjustment found Γ_{PyC} = 3.6 J/m^2 which is close to that of Γ_{PyC} at steep inclines (>60°) = ~2.5 J/m^2 as observed in figure 9.

Insert FIG. 10.

This evaluation may explain the scatter observed at shallow inclines, where local surface roughness and therefore increased mechanical resistance to debond may play a stronger role. It is

believed that steep incline interface property values are more characteristic of true PyC fracture energy release rate. Therefore, our analysis presents 2.5 J/m^2 as an additional data point for PyC mode I fracture energy release rate. This value is presented in Table III amongst others found in literature. It can be noted that Γ_{PyC} varies significantly from different experiments, however the value presented here, 2.5 J/m^2, would satisfy the HH criterion (compared with Γ_{SiC} ~20 J/m^2 from table III) with respect to experimental micro-crack deflection observed in the bulk SiC composites. It is believed that this micro-mechanical approach to PyC property extraction shows promise for experimental validation of crack deflection and propagation criterion. With respect to CFMC design and modelling, providing a method for property validation may open doors for improved finite element models that can build at a fundamental level, incorporating crack deflection logic and phenomena. This may improve computer prediction and for allow for iterative interface tailoring and optimization.

Table III is a comprehensive summary of literature that has identified and extracted governing interface properties specific to SiC/PyC/SiC. Data presented for stage ii and iii are representative of samples with thin (~50-100μm) first layer PyC except those explicitly acknowledged (i.e. irradiated and thick PyC of this manuscript). It is observed that fiber push-out testing has significant scatter for stage ii debond strength ranging from 5 to 400 MPa. This scatter is likely due to the aforementioned challenges and assumptions relating to experimental operation (i.e. fiber and indenter alignment) and correct application of property extraction models (i.e. shear lag analysis). Additionally, fiber push-out was unable to extract a friction parameter. Micro-pillar compression provided debond shear strength values on the same order of magnitude, 100 to ~300 MPa, but with improved uncertainties. The lower bound of τ_{debond} = 100MPa (and accompanying μ_i = 0.7) from the pioneering work of Shih et al. [68] shows significant deviation from pillars of sample A that hosted similar ~50μm first layer PyC. The original effort captured data from a total of seven pillars, limiting robustness and property confidence. However, when combined with pillars from sample A as shown in figure 8B of Kabel et al. [69], there is only a minor shift in the extracted values with τ_{debond} ~244MPa and μ_i ~0.28. As micro-pillar compression characterization continues, it is expected that this fundamental approach will continue to narrow the uncertainties for interfaces of different PyC parameters and conditions. Improved characterization of the as-deposited PyC structure and the as fabricated residual clamping stress will improve data fidelity and understanding of failure

phenomenon. Although capable of stage i and ii property extraction, it is important to note that micro-pillar compression is not well equipped for the extraction of kinetic properties of stage iii. To date, fiber push-out testing continues to be the most viable option for stage iii property characterization. However, it is believed that development of novel SSMT structures can provide appropriate avenues for refined property extraction at all stages.

Insert Table III *– Governing interface properties for toughening stages i, ii, and iii*

IV. CONCLUSION

This manuscript provides a) a literature review on the role of interfaces in CFMC failure and associated laboratory methods for extracting the governing properties, and b) a demonstration of SSMT as a promising technique to improve characterization and quantification of CFMC interface properties. Three primary stages for CFMC toughening were identified; i) crack deflection, ii) crack propagation along the fiber, and iii) fiber pull-out. Each stage exhibits fundamental properties including, respectively, fracture energy release rate, internal friction and debond shear strength, and kinetic friction and debonded shear stress. Traditionally, fiber push-out testing is performed to identify some of these properties. For this method, it was noted that both the physics-based models for data interpretation and the experimental procedures present inherent difficulties that lead to significant data scatter, see table III. *In-Situ* micro-pillar compression was presented as an alternative method to overcome many experimental hurdles and analysis difficulties. Pillar analysis extracted properties related to stage i and ii with higher fidelity than fiber push-out. For thin ~50nm PyC interfaces, $\mu_i = 0.25 \pm 0.03$ and $\tau_{debond} = 266 \pm 23$, as shown here and by Kabel et al. [69]. Thick ~1500nm PyC interfaces showed a reduction in both debond shear strength and internal friction coefficient with $\mu_i = 0.17 \pm 0.03$ and $\tau_{debond} = 133 \pm 14$. Across the varying thickness, a fundamental value for fracture energy release rate was observed, $\Gamma = \sim 2.5$ J/m^2. Finally, it was shown that irradiation at 350C to ~1 dpa on ~50nm PyC resulted in a reduction of debond shear strength with an increase in internal friction coefficient with $\mu_i = 0.36 \pm 0.03$ and $\tau_{debond} = 103 \pm 11$. It is recommended that stage i and stage ii property

values of this effort be applied in modelling efforts attempting to capture fundamental physics of crack propagation.

ACKNOWLEDGMENTS:
This work was supported by the U.S. Department of Energy (DOE), Office of Nuclear Energy's Nuclear Science User Facilities (NSUF) program. A portion of this study was also supported by the U.S. DOE, Office of Nuclear Energy for the Advanced Fuels Campaign of the Fuel Cycle R&D program under contact DE-AC05-00OR22725 with Oak Ridge National Laboratory managed by UT Battelle, LLC. In addition, we would like to thank the Nuclear Regulatory Commission (NRC) fellowship program and the DOE-NEUP program for student and project support. We also acknowledge the EPSRC for their support through grant number EP/N017110/1. Lastly, we would like thank those involved with the UC Berkeley BNC facility and the Lawrence Berkeley National Laboratory National Center for Electron Microscopy (LBNL NCEM) for enabling this research through access and expertise to the necessary facilities.

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FIGURE CAPTIONS:

FIG. 1. (a) SiC/PyC/SiC with alternating PyC-SiC interlayer architecture including varying thickness and spacing, reproduced with permission from ref. 21. Copyright 2014 Elsevier. (b) Deformation and debonding of a ductile platinum coating in Al_2O_3/Al_2O_3 composite (c) LaPO4 coating on alumina reinforced with alumina fiber composite. Images (b) and (c) are reproduced with permission from ref. 24. Copyright 2002 John Wiley and Sons.

FIG. 2. (a) Graphical representation of the He-Hutchinson criterion. A representative debond length due to mode II shear is pointed to on the deflection zone schematic. (b) Schematic displaying the load sharing characteristics between the fiber and matrix on a bridged micro crack as a function of debond length, modified and reproduced with permission from ref. 41. Copyright 2015 John Wiley and Sons.

FIG. 3. (a) Crack propagation occurring around a notch defect, where pull-out traction redistributes the stress. (b) Three stages related to CFMC toughening and the governing interface properties; i) Γ_i , ii) τ_{debond} and μ_i, and iii) $\tau_{sliding}$ and μ. Extrinsic influences such as fiber surface roughness, interface thickness, and residual clamping stress (N_R) are illustrated. Inspired by and adapted from Evans and Lamon and reproduced with permission from ref. 14. Copyright 1994 Springer. and ref. 41. Copyright 2015 John Wiley and Sons.

FIG. 4 (a) Cracking of fiber before push-out and observation of indenter tip misalignment (b) Indenter tip interference with matrix material limiting push-out displacement and impacting push-back testing. Reproduced with permission from ref. 21. Copyright 2014 Elsevier. (c) Transmission Electron Micrograph of two fibers 15um apart from each other embedded in the same matrix. It can be seen that the interphase has different structures that are likely to cause difficulties without push-out testing and data interpretation.

FIG. 5. (a) Representative schematic of pillar fabrication, adapted and reproduced with permission from ref. 69. Copyright 2017 Elsevier. (b) Stress state and force balance of a representative micro-compression structure. (c) STEM image of HNLS fiber and interphase with alternating PyC (light) and SiC layers (dark).

FIG. 6. Typical micro-pillar fabrication process using FIB milling techniques. (a) Candidate fiber selection and fiber incline calculation. (b) Initial FIB rough cut for micro-pillar mid-fabrication. (c) Final micro-pillar structure after finishing cuts, and resulting interface area equation.

FIG. 7. (a) Load vs diplacement curve of pillar compresssion showing failure load and shaded area under the curve (work of fracture) for extraction of the fracture release rate energy. (b)HNLS_B micro-pillar with thick PyC interphase prior to compression.

FIG. 8. (a) Comparison of raw data for control sample A, A_{rad}, and B to show fundamental reduction in strength with irradiation and thickness. (b) Application of the Mohr-Coulomb criterion to extract τ_{debond} and μ_i via linear regression.

FIG. 9. Energy release rate as a function of interface angle grouped in three and interface layer thickness (data labels in nanometers). The mode I energy release rate was calculated using Eq.3 Cedric's relationship $\Gamma_{II} = 3.5 * \Gamma_{I}$.

FIG. 10. Isolation of chemical bonding contribution to fracture energy release rate. The area under the curve. Post interface failure of micro-pillar from HNLS_A with pillar cap still intact, adapted and reproduced with permission from ref. 69. Copyright 2017 Elsevier

TABLES:

Table I – Test matrix

Sample	PyC 1st layer (nm)	Inclines tested (°)	Successful pillars
A [67]	40 ± 6	~25°, 44°, 63°	17
A_{rad}	41 ± 12	~35°, 50°, 60°	16
B	1330 ± 176	~20°, 42°, 56°	8

Table II – Interphase Property Values

Fiber	τ_{debond} (MPa)	Internal friction coefficient. (μ)
A [67]	266 ± 23	0.25 ± 0.03
A_{rad}	103 ± 11	0.36 ± 0.03
B	133 ± 14	0.17 ± 0.03

Table III – Governing interface properties for toughening stages i, ii, and iii

Material/sample	Test method	Property	Reference
Stage i (deflection)			
		Γ_{PyC} (J/m^2)	
Monolithic PyC	K_{IC} test	~21-34	[81]
		~28	[41], [58],
HNLS/PyC/CVI	Permanent strain &	~2*	[59]
	Residual crack opening	~0-5	[6]
HNLS/PyC/CVI	Micro-pillar	~2.5	(this work)
		Γ_{fiber} (J/m^2)	
HNLS Fiber	Tensile	~22*	[18], [84]
HNLS/PyC/CVI	Tensile	~8 *	[41]
		Γ_{Matrix} (J/m^2)	
CVI SiC	K_{IC} test	~22*	[18]
CFMC	Micro-crack spacing	~5-50	[14]
Stage ii (debonding)			
		τ_{debond} (MPa)	
HNLS/PyC/CVI	Push-out	~267	[20]
(PyC~50-150nm)		~208 (0.8dpa 380C)	[20]
		~350	[21]
		~71-212	[85]
		~105	[61]
		~5-400	[60]

HNLS/PyC/CVI (PyC~50-150nm)	Micro-pillar	~100	[68]
		~266	[69]
		~133 (~1300nm PyC)	(this work)
		~103 (1 dpa 350C)	(this work)
		μ_i (internal friction)	
HNLS/PyC/CVI (PyC~50-150nm)	Micro-pillar	~0.7	[68]
		~0.25	[69]
		~0.17 (~1300nm PyC)	(this work)
		~0.36 (1 dpa 350C)	(this work)
Stage iii (pull-out)			
		$\tau_{sliding}$ (MPa)	
HNLS/PyC/CVI (PyC~50-150nm)	Push-out	~338	[20]
		~63 (0.8dpa 380C)	[20]
		~100	[21]
		~90-270	[41],[33]
		~160-273	[57]
		~13-37	[85]
		~300	[86]
HNLS/PyC/CVI (Treated fibers) (PyC~50-150nm)	Hysteresis loops and micro-crack spacing	~1-200	[14]
		~50-370	[41],[87]
		~190-370	[57]
		~9-33	[74]

*Converted from K_{IC}