With a unique combination of properties including high hardness, low density, wear and corrosion resistance, thermal stability, high neutron absorption, and semi-conductivity, boron carbide (B\textsubscript{4}C) is a candidate material for various engineering applications that involve extreme environment. The current applications of boron carbide, however, are limited by its intrinsic brittleness due to its strong covalent bonding. To toughen boron carbide, in this work hierarchical microstructure designs was used to provide multiple toughening mechanisms including crack deflection/bridging, micro-crack toughening, etc. Using field assisted sintering, B\textsubscript{4}C composites with hierarchical microstructure features including graphite platelets, micron and sub-micron sized TiB\textsubscript{2} reinforcements were fabricated. The fracture toughness of fabricated B\textsubscript{4}C composites were previously measured at micro-scale using micro-indentation followed by post-testing microstructure inspection. However, questions including whether the fracture toughness enhancement measured at micro-scale can translate to macro-scale mechanical properties, and what are the fundamental mechanisms behind observed fracture toughness enhancement, remain to be answered. In this study, the fabricated B\textsubscript{4}C composites were tested using standardized four-point bending method to obtain fracture toughness at macro-scale. In addition, micromechanics modeling was conducted using MAC/GMC code and crack-band model to study the effect of residual stress and weak interphases on fracture behaviors of B\textsubscript{4}C composites reinforced with TiB\textsubscript{2} particles. Through standardized four-point bending tests, fracture toughness enhancements up to 2.85, 3.32, and 3.65 MPa-m\textsuperscript{1/2} (from 2.38 MPa-m\textsuperscript{1/2}) were achieved for B\textsubscript{4}C composites with graphite platelets addition (micro/nano B\textsubscript{4}C), with TiB\textsubscript{2} formation (micro B\textsubscript{4}C-TiB\textsubscript{2}), and with both graphite and TiB\textsubscript{2} addition (micro/nano B\textsubscript{4}C-TiB\textsubscript{2}) respectively. Micromechanics modeling indicated that introduction of thermal residual stress and weak interphases caused enhanced micro-cracking behavior and resulted in the observed fracture toughness enhancement. These results furthered understanding about the mechanical behaviors at macro-scale and the mechanisms behind observed fracture toughness enhancement for B\textsubscript{4}C composites with hierarchical microstructures and can provide reference data for the future design of B\textsubscript{4}C composites with optimized microstructures for further fracture toughness enhancement.

I. Introduction

With a unique combination of properties including high hardness (~29.1 GPa [1]), low density (2.52 g/cm\textsuperscript{3} [1]), high stiffness (Young’s modulus: ~448 GPa [2]), high melting point (~2450 °C [3]), corrosion and wear resistance, semi-conductivity [1], and high neutron absorption ability [4], boron carbide (B\textsubscript{4}C) can be used in various structural and multi-functional applications, such as body armor, protective coating, radiation shielding, etc. However, current applications of B\textsubscript{4}C are largely limited due to its intrinsically low fracture toughness (K\textsubscript{IC}: ~ 2.9 MPa-m\textsuperscript{1/2} [5]). Traditionally, boron carbide is often toughened through introduction of a secondary phase, such as various transition metal carbides and borides [6], among which titanium diboride (TiB\textsubscript{2}) [7–11] and zirconium diboride (ZrB\textsubscript{2}) [12] are the most common. Various carbon-based nanofillers, such as carbon nanotubes (CNTs) [13,14] and graphene platelets...
Materials and Methods

Macro C and TiB

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composites were sintered through reactive sintering method, where TiB powder and B µm B

Table A.  of TiB structured B

contribution from each

second, with multiple toughening mechanisms functioning together, it is difficult to identify individual toughness measured using indentation methods at micro/nano B

While introduction of softer phases resulted in degradation in hardness and 4.65 MPa∙m

Comparison of toughness for B

micro/nano B

Toughening microstructure, including grain boundary sliding and nano-pore compression [17].

Figure 1. Typical toughening mechanisms for B4C composites with hierarchical microstructures: (a) crack deflection for micro/nano B4C samples, (b) crack deflection, micro-crack toughening for B4C-TiB2

composites.

In previous studies, the authors pursued toughening of B4C by a hierarchical microstructure design that utilizes both secondary reinforcement phases (TiB2) and ‘soft’ grain boundary phases (graphite platelets and nanocrystalline B4C phase) [22,23]. Three types of B4C composites were fabricated which exhibited multiple toughening mechanisms: micro/nano B4C samples with graphite platelets distributed between B4C micro-grains showed crack-deflection toughening (see Figure 1(a)) and graphite delamination; micro B4C-TiB2 composites with micron-sized B4C and TiB2 grains and micro/nano B4C-TiB2 composites, with B4C micro-grains, sub-micron TiB2 reinforcements, and introduced graphite platelets, both exhibited crack-deflection/bridging and micro-crack toughening behaviors (see Figure 1(b)). When compared with monolithic B4C samples (K1 c: 2.98 MPa·m1/2), fracture toughness enhancement up to 4.16, 4.67, and 4.65 MPa·m1/2 were achieved for micro/nano B4C, micro and micro/nano B4C-TiB2 composites respectively. While introduction of softer phases resulted in degradation in hardness: from 32.46 GPa to 18.19 and 29.43 for micro/nano B4C and micro B4C-TiB2 composites with 15 vol% secondary phase introductions, the micro/nano B4C-TiB2 composites demonstrated high fracture toughness while maintaining high hardness (31.88 GPa).

Despite the promising results, two main challenges remained in this study: first, the fracture toughness was measured using indentation methods at micro-scale, and might not translate to macro-scale behaviors and properties; second, with multiple toughening mechanisms functioning together, it is difficult to identify individual toughness contribution from each type of microstructure features. In this study, macro-scale standardized fracture toughness testing (four-point bending) was carried out to establish microstructure-property relationships for hierarchical micro-structured B4C composites at macro-scale. And the fracture behavior for B4C composites, specifically the ones with TiB2 introduction, was modeled using micromechanics analysis code MAC/GMC with crack-band model. The effects of the weak interphases at B4C-TiB2 boundaries and the thermal residual stress caused by the large coefficient of thermal expansion mismatch between B4C and TiB2 were studied.

II. Materials and Methods

A. Macro-scale fracture toughness testing

For macro-scale fracture toughness characterizations, B4C composites samples with various compositions (see Table 2) were fabricated using field assisted sintering technology (FAST). A monolithic B4C reference sample (micro B4C) was fabricated using commercially available B4C micro-powder (H.C. Stark, Grade HS, particle size: ~0.6-1.2 µm). For hierarchical micro-structured B4C composites, two micro/nano B4C samples were sintered using B4C micro-powder and B4C-C nano-powder (US-Nano Inc, 55 wt% B4C and 45 wt% graphitic carbon, particle size: ~45-55 nm) using 90/10 and 80/20 volume fraction ratios. In addition, three micro B4C-TiB2 and three micro/nano B4C-TiB2 composites were sintered through reactive sintering method, where TiB2 grains were introduced through in-situ reaction between B4C, TiO2, and free carbon through reaction (1).
B₄C + 2 TiO₂ + 3 C → 2 TiB₂ + 4 CO  \hspace{1cm} (1)

The micro B₄C-TiB₂ composite samples were sintered using B₄C micro-powder, TiO₂ nano-powder (US-Nano Inc, particle size: ~40 nm, anatase phase), and carbon black nano-powder (Alfa Aesar, particle size: ~42 nm) to yield 5, 10, and 15 vol% TiB₂ phases accordingly. For the micro/nano B₄C-TiB₂ composites, the samples were sintered using B₄C micro-powder, B₄C-C nano-powder and TiO₂ nano-powder without the addition of carbon black, as the free carbon within B₄C-C nano-powder can provide sufficient carbon source for reaction (1) to happen. The starting powder compositions were selected to yield 5, 10, and 15 vol% of TiB₂ phases in the sintered samples. A full list of sintered samples and their target compositions are listed in Table 2. The starting powders were ball-milled (Tencan XQM-0.4A) in methanol for 1 hour, dried in air at 110 °C for 12 hours, and grinded before use. The FAST sintering was performed using an FCT HP D25 unit with 25 tons load capacity. The starting powders were poured into a 40 mm-diameter graphite die and sintered using a 100 °C/min heating rate, 45 MPa applied pressure, 20 min holding time at 2100 °C in vacuum environment before naturally cooled down. Starting powders were measured to yield samples with at least 5 mm thickness upon complete densification.

In author’s previous works [22,23], the reactive sintered micro and micro/nano B₄C-TiB₂ composites exhibited inhomogeneous microstructure after sintering, where the edges of the sample fully densified while the center parts of the sample remained porous. The origin of this inhomogeneity was identified to be the lack of degassing for CO during the reaction. According to Huang et al [10,11], reaction (1) can be divided into 2 reactions:

1. 2.5 B₄C + 3 TiO₂ → 3 TiB₂ + 2 B₂O₃ + 2.5 C \hspace{1cm} (2)
2. 2 B₂O₃ + 7 C → B₄C + 6 CO \hspace{1cm} (3)

The formation of TiB₂ according to reaction (2) happens at ~1600 °C, forming excessive free carbon and liquid phase B₂O₃ in the process, while carbothermal reduction between B₂O₃ and C happens at a higher ~2000 °C temperature [24–26]. Without a degassing step (pressure applied at the beginning of sintering processes), the CO gas formed during reaction (3) can be trapped at the center of the sample during sintering, preventing reaction (3) from completion, resulting in poor densification and microstructure inhomogeneity. In order to fabricate homogeneous B₄C-TiB₂ samples required for macro-scale testing, an updated sintering profile with an additional degassing step (see Figure 2) was used in the current study, where pressure was applied nine min after reaching the sintering temperature. With the updated sintering profile, samples with near full density (Table 2) and homogeneous microstructures that satisfy the geometry requirements for macro-scale fracture toughness testing were successfully fabricated.

**Figure 2. Representative sintering profile with degassing step for reactive sintering of B₄C-TiB₂ composite.**

Four-point bending method according to ASTM standard C-1421 [27] was used in this study for macro-scale fracture toughness characterization. The sintered B₄C composites pellets were cut and machined into beam specimens with a dimension of 25 mm × 4 mm × 3 mm (see Figure 3 (b)). A surface pre-crack was created at the center of each beam samples on the surface with 4 mm width using micro-indentation with 2 kgf load, 20 sec holding time and a Knoop indenter tip (Figure 3(c)). The indented surfaces were polished by hand grinding to remove indentation impression and surface layers with residual stress followed by drying at 110 °C for 1 hour in air before bending tests. Four-point bending tests were conducted using an MTS Criterion electro-mechanical universal test system with a fixture with 20 mm and 10 mm outer and inner roller spans (Figure 3 (a)), and a constant crosshead speed of 0.02 mm/s (~70-80 N/s equivalent loading rate). At least five samples were tested for each composition. The fractured
surfaces were inspected by optical microscopy after testing to measure half width and depth of the pre-crack (see Figure 3 (d)). Fracture toughness can be calculated according to the following equation:

\[ K_{Isc} = Y \left( \frac{3 P_{max} (S_o - S_i) 10^{-6}}{2 BW^2} \right)^{1/2} \sqrt{a} \]  

(4)

Where \( K_{Isc} \) denotes the fracture toughness measured using the surface crack method, \( Y \) is the stress intensity factor calculated from the pre-crack geometries, \( P_{max} \) is the maximum force (fracture load), \( S_o \) and \( S_i \) are the outer and inner spans of 4-point bending fixture, \( B \) and \( W \) are the width and thickness of the sample, and \( a \) is the depth of the pre-crack.

Figure 3. (a) Four-point bending test set-up, (b) image of a beam sample and pre-crack location, (c) a typical Knoop indentation impression on sample surface, (d) typical pre-crack geometry observed after bending tests.

B. Micromechanics modeling of fracture behaviors

Modeling of fracture behaviors for hierarchical micro-structured \( B_4C \) composites, specifically the ones with TiB\(_2\) reinforcement phases (micro and micro/nano \( B_4C \)-TiB\(_2\)), was performed using the high-fidelity generalized method of cells (HFGMC) [28–30] incorporated in the micromechanics analysis code with generalized method of cells (MAC/GMC) [31,32] developed at NASA Glenn Research Center. The crack band model, initially developed to model failure of concrete [33], have previously been used to model progressive failure of polymer and ceramic matrix composites [34–36], and was used to model fracture behavior of \( B_4C \) composites in this study.

Figure 4. Representative RVEs (10 \( \mu m \times 10 \mu m \)) constructed from SEM images of \( B_4C \)-TiB\(_2\) composites (15 vol\% TiB\(_2\)); green represents \( B_4C \) matrix, blue represents TiB\(_2\) grains, and yellow represents inter-phases.

The modeling was carried out on 2-D representative volume elements (RVEs) of micro and micro/nano \( B_4C \)-TiB\(_2\) composites to study the effect of residual stresses and weak interphases introduced through TiB\(_2\) formation. As \( B_4C \) grain boundaries have high strengths, observed to result in mostly trans-granular fracture in previous study [23], the grain boundary of \( B_4C \) was neglected in the current model. Thus, \( B_4C \)-TiB\(_2\) composites were modeled as a two or three-phase material consisting of \( B_4C \) matrix, TiB\(_2\) reinforcements, and weak inter-phases. To construct RVEs that can represent microstructures observed for fabricated \( B_4C \)-TiB\(_2\) composites, SEM images taken on polished surfaces of \( B_4C \)-TiB\(_2\) composite samples were converted into the binary format, cropped, and transformed as the microstructure...
input for the MAC/GMC code. Weak inter-phases between B\textsubscript{4}C matrix and TiB\textsubscript{2} grains were introduced by tracing the boundaries of TiB\textsubscript{2} particles. Representative RVEs generated through this procedure are shown in Figure 4.

Table 1. Mechanical and thermal properties of B\textsubscript{4}C and TiB\textsubscript{2} used for MAC/GMC modeling.

<table>
<thead>
<tr>
<th></th>
<th>E (GPa)</th>
<th>ν</th>
<th>α (K\textsuperscript{−1})</th>
<th>ε\textsubscript{fail}</th>
<th>σ\textsubscript{fail} (GPa)</th>
<th>K\textsubscript{IC} (MPa\textcdot m\textsuperscript{1/2})</th>
<th>G\textsubscript{I} (J/m\textsuperscript{2})</th>
<th>Sub-cell size H (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B\textsubscript{4}C [1,2]</td>
<td>432.6</td>
<td>0.151</td>
<td>5.7 \times 10\textsuperscript{−6}</td>
<td>0.5</td>
<td>2.16</td>
<td>2.9</td>
<td>19</td>
<td>0.1</td>
</tr>
<tr>
<td>TiB\textsubscript{2} [37]</td>
<td>584.7</td>
<td>0.106</td>
<td>8.7 \times 10\textsuperscript{−6}</td>
<td>0.4</td>
<td>2.34</td>
<td>5.7</td>
<td>54.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Interphase</td>
<td>432.6</td>
<td>0.151</td>
<td>5.7 \times 10\textsuperscript{−6}</td>
<td>0.3</td>
<td>1.30</td>
<td>1.7</td>
<td>6.8</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure 5. Traction-separation curves for B\textsubscript{4}C and TiB\textsubscript{2} used for modeling.

To simplify the model, both B\textsubscript{4}C and TiB\textsubscript{2} were treated as linear elastic, isotropic materials before failure. The mechanical and thermal properties used to model B\textsubscript{4}C and TiB\textsubscript{2} phases are listed in Table 1. For failure modeling, only Mode I fracture under uniaxial loading was considered, and the material degradation properties were governed by the post-(crack) initiation tangent stiffnesses, which are the slopes of the softening stress-strain or traction separation curves. In this study, the traction-separation constitutive behavior was used. As shown in Figure 5, the post-initiation behaviors of B\textsubscript{4}C and TiB\textsubscript{2} were determined by their elastic modulus, failure strain/stress, the characteristic length (element or sub-cell size), and the area underneath the unloading/degradation curve which equals to the Mode I critical energy release rate G\textsubscript{I}. For the plane-strain condition used in this study, G\textsubscript{I} was calculated from fracture toughness K\textsubscript{IC} using equation (5):

\[
G \textsubscript{I} = K \textsubscript{IC}^2 \cdot (1-\nu^2) / E
\] (5)

Where ν is Poisson’s ratio and E is the elastic modulus. While properties including modulus, fracture toughness can be obtained from previous studies, the actual failure strain/stress for B\textsubscript{4}C and TiB\textsubscript{2} at micro-scale cannot be directly obtained. As the focus of this modeling study is to capture the fracture behaviors instead of accurately predicting material properties, the failure strains for B\textsubscript{4}C and TiB\textsubscript{2} were decided through a parametric trial study on various combinations of failure strains for B\textsubscript{4}C and TiB\textsubscript{2}, where the resulting fracture behaviors of the RVEs were compared with experimental observations. A combination of 0.5 % failure strain for B\textsubscript{4}C and 0.4 % failure strain for TiB\textsubscript{2} was selected, as this combination resulted in trans-granular fracture in both B\textsubscript{4}C and TiB\textsubscript{2}, resembling the fracture behaviors observed in previous studies. For weak inter-phases, the elastic, thermal properties, and post-initiation stiffness of B\textsubscript{4}C are currently used, with failure strain reduced from 0.5 % to 0.3 %, resulting in a 64 % decrease in corresponding energy release rate (Table 2).

To model the mechanical responses of the B\textsubscript{4}C-TiB\textsubscript{2} composites, the 2-D RVEs were subjected to plane strain condition, uniaxial tensile strain up to 0.5%, with periodic boundary conditions applied to all the RVE edges. To simulate residual stress due to the large coefficient of thermal expansion (CTE) mismatch between B\textsubscript{4}C and TiB\textsubscript{2}, a stress-free cooling section (from 1000 °C to 23 °C) was added before the uniaxial tension. The thermal and mechanical loading applied to RVEs in this study is shown in Figure 6. To investigate the effects of thermal residual stress and weak interphases, RVEs constructed from the microstructures of the micro B\textsubscript{4}C-TiB\textsubscript{2} composites with 15 vol% TiB\textsubscript{2} were modeled in three cases: 1) without cooling, without weak interphases, 2) with cooling, without weak interphases, and 3) with cooling, with weak interphases. The results including stress-strain relations, change in elastic modulus,
stress/strain fields obtained from the three simulated cases were compared to separately study the effect of individual mechanisms.

![Figure 6. Thermal and tensile loads applied to the RVEs.](image)

III. Results

A. Macro-scale fracture toughness measurement

For macro-scale fracture toughness testing, B₄C-composite samples with homogeneous microstructure and near full density have been successfully fabricated. As shown in Table 2, with the updated sintering profile with degassing step, all the reactive sintered micro and micro/nano B₄C-TiB₂ composite samples exhibited consistently high density (> 97 % relative density). Upon inspection, all reactive sintered B₄C-TiB₂ composites exhibited homogeneous microstructure. SEM images showing representative microstructures for fabricated B₄C composites are shown in Figure 7. The reference micro B₄C sample exhibited densely packed grains with an average size of ~3 µm (see Figure 7(a)). With addition of B₄C-C nano-powders, graphite platelets formed after FAST process were observed in fabricated micro/nano B₄C samples (see Figure 7(b)). For both micro and micro/nano B₄C-TiB₂ composites, TiB₂ particles formed through reactive sintering were observed (see Figure 7(c, d)). Due to the usage of B₄C-C nanopowder, the formed TiB₂ particles in micro/nano B₄C-TiB₂ composites were smaller than those in micro B₄C-TiB₂ composites and were distributed at grain boundaries of B₄C grains where graphite platelets were also observed. More detailed inspection of fabricated B₄C composites with hierarchical microstructures can be found in authors’ previous works [22,23].

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Target Composition (vol%)</th>
<th>Sintering Conditions</th>
<th>Measured Density (g/cm³)</th>
<th>Theoretical Density (g/cm³)</th>
<th>Relative Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>micro B₄C</td>
<td>100</td>
<td>2100 °C 100 °C/min, 45 MPa, 20 min</td>
<td>2.514</td>
<td>2.52</td>
<td>99.8</td>
</tr>
<tr>
<td>micro/nano B₄C</td>
<td>90 4.9 5.1</td>
<td>2100 °C 100 °C/min, 45 MPa, 20 min</td>
<td>2.497</td>
<td>2.494</td>
<td>100.0</td>
</tr>
<tr>
<td>micro B₄C-TiB₂</td>
<td>95 9.8 10.2</td>
<td>2100 °C 100 °C/min, 45 MPa, 20 min</td>
<td>2.467</td>
<td>2.468</td>
<td>99.9</td>
</tr>
<tr>
<td>micro/nano B₄C-TiB₂</td>
<td>90 2.1 2.9 5</td>
<td>2100 °C 100 °C/min, 45 MPa, 20 min</td>
<td>2.624</td>
<td>2.62</td>
<td>100.0</td>
</tr>
</tbody>
</table>

† Assume no grain growth and no reaction between carbon and oxidization layers on B₄C powders; for reactive sintered micro/nano B₄C-TiB₂ composites, complete reaction between TiO₂, carbon and nano-sized B₄C is assumed.
Figure 7. Representative microstructures of fabricated (a) micro B₄C, (b) micro/nano B₄C, (c) micro B₄C-TiB₂, and (d) micro/nano B₄C-TiB₂ composites.

For micro/nano B₄C samples, four-point bending tests have been conducted on two micro/nano B₄C samples with 10 and 20 vol% B₄C-C nano-powder addition and compared to the fracture toughness measured on the reference micro B₄C sample. With 10 and 20 vol% B₄C-C nano-powder addition, the micro/nano B₄C samples exhibited increased fracture toughness of 2.62 and 2.85 MPa·m⁰.⁵ when compared with micro B₄C (2.38 MPa·m⁰.⁵) (see Figure 8). Although lower than the values measured using micro-indentation: 3.71 and 4.00 MPa·m⁰.⁵ for micro/nano B₄C, and 2.98 MPa·m⁰.⁵ for micro B₄C samples, both micro-indentation and 4-point bending results showed increasing trend for fracture toughness with higher volume fraction of B₄C-C nano-powder addition. Such trend can be attributed to the increasing volume fractions of formed graphite, which toughens B₄C through crack deflection and graphite platelet delamination. The discrepancy between fracture toughness measured using micro-indentation and four-point bending is a result of the complex fracture behaviors beneath indentation impressions after the micro-indentation tests [23]. While the 4-point bending tests create mostly mode-I fracture under flexural load, the compressive load under indentation can lead to mixed mode fracture and deformation behaviors including shear-band formation, resulting in over-estimated fracture toughness. Regardless of the overestimation, the general fracture toughness enhancement due to the formed graphite platelets is verified by the standardized 4-point bending tests.

Figure 8. Fracture toughness measured using micro-indentation and four-point bending methods for fabricated B₄C composites.
The fracture toughness measured for micro and micro/nano B$_4$C-TiB$_2$ composites using the four-point bending method are summarized in Figure 8. Compared to the reference micro B$_4$C sample (2.38 MPa∙m$^{1/2}$), both micro and micro/nano B$_4$C-TiB$_2$ composites exhibited enhanced fracture toughness with higher volume fraction of TiB$_2$ particles: fracture toughness of 3.32 and 3.65 MPa∙m$^{1/2}$ were achieved for micro and micro/nano B$_4$C-TiB$_2$ composites with 15 vol% TiB$_2$ respectively. The micro/nano B$_4$C-TiB$_2$ composites achieved higher fracture toughness than micro B$_4$C-TiB$_2$ composites, due to the additional toughening contribution from the graphite platelets formed from B$_4$C nano-powders. These results are consistent with observations from micro-indentation data; introduction of TiB$_2$ and graphite platelets promoted toughening mechanisms including crack deflection/bridging, micro-crack toughening, and graphite delamination, resulting in enhanced fracture resistance for hierarchically microstructure B$_4$C composites [23]. Comparing the fracture toughness values measured using the macro-scale four-point bending tests and the micro-scale indentation tests (see Figure 8), overestimation of fracture toughness was again observed for the micro-indentation testing data. Such discrepancy stems from the complex fracture behaviors beneath indentation impressions during the micro-indentation testing as opposed to mostly mode-I fracture under flexural load in the four-point bending tests. The high compressive load (in the range of ~30 GPa) beneath the indentation impressions can also trigger deformation behaviors including shear band formation in B$_4$C grains and dislocation inside TiB$_2$ grains. These deformation behaviors will be less common under the lower flexural load (~400 MPa for an uncracked beam under testing load of 1 kN) in four-point bending testing.

B. Modeling effects of thermal residual stress and weak interphases on fracture behaviors

Based on previous studies [38–40], weak interphases and thermal residual stress are expected to be two contributing factors for the observed micro-cracking behaviors and fracture toughness enhancement for micro and micro/nano B$_4$C-TiB$_2$ composites. To study the effects of thermal residual stress and weak interphases on fracture behaviors of B$_4$C-TiB$_2$ composites, micromechanics modeling was performed on micro B$_4$C-TiB$_2$ composite RVEs (~15 % TiB$_2$) with three different conditions: 1) without cooling, without weak interphases, 2) with cooling, without weak interphases, and 3) with cooling, with weak interphases. Modeling was performed on four RVEs for each case. The stress-strain behavior in tensile direction ($\sigma_{22}$-$\epsilon_{22}$), the change in elastic modulus, and the stress/strain field were monitored at different stages of mechanical and thermal loadings. The resulting stress-strain curves and change in modulus with respect to strain in loading direction ($\epsilon_{22}$) were used to identify the onset of failure and complete fracture. The $\sigma_{22}$ stress field right before damage initiation and the $\epsilon_{22}$ strain field before and after brittle failure of the RVEs were used to examine the progressive failure behaviors for B$_4$C-TiB$_2$ composite RVEs. The simulation results of the four cases are presented below (see Figures 9-11).

Figure 9. Simulation results of a B$_4$C-TiB$_2$ composite (~15 vol % TiB$_2$) RVEs without weak interphases and without thermal residual stress: (a) stress-strain ($\sigma_{22}$-$\epsilon_{22}$) curves, (b) modulus-strain plots, (c) stress ($\sigma_{22}$) distribution before damage initiation, strain ($\epsilon_{22}$) distribution (d) before and (e) after brittle failure.
First, for micro B$_4$C-TiB$_2$ composite RVEs (~15 vol% TiB$_2$) without weak interphases and without thermal residual stress, the RVEs behaved in a mostly linear elastic manner until fracture initiation at ~0.41% tensile strain ($\varepsilon_{22}$) and ~1800 MPa tensile stress ($\sigma_{22}$) (see Figure 9 (a, b)). At the beginning of fracture initiation, high stress level was observed inside and near TiB$_2$ particles, due to the contrast in stiffness between B$_4$C and TiB$_2$ (see Figure 9 (c)). The irregular shapes of TiB$_2$ particles also contributed to stress concentration in a few TiB$_2$ particles. At the ‘necking’ location of an elongated TiB$_2$ grain (Figure 9 (c)), stresses in tensile direction up to ~2.3 GPa was observed. When loaded further, the RVEs went under limited progressive failure by micro-cracking. In these micro-cracks at boundaries of B$_4$C and TiB$_2$ and locations of high stress concentration, high strain ($\varepsilon_{22}$) resulted from the post-failure softening stress-strain behavior was observed (see Figure 9 (d)). These micro-cracks eventually propagated into the surrounding B$_4$C matrix, connected to form a major crack going through the B$_4$C-TiB$_2$ composite RVEs leading to complete fracture. Without weak interphases and without thermal residual stress, the simulated micro-cracking behaviors can be solely attributed to the TiB$_2$ grain geometry and stiffness/strength contrast.

![Figure 10. Simulation results of a B$_4$C-TiB$_2$ composite (~15 vol% TiB$_2$) RVEs without weak interphases and with thermal residual stress: (a) stress-strain ($\sigma_{22}$-$\varepsilon_{22}$) curves, (b) modulus-strain plots, (c) stress ($\sigma_{22}$) distribution before damage initiation, strain ($\varepsilon_{22}$) distribution (d) before and (e) after brittle failure.](image)

Second, for micro B$_4$C-TiB$_2$ composite RVEs without weak interphases and with thermal residual stress, failure initiation happened at ~0.21% tensile strain ($\varepsilon_{22}$) (see Figure 10 (a, b)), which was much lower when compared with the case without thermal residual stress (at ~0.41% tensile strain ($\varepsilon_{22}$), see Figure 9 (a, b)). Despite the early fracture initiation at ~0.21% tensile strain, the composite RVEs sustained ~0.2% increase in tensile strain during inelastic deformation before complete fracture at ~0.40-0.43% tensile strain ($\varepsilon_{22}$). The enhanced progressive fracture behavior can be attributed to the thermal residual stress distribution. In Figure 10 (c), high tensile stress (up to ~2.0-2.4 GPa) was observed inside and near TiB$_2$ grains, while compressive stress (~500 MPa) was seen in B$_4$C matrix surrounding the TiB$_2$ grains. This high stress contrast originated from the thermal residual stress due to B$_4$C and TiB$_2$’s high CTE mismatch (B$_4$C: $5.7 \times 10^{-6}$/K and TiB$_2$: $8.7 \times 10^{-6}$/K). During the cooling process, TiB$_2$ grains shrank more than the surrounding B$_4$C matrix, creating tensile residual stress inside TiB$_2$ and at B$_4$C-TiB$_2$ boundaries, and compressive residual stress in B$_4$C matrix surrounding B$_4$C grains. The high tensile stress inside and at boundaries of TiB$_2$ grains contributed to the micro-cracking behavior (see Figure 10 (d)) and led to fracture initiation at lower tensile load. The compressive thermal residual stress inside B$_4$C matrix delayed complete fracture of the material by containing the micro-cracks with regions under compression or much lower tensile stress.

Third, for micro B$_4$C-TiB$_2$ composite RVEs with weak interphases and with thermal residual stress, both early onset of damage and extensive progressive failure behaviors were observed. The combination of weak interphases’ low failure strain (0.3%) and thermal residual stress resulted in micro-cracking and drop in material stiffness at low tensile strain of ~0.1% (see Figure 11 (a, b)). Similar to the case of RVEs without weak interphases but with thermal
residual stress (see Figure 10), the regions under compressive residual stresses surrounding the opening micro-cracks inhibited them from further opening, leading to the progressive failure behavior between ~0.1% to ~0.3% tensile strain. About the behavior right before complete fracture, more extensive micro-cracking and their conforming to the TiB₂ boundaries were observed with weak interphases (see Figure 11 (d)) than the case without weak interphases (see Figure 10 (d)). With weak interphases, high local strain in the tensile direction within the weak interphases (up to 3.0%, see Figure 11 (d)) was observed despite the lower global tensile strain, while local strains within the micro-cracks for RVEs without weak interphases was observed at 1.5% (see Figure 10 (d)).

Figure 11. Simulation results of a B₄C-TiB₂ composite (~15 vol% TiB₂) RVEs with weak interphases and with thermal residual stress: (a) stress-strain (σ<sub>22</sub>-ε<sub>22</sub>) curves, (b) modulus-strain plots, (c) stress (σ<sub>22</sub>) distribution before damage initiation, strain (ε<sub>22</sub>) distribution (d) before and (e) after brittle failure.

The micro-cracking behavior observed in fabricated B₄C-TiB₂ composites was captured in all three cases modeled using micromechanics. However, extensive progressive failure behavior was only achieved when thermal residual stress was introduced. The high CTE mismatch between B₄C and TiB₂ induced tensile residual stress of ~1.5 GPa within TiB₂ grains and at B₄C-TiB₂ boundaries, and compressive residual stress of ~500 MPa within B₄C matrix near the TiB₂ grains. The high tensile residual stress promoted micro-cracking behavior, while the surrounding compressive residual stress contained the propagation of micro-cracks, leading to gradual failure of the composites. The existence of weak interphases along B₄C-TiB₂ boundaries further promoted the progressive failure behavior by inducing micro-cracks at lower load. The modeled behaviors agreed with experimental observations and offered insights on the mechanisms behind observed fracture toughness enhancement.

IV. Conclusion and Future Work

In this study, the fracture toughness for B₄C composites with hierarchical microstructures was measured at macro-scale using standardized four-point bending tests. Fracture toughness enhancement from 2.38 MPa·m<sup>1/2</sup> to 2.85, 3.32, and 3.65 MPa·m<sup>1/2</sup> were observed for micro/nano B₄C with graphite formation, micro B₄C-TiB₂ composites with micron sized TiB₂ grains, and micro/nano B₄C-TiB₂ composites with sub-micron sized TiB₂ grains and graphite platelets respectively. These measurement results using the macro-scale bending tests were smaller than those obtained using the micro-scale indentation method but exhibited the same trend. Such discrepancy can be attributed to the mixed-mode fracture and complex deformation behaviors (shear bands, dislocations) induced during indentation tests. In addition to macro-scale mechanical testing, micromechanics modeling of fracture behaviors was performed on B₄C-TiB₂ composites which exhibited the highest fracture toughness enhancement in this study. The effects of thermal residual stress and weak interphase on fracture behaviors of B₄C-TiB₂ composites were investigated using the micromechanics-based modeling. The residual stress resulted from the high CTE mismatch between B₄C and TiB₂ was found to promote initiation of micro-cracks at B₄C-TiB₂ boundaries; their gradual opening lead to enhanced
progressive failure behavior. Such behavior was further enhanced by the introduction of weak interphases which caused early onset of micro-cracks and thus more extensive progressive failure behaviors. Along with knowledge obtained in the authors’ previous works [22,23], this study offers a fuller picture on the mechanical properties at both micro and macro-scale for fabricated B₄C composites and further understanding towards the mechanisms behind observed fracture toughness enhancement.

In future, material properties including the impact resistance, thermal and electric properties for B₄C composites with hierarchical microstructures can be measured to study the effects of hierarchical microstructure designs on properties other than fracture toughness. Micromechanics modeling can be conducted on polycrystalline RVEs to consider the effects of anisotropic single crystalline properties of individual grains and the existence of grain boundaries. The proposed hierarchical microstructure designs can also be optimized based on micromechanics modeling results to yield B₄C composites with enhanced fracture toughness without sacrificing other physical properties.

V. Acknowledgement

This material is based upon research partly supported by the U. S. Office of Naval Research under award number N000141712361. The authors are thankful for technical support from Charis Lin, Ricardo Braga Nogueira Branco, and Austin (Kirk) Heller from the Department of Aerospace Engineering (PSU), Kevin Busko and Petr Kolonin from the Applied Research Lab (PSU), Julie Anderson, Ke Wang, Haiying Wang, Jenny Gray, Manuel Villalpando, Tim Tighe, Beth Last, Trevor Clark, and Nichole Wonderling from Materials Characterization Lab (PSU).

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