Measurement of Microscale Residual Stresses in Multi-Phase Ceramic Composites Using Raman Spectroscopy

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Abstract

A methodology is described for characterizing the spatial distribution of thermal mismatch stresses at grain level in B₄C-SiC-Si ceramic composites using Raman spectroscopy. Unlike traditional methods to detect residual stress (e.g., X-ray diffraction) which provide average values over the entire specimen surface, Raman peak-shift analysis provides residual stress distributions within the microstructure at high spatial resolution. While the classical formulation predicts uniform compressive stress within a Si-phase surrounded by the ceramic matrix, the Raman measurements revealed non-uniform residual stress distributions in Si when the particle size was larger than 5 microns. For large irregular shaped particles, the two methods coincide only along the interface between the particle and matrix, but vary drastically both in magnitude and nature in the interior of the particle where large tensile stresses have been measured. The average residual stress within the microstructure was found to correlate well with the volume fraction of the constituents and material properties. The presence of anomalous tensile stress in the interior of the minor Si-phase results in defect generation and structural disorder which has been confirmed by a subsequent TEM analysis.

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1. Introduction

Structural ceramics, such as boron carbide (B_4C) and silicon carbide (SiC), offer exceptional mechanical properties and have applications ranging from lightweight armor to wear-resistant tooling [1-3]. These ceramics are commonly produced by hot pressing or pressureless sintering. Recently, reaction bonding has become a promising alternative because it offers rapid fabrication times, reduced processing temperatures, and can produce complex, near net-shape parts [4], e.g., a one-piece ceramic helicopter seat [5,6]. In this method, a porous ceramic (B_4C and/or SiC) powder preform is placed in a vacuum furnace along with Si lumps. As the temperature is raised above the melting point of silicon ($1410\text{ }^{\circ}C$), the molten silicon (Si) infiltrates the ceramic preform [7] and reacts with a carbon (C) source (free carbon or residual carbon in B_4C) to form SiC . The reaction-formed SiC and residual (unreacted) Si bond the microstructure together. Due to the complex microstructure of reaction bonded ceramics, an in-depth understanding of microstructure-property relationships is crucial for their effective use in intended applications.

An important consideration in these multiphase ceramic composites processed at high temperatures is residual misfit stress that evolves due to coefficient of thermal expansion mismatch and in some cases, even defect generation [8]. Patent literature [9] has revealed that residual compressive stresses in the Si phase can be leveraged as a “toughening” mechanism. Because Si is the weakest mechanical constituent in the composite microstructure it is of utmost interest in this study [10,11].

The current work is motivated by three considerations: (i) Limited work has been reported on thermal mismatch stresses in reaction bonded materials, especially at microstructural level; (ii) A method for evaluating the spatial distribution of stress across different phases of

varying size and shape is not readily available. Such an effort is critically important to understand the failure behavior of multi-phase composites. Traditional techniques to measure residual stresses, such as X-ray diffraction, yield only global average values and cannot provide stress distributions at the micron-scale with high spatial resolution. Lastly, (iii) classical formulation for calculation of residual stress in a small region (or a particle) surrounded by semi-infinite matrix assumes a perfect spherical geometry and uniform residual stress within the particle. In reality, these particles occur in various shapes and sizes, and the residual stress within the particles cannot be assumed constant. In this manuscript, a methodology is described to quantify the magnitude and spatial distribution of residual stress at micron-scale spatial resolution using micro-Raman spectroscopy on the Si phase of the reaction bonded B₄C and SiC ceramics. Transmission electron microscopy (TEM) was then used to identify structural disorder resulting from these stresses.

2. Experimental

2.1 Materials and Microstructure

Three reaction bonded ceramics (see Table 1), with a naming convention based on starting powder composition, were examined: (i) B₄C powder (BC ceramic), (ii) B₄C-SiC powders (BSC ceramic), and (iii) SiC powder (SC ceramic). Two types of BC ceramics were assessed: one contained only B₄C particles with no preform additives (BC-1) and the other contained 10 wt.% of diamond particles (BC-D) in the preform as an additional carbon source to reduce the residual Si content [12]. Three BSC ceramics with varying ratios of B₄C and α -SiC powders (BSC-1, BSC-2, and BSC-3) were used. Finally, the SC ceramic containing only α -SiC powder in the preform (called SC-1). After reaction bonding, the final ceramic compositions are reported in volume percentage (vol.%) as shown in Table 1. Exact details of the process

parameters were proprietary and only the starting and final compositions were revealed by the manufacturer.

The typical microstructure for each type of reaction bonded ceramics is shown in Fig. 1. Raman spectroscopy was used for identification of phases present based on characteristic Raman peaks shown in Fig. 1(d). The residual Si phase has one strong peak at 520 cm^{-1} , with a broad spectral feature at 965 cm^{-1} [13]. The SiC polytypes found in the reaction bonded ceramics are α -SiC and β -SiC. The α -SiC (the starting powder) exhibits peaks at 769, 789, 798, and 971 cm^{-1} , while the peaks of β -SiC (reaction formed) are at 793 and 973 cm^{-1} [14,15]. The α -SiC appears as polygonal-shaped grains, while β -SiC appears as needle-like whiskers (see Fig. 1(a)). The B_4C has a multitude of peaks between $200\text{-}1200\text{ cm}^{-1}$, specifically 264, 324, and 1090 cm^{-1} [16,17].

2.2 Raman Spectroscopy

A Raman spectroscope (Renishaw InVia, 532 nm laser, 1 micron spatial resolution) was used to evaluate thermal stresses and structural disorder in the ceramic composites. Raman spectroscopy utilizes a focused laser to probe a specific region in a material. The laser light is scattered by the material causing an increase or decrease in energy which is characteristic of specific molecular vibration modes and chemical bonds [18,19]. The shifts in energy are interpreted and visualized as specific peaks in the collected spectra. To prevent localized heating of scanned regions, a low laser power of 10 mW was used.

Silicon was chosen for analysis because it is the weakest constituent in the microstructure. Raman spectral scans were collected from pure Si powder (reference material used for calibration), Si lumps used for reaction bonding (obtained from manufacturer), and Si regions within the reaction bonded ceramics. The characteristic stress-free peak at 520 cm^{-1} of Si was used as the reference and chosen for analysis. Peak shifts relative to this position were

related to residual stress, while peak broadening and reduced peak intensity were related to structural disorder [20]. In numerous Raman spectroscopic investigations, the shift (Δw) in the position of the most dominant Si peak from the virgin state (520 cm^{-1}) to stressed state was related to residual stress (σ_{Si}) as [21-23]:

$$\sigma_{Si} = -250 (\Delta w) \text{ {MPa}} \quad (1)$$

When the local residual stress is larger than the yield strength of the material, defects may be nucleated. Strain associated with structural disorder can cause peak asymmetry and peak broadening in the Raman spectrum which was then monitored for further analysis.

2.3 Transmission Electron Microscopy (TEM)

To corroborate peak asymmetry and broadening in the Raman spectrum to the structural disorder in the processed material, TEM analysis was undertaken on raw Si used for infiltration (prior to reaction bonding) and on Si in the reaction bonded BC-1. The TEM samples were prepared using a focused ion beam (FEI Dual-Beam Strata DB235) and were observed in a field-emission TEM (JEOL 2010F, Peabody, MA, USA).

2.3 Mechanical Properties

Static indentation hardness measurements were conducted with a standard hardness tester (Wilson® Instruments Tukon™ 2100B) on the ceramic composites using Vickers and Knoop indentations at 1 kg and 2 kg, respectively. The indentation loads were chosen to generate measurable indents and minimal cracking. At least 30 indentations were performed on several samples to generate a representative average value. All indentations were measured using an optical microscope (Olympus model BX51).

Uniaxial compression experiments were performed using 3.4 x 3.4 x 5 mm rectangular bar specimens with their surfaces polished to a 15-micron finish. Quasi-static testing was

conducted in a servo-hydraulic testing machine (MTS model 309.2) at two nominal strain rates of 5×10^{-3} and $5 \times 10^{-4} \text{ s}^{-1}$. The dynamic experiments were conducted using a split Hopkinson pressure bar (SHPB) suitably modified for testing ceramics at a nominal strain rate of 10^3 s^{-1} [24]. The incident and transmission bars were made of maraging steel and were 19 mm in diameter, and 1219 mm and 914 mm in length, respectively. Impedance-matched tungsten carbide platens of 12.7 mm diameter and 9.5 mm height were used to protect the loading surfaces from indentation by the intact or failed ceramic fragments during testing. The platen surfaces in contact with test specimens were lubricated to eliminate frictional effects and ensure a uniform stress state in the specimen. Ten specimens of each material were tested at each strain rate.

3. Theoretical Estimation of Residual Stress

If the microstructure is assumed to be an assembly of uniformly sized, elastic, spherical Si particles (p) surrounded by a semi-infinite ceramic (B_4C or SiC) matrix (m), the magnitude of residual stress (σ) in Si regions can be approximated using the following classical equation [25],

$$\sigma_{m-p} = - \frac{\Delta\alpha \cdot \Delta T}{\left[\frac{0.5(1+v_m)+f_p(1-2v_m)}{E_m(1-f_p)} + \frac{1-2v_p}{E_p} \right]} \quad (2)$$

where the misfit stress developed in the particle is a function of the difference (ΔT) between processing and ambient temperatures, elastic modulus (E) and Poisson's ratio (ν), the coefficient of thermal expansion (CTE) mismatch ($\Delta\alpha = \alpha_m - \alpha_p$) between the matrix and particle phases, and the volume fraction of particle phase (f_p). Although Eq. (2) is derived for a two-phase composite, a multi-phase material microstructure can be discretized into localized regions of two-phase materials. Thus, one can compute the thermal mismatch stress between each combination of matrix and particle phases (e.g., B_4C -Si and SiC -Si mismatches) as shown in Table 2. The CTE for B_4C , SiC , and Si are approximately 6.0, 4.6, and $3.6 \times 10^{-6}/^\circ\text{C}$,

respectively (i.e., $\alpha_{B_4C} > \alpha_{SiC} > \alpha_{Si}$). The elastic moduli and Poisson's ratios of B_4C and SiC are very similar and taken to be ~ 450 GPa [1,26-33] and 0.17 [1,26,28-30,33,34], respectively, and for Si these values are taken to be 150 GPa [26,35,36] and 0.22 [26,35], respectively. Using a nominal volume fraction of Si phase of 20% (e.g., BC-1 and SC-1) for illustrative purposes, the predicted values of residual stress in B_4C - Si , SiC - Si , and B_4C - SiC would be 583, 243, and 563 MPa, respectively. This value can be compression or tension depending on the phase in consideration, i.e., whether the phase being considered has higher or lower CTE than the adjacent phase. The actual stress developed in each region and each phase differs based on local volume fraction of particle phase, properties of the surrounding phase, and the size and shape of the particle.

Based on Eq. (2), as the composite is cooled from processing temperature down to ambient temperature, a matrix phase with higher CTE than the particle ($\alpha_m > \alpha_p$) should shrink more, placing the low CTE particle in residual compression, while the matrix is left in tension. The opposite is true for a matrix with lower CTE than the particle ($\alpha_m < \alpha_p$), where the particle is left in tension and the matrix is placed in compression. Thus, Si is expected to always be in residual compression. Furthermore, the largest beneficial compressive stress would develop in Si for primarily B_4C -containing ceramics (BC and BSC) due to large B_4C - Si thermal mismatch, compared to lesser SiC - Si thermal mismatch in predominantly SiC -containing ceramics (SC). Large residual compressive stresses should be beneficial in improving mechanical performance, but understanding their spatial distribution and variation will be of primary importance.

Recall that because Eq. (2) only provides residual stress between two phases, it must be suitably modified for multi-phase materials. We assume that the microstructure can be discretized into local regions of two phase materials and then weigh the resulting mismatch stress

between B₄C-Si or SiC-Si according to relative volume fraction of each contributing mismatch. Thus, the stress in any one phase becomes a weighted average of the stress due to its mismatch with the other two phases and is calculated as

$$\sigma_i = \frac{1}{f_j + f_k} (f_j * \sigma_{i-j} + f_k * \sigma_{i-k}) \quad (3)$$

where i , j , and k take the values 1, 2 and 3. For example, the stress in phase 1 (σ_1) is a weighted average of the stress developed due to mismatch between phases 1-2 and between 1-3 (i.e., σ_{1-2} and σ_{1-3} given by Eq. (2)). The sign of the stress value for each phase is assigned based on the CTE values of included phases (known *a priori*). A major assumption is that the local volume fraction in the region being analyzed is the same as the global average volume fraction value being used. Also, it is assumed a larger area can be discretized into localized regions of two-phase materials. Thus, based on relative quantities of one phase compared to another, a residual stress value can be determined for any phase in a multi-phase material as shown in Table 3. For regions with highly irregular particles it is unrealistic to assume uniformity in residual stresses with in each particle as will be demonstrated by Raman peak shift.

4. Results and Discussion

4.1 Residual Stress

The vast differences in thermo-mechanical properties of B₄C, SiC, and Si, shown in Table 2, cause thermal residual stress in the microstructure. Because residual Si is the weakest mechanical phase in the composite, it was of utmost interest in this analysis. Shown in Fig. 2 are Raman spectra for a silicon standard (reference material), raw Si used for infiltration (prior to reaction bonding) in its bulk and powder form, and selected scans of residual Si in a reaction bonded ceramic with predominantly B₄C, BC-1, due to greater anticipated peak shifting (higher

mismatch and residual stress). Both the Si standard and bulk Si show a high intensity sharp (narrow line width) peak at 520 cm^{-1} , representing high-crystalline quality and negligible residual stress, respectively. The bulk Si was powdered, and was re-scanned (to verify its stress-free condition). The same strong, narrow peak at 520 cm^{-1} was observed, suggesting negligible stress and structural disorder prior to processing. On the contrary, residual silicon in the reaction bonded ceramic showed observable peak shifting due to residual stress as well as peak broadening, reduced peak intensity, and peak asymmetry likely due to defects generated during processing.

Recall from Table 2 that Si exhibits lower coefficient of thermal expansion (CTE) than B_4C and SiC. Thus, as the ceramic composite cools after reaction bonding the carbide phases shrink more than Si, placing Si in residual compression and causing Raman peak shifts to higher wavenumbers. Using Eq. (2), for a spherical Si region encased in B_4C matrix, it was predicted that a uniform compressive stress up to around -583 MPa would develop in Si (see Table 2), i.e., the peak would shift to higher wavenumbers (compression) everywhere in the Si region. However, based on experimentally observed peak shifts for the perimeter and interior regions of a typical Si region in the final ceramic (Fig. 2), it was seen that the Si peak shifted to higher wavenumbers (compression) in perimeter regions and to lower wavenumbers (tension) in interior regions. These peak shifts suggest non-uniformities in the stress state within each particle, contrary to the predictions of uniform compressive stress by the classical formulation (Eq. (2)). To determine the range of validity of classical formulation and to better understand the nature of residual stress developed, Si regions of varying size and shape were investigated (see Fig. 3). Raman maps scans were conducted using a 100X objective and encompassed only a single Si region in each scan. The collected Raman maps were color-coded and analyzed as a function of

peak position, to create a residual stress map (Figs. 3 and 4). It was found that Si regions smaller than $\sim 5\text{ }\mu\text{m}$ in size were in a state of uniform compression as shown in Fig. 3(a) but those larger than $5\text{ }\mu\text{m}$ and of irregular shape revealed an anomalous tensile stress (see Fig. 3(b-d)) in the interior of the Si phase. This observation was accompanied by increased stress non-uniformity (indicated by color gradation) in both the perimeter compression and interior tension.

The predicted compressive stress value of -583 MPa (with Eq. (2)), compared well with magnitude of residual compressive stress measured in small regions (Figs. 3(a-b)) or along the periphery of large Si regions (Fig. 3(c-d)) between -575 to -590 MPa . Recall that Eq. (2) assumes a two phase material with spherical particle surrounded by a semi-infinite matrix and predicts a uniform state of compression in the Si regions. Clearly, the small Si regions better matched the predictions because they represented the ideal case. However, as particle size and shape deviated from the ideal case, experimentally measured stresses deviates from the predicted values. Thus, the Raman technique not only measures the theoretically predicted residual stresses (in ideal microstructures) but also sheds light on the unforeseen microscale stress heterogeneities, i.e., interior tensile stresses in highly irregular and large size particles.

The reasons for non-uniform stress distribution and tensile stress in Si particles can be rationalized as follows: (i) For a large particle, the exterior region cools more rapidly than the interior, and as a result, the exterior is in compression and interior is in tension; (ii) The irregular shape of the particle induces non-hydrostatic stress state on the particle resulting in high magnitude of shear and tensile stresses at various points within the particle; and finally, (iii) the Si is surrounded by ceramic particles of different sizes with different crystallographic orientations, and as is well known the elastic modulus and the CTE differ in each orientation resulting in uneven application of compressive stress on the Si phase boundary. All these factors

can contribute to the development of stress non-uniformities, interior balancing tension, and appreciable gradients in the developed stress state.

With this knowledge, it was of interest to assess the influence of the surrounding ceramic phase (either B_4C or SiC) on the thermal stress developed in Si phase of a multicomponent ceramic composite. Raman maps were obtained for silicon regions when surrounded primarily by either B_4C or SiC , as shown in Figs. 4(a) and 4(b), respectively. Based on the first-order approximation of thermal stress (Eq. (2)) for Si encased solely in B_4C matrix, it was predicted that compressive stress up to -583 MPa would develop in Si . Experimentally, for a Si region surrounded solely by B_4C (BC ceramic; BC-1), it was observed that residual compression was on average -390 MPa, reaching up to -590 MPa on the periphery depending on size and shape of particles considered. Conversely, the average tensile stress was +80 MPa, with stresses up to +320 MPa in the interior. When Si is encased by only SiC , a residual compression of -243 MPa was predicted (see Table 2). Similarly, for a Si region surrounded solely by SiC (SC ceramic; SC-1), stress non-uniformities similar to that observed for BC ceramic were observed. Again, the interior was found in a state of residual tension, while the perimeter was in compression. The average level of residual compressive stress was -50 MPa, with stress up to -260 MPa at the periphery of the Si region. On average, the tensile stresses were around +104 MPa, reaching up to +530 MPa in the Si interior. Thus, due to lower CTE mismatch between Si and SiC (compared to Si and B_4C), lower levels of residual compressive stresses were developed.

Clearly, in both examples above, the Raman technique was not only able to accurately measure the maximum residual compressive stress near the Si periphery, but also identified stress non-uniformities which deviated from the classical formulation. In order to expand the utility of this method and examine compositional influences on the developed stresses in more

complex ceramic composites, large areas consisting of many Si regions of varying sizes and shapes were examined to sufficiently account for microscale heterogeneities: 2100-10,600 μm^2 of Si or 3,300-16,600 unique Si spectra are collected (depending on volume fraction of Si present in each material). The peak shift value was determined for each collected spectrum and converted into a residual stress value using Eq. (3). The results are summarized in Figs. 5 and 6, which illustrate the distribution of residual stresses for the various compositions.

In Fig. 5, the influence of Si region size/shape and composition are depicted. The larger the Si region, the more non-uniform (greater color variation) the resulting stress distribution, and the greater the interior tension (blue regions). Also, increased B_4C content resulted in a higher level of compressive stress (i.e., green regions). Notice that outer regions of BC materials are highly compressive (green), while for the SC material they are mildly compressive (white). In addition to revealing local stress variation, these large map scans allow a single representative stress value to be determined for each material composition. These values can be used to make quantitative comparisons between mechanical properties and average residual stress for various microstructures.

Averaged values of residual stress in Si were extracted from the large maps in Fig. 5 for each material composition and plotted as a function of the volume fraction of various phases in Fig. 6. The data was examined in terms of average compressive stress (average value of all compressive points in Si regions), average tensile stress (average value of all tensile points in Si regions), or average residual stress (average value of all points in Si regions). The influence of volume fraction of carbide phase on the stress developed in Si is demonstrated in Figs. 6(a) and 6(b) (see solid green line). It can be noted that the average compressive stress in Si transitions from high compression (-330 to -445 MPa) for predominantly B_4C ceramics (BC), to moderate

compression (-200 to -350 MPa) for ceramics with comparable B_4C/SiC content (BSC), to weak compression (-50 MPa) for predominantly SiC ceramics (SC). Because B_4C has higher thermal mismatch with Si compared to SiC, increased volume fraction of B_4C leads to an increased magnitude of residual compression in the Si regions as in Fig. 6(a). It was also observed that average stresses in Si (see dashed red line) trended from highly compressive (-270 to -435 MPa) for BC materials to mildly tensile (+57 MPa) for SC materials. The low level of compressive stress in SC materials was overwhelmed by anomalous tensile stresses, leading to an average tensile state of stress. Lastly, the average value of residual tensile stress in each material did not show a strong dependence on B_4C or SiC content (see solid blue line in Fig. 6(a-b)).

Interestingly, trends in average stress, average compression, and average tension were observed as strong functions of the vol.% Si (see Fig.6(c)). It was noted that increased Si volume fraction correlated with decreased residual compression (see solid green line) and correspondingly greater residual tension (see solid blue line). As the Si content increased, the size of the Si regions also increased (see Fig. 5) and subsequently a higher likelihood of non-uniform cooling in each Si region. This lead to non-uniform residual stresses with compression only along the periphery and tension in the interior of the large Si regions. When Si volume fraction was low, most of the Si is in compression and the average stress is highly compressive (see dashed red line in Fig. 6(c)). With increased Si content, more number of large irregular shapes form with high interior tension, and so the average stress became less compressive. This observation is an extension of what was seen for the mapped regions shown in Fig. 3, which demonstrated that smaller Si regions are more likely to develop only compression, while larger Si regions have higher tendency to develop interior tension.

The above experimental results were found to follow the same trend but differ in

magnitude from the predicted values of stress in Si computed using Eq. (3) (see dotted black lines in Fig. 6(a-c)). The two major differences were: (i) non-existence of tensile stress in the microstructure and (ii) greater compressive stress values from theoretical calculations compared to experimental data. From theoretical calculations (Eq.(3)) it was expected that the thermal mismatch would result only in uniform compression in the Si. However, non-uniformities in the nature and distribution of stress were observed experimentally due to size, shape and surrounding matrix properties. The stress gradients and interior tensile stresses all decrease the level of compressive stress developed in each material with changes in composition. Simply put, if one were to add the average compressive and tensile stress magnitudes found for each material experimentally, i.e., $|\sigma_c| + |\sigma_t|$, then reasonable agreement is found between the experimental and predicted values. This demonstrates that the discrepancy between experimental and predicted values is primarily due to the fact that the theoretical approximations (assumptions of spherical shape and uniform matrix properties) do not account for the experimental factors such as irregular shape and size, which give rise to local tension.

4.2 Structural Disorder

The Raman peak broadening and peak intensity reduction observed in the Si regions of reaction bonded ceramics (see Fig. 2) are commonly related to structural disorder. Similar spectral changes were seen in the interior of Si regions, which have been demonstrated to be in a state of residual tension which can result in lattice strain and structural disorder. Previous work [8] has suggested the development of defects in the Si regions for sufficiently large thermal mismatch. Thus, Raman mapping was carried out to assess the spatial evolution of the Si peak width and peak intensity (see Fig. 7(a-b)) as well as to examine the presence of disorder induced by processing. For brevity, only a Si region surrounded by B₄C is shown. For the outer

compressive region, the peak width is narrower at 11-14 cm^{-1} , (i.e., less broadening), compared to interior tensile regions which showed peak widths of 20-30 cm^{-1} (see Fig. 7(a)). This result suggested more disorder in the interior tensile regions. Additionally, interior Si regions yielded significantly lower intensity (1,500-6,000 counts) compared to the perimeter regions (10,000-20,000 counts) suggesting increased distortion of the Si crystal in the interior (see Fig. 7(b)). Thus, highly compressive regions are expected to have less structural disorder than highly tensile regions. The observed peak broadening and reduced peak intensity are proposed to be due not only to lattice strain but also to high defect generation, i.e., high structural disorder. TEM analysis of Si phase was undertaken to assess the presence of volume defects in a virgin Si region (taken from a Si lump) and a residual Si region (take from BC-1). Recall that in TEM, defective regions appear dark in contrast against the light background [44].

From Fig. 8(a), it was observed that minimal defectiveness existed in the virgin Si. Only one volume defect could be found in the center of the specimen. On the other hand, the residual Si phase in the reaction bonded ceramic was found to contain a higher concentration of defects (e.g., dislocations and point defects) as seen in Fig. 8(b). Lattice strain due to thermal mismatch led to lattice disorder and some level of defect generation. Because only a finite amount of tensile strain energy can be stored in the lattice, defect generation allows strain relaxation. It would be anticipated that the level of defectiveness would ideally scale with the level of thermal mismatch, suggesting that a higher defect density should prevail in BC ceramics than BSC or SC ceramics.

Additionally, boron (B) and carbon (C) in the starting powder can dissolve into molten Si during processing leading to residual stress and/or structural disorder. Doping Si with smaller atoms, such as B, results in lattice contraction due to substitution, leading to tensile stresses [45-

49]. Based on large tensile stresses and disorder observed in interior regions of the Si, increased dopant concentrations would exist primarily in interior regions of the Si. Dopant material (B and/or C) in perimeter regions would likely form reaction phases ($B_{12}(B,C,Si)_3$ or SiC) on the boundary of carbide phases [17], leaving remaining dopant concentrated in the interior regions of the residual Si phase. P-type dopants, like B, have also been reported to cause asymmetry in the Si peak and broadening towards higher wavenumbers [19,50,51], similar to that shown in Fig. 2. Additionally, B doping can cause decreased signal intensity [52]. Although, little or no B was detected using energy dispersive spectroscopy (EDS), future studies utilizing compositional analyses which are more sensitive to low concentrations of light elements is warranted.

4.3 Mechanical Properties

The average residual stress values in Si, determined using this Raman technique, were compared with the mechanical properties, such as hardness and uniaxial compressive strength, of the composites to determine a link between microstructure (i.e., residual stress) and properties. It is seen from Fig. 9 that compressive strength and hardness are highest when the average residual stress state of the Si phase was highly compressive. As the average residual stress value became increasingly tensile, the mechanical properties were observed to decrease. This observation is consistent with some previous works on brittle materials such as glasses [53] where the residual compressive stress yielded an increase in hardness, and the residual tensile stress resulted in lower hardness values. This result is attributed to the fact that residual compression resists against the indentation loading whereas the residual tension promotes easy penetration and fracture. For uniaxial compressive strength, a similar trend was observed. Greater compressive residual stresses yielded greater fracture strength. At higher strain rates this increase was even steeper.

Recall that materials with increased vol.% of B_4C have greater residual compressive stress than those with equal vol.% SiC because of greater thermal mismatch with Si. Also, materials with low Si content and correspondingly small pockets of Si develop high levels of uniform compressive stresses. As the Si vol.% increased, large irregular pockets developed with interior tension and lower average compression levels. Thus, an ideal reaction bonded ceramic would be B_4C -based with low vol. % Si to maximize beneficial compressive stress.

Clearly, measuring residual stresses using micro Raman spectroscopy at high spatial resolution allows the composition, microstructure and some properties to be described by a single metric, namely residual stress. Such analysis may enable materials engineers to tailor the microstructure and optimize the mechanical performance. Determination of residual stress at high spatial resolution allows assessment of potential fracture initiation sites in a complex microstructure and can be beneficial in accurate modeling of the process and eventually predict microstructural influences on mechanical properties. In the long run, such knowledge can assist in development of improved processing-structure-property relationships.

5. Conclusions

Raman spectroscopy has been effectively used in this investigation to assess residual stress and the level of defectiveness developed in processed multi-phase ceramics. The method provides a convenient route for characterizing local microscale stress heterogeneity at high spatial resolution. It was determined that Si regions smaller than 5 microns in diameter are in a nearly uniform state of compression as predicted by analytical equations. However, the classical formulation breaks down when the particle size is large or highly irregular, which leads to stress gradients and interior tensile stresses. Raman mapping was also shown to provide the ability to extract a bulk, macroscale residual stress value for a given material. The ability to quantify a

microstructure or composition and represent it by a single metric allows links to be developed between processing, microstructure and properties. Lastly, Raman peak broadening and intensity reduction in the Si regions, which are indicative of lattice disorder, have been correlated with processing-induced defects through TEM investigation.

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7. List of Figure Captions

Fig. 1. Scanning electron micrographs of the three types of reaction bonded ceramics, where the starting powders were (a) boron carbide (BC), (b) boron carbide and silicon carbide (BSC), and (c) silicon carbide (SC). Phase constituents in the reaction bonded ceramic microstructure were verified by their characteristic Raman peaks given in (d). In the SEM images, the phases can be distinguished by their light/dark contrast, with B_4C being the darkest grey phase, followed by the residual Si which is medium grey, and with SiC being the lightest (almost white) phase.

Fig. 2. Characteristic Raman peaks for the stress-free and as-processed Si phase.

Fig. 3. Residual stress maps for Si regions of varying size and shape in a BC ceramic composite. The inset displays the color-coding based on both Raman peak position and residual stress value.

Fig. 4. Residual stress maps based on peak shift in Si regions surrounded by (a) B_4C or (b) SiC.

Fig. 5. Raman maps color-coded according to (a) phase and (b) residual stress in Si regions. In the phase maps (a), red represents B_4C , green denotes SiC, and blue indicates Si regions. In the stress maps (b), only the residual Si phase is color-coded, while the other phases are greyed-out. The color-coded legend at the top indicates stress magnitude.

Fig. 6. The average measured residual stress (red line) in Si regions of various reaction bonded ceramics with differing composition given as a function of vol.% (a) B_4C , (b) SiC, and (c) Si. The average measured stress is split into compressive (green line) and tensile (blue line) components. Also shown is the predicted stress (black line) according to Eq. (3).

Fig. 7. Raman maps of (a) peak width and (b) peak intensity for a Si region surrounded by B_4C . The reduced peak intensity and larger peak width in the interior of the Si regions suggest

increased structural disorder.

Fig. 8. Bright-field TEM images showing (a) only one defect in virgin Si sample and (b) numerous defects and dislocations in Si of a reaction bonded ceramic (BC-1). Defects are shown in magnified views.

Fig. 9. The influence of average residual stress on indentation hardness (triangle data points) and uniaxial compressive strength (square data points). The blue 'circle' data point was Vickers hardness data taken from Pittari et al. [54].

8. List of Tables

Table 1. Material compositions in the starting powder preforms and final ceramic composites.

Material	Preform Composition (wt.%)			Final Composition (vol.%)			
	B ₄ C	SiC	Diamond	B ₄ C	SiC	Diamond	Si
BC-1	100	0	0	75	8	0	17
BC-D	90	0	10	75	12	4	9
BSC-1	80	20	0	63	27	0	10
BSC-2	80	20	0	63	23	0	14
BSC-3	60	40	0	49	37	0	14
SC-1	0	100	0	0	78	0	22

Table 2. Selected properties for B₄C, SiC, and Si.

Property	B ₄ C	SiC	Si
Elastic Modulus (GPa)	372-480 [1,30-33]	386-460 [26-29]	123-175 [26,35,36]
Poisson's Ratio	0.14-0.21 [1,30,33]	0.14-0.17 [26,28,29,34]	0.22 [26,35]
Average Coefficient of Thermal Expansion, CTE (10 ⁻⁶ /°C)	6.0 [37]	4.6 [34,37-40]	3.6 [37,38,41-43]
Predicted B ₄ C-Si misfit stress (Eq. (2))	+583	—	-583
Predicted SiC-Si misfit stress (Eq. (2))	—	+243	-243
Predicted B ₄ C-SiC misfit stress (Eq. (2))	+563	-563	—

Table 3. Calculated average residual stresses in each phase in the microstructure (Eq. (3)).

Material	Average vol.% of Composition				Residual Stress (MPa)		
	B ₄ C	SiC	Diamond	Si	B ₄ C	SiC	Si
BC-1	75	8	0	17	+604	-495	-545
BC-D	75	12	4	9	+613	-520	-563
BSC-1	63	27	0	10	+524	-393	-496
BSC-2	63	23	0	14	+544	-384	-488
BSC-3	49	37	0	14	+448	-261	-425
SC-1	0	78	0	22	0	+239	-239

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9