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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 B_4C-SiC-Si ceramic composites using Raman spectroscopy. Unlike traditional methods to detect residual stresses (e.g., X-ray diffraction) which provide average values of stress over the entire specimen surface, Raman peak-shift analysis provides residual stress distributions within the microstructure at high spatial resolution. While 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 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 TEM analysis. Raman spectroscopic mapping was also used to compute an average macroscale residual stress value for a given material composition allowing links to be drawn between processing, microstructure and properties. The average residual stress within the microstructure was found to correlate well with the estimates based on volume fraction of the constituents and material properties.

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 °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

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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 B_4C 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) B_4C powder (BC ceramic), (ii) B_4C-SiC powders (BSC ceramic), and (iii) SiC powder (SC ceramic). Two types of BC ceramics were assessed: one contained only B_4C 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 B_4C 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 and 1200 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.

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

Material	Preform Composition (wt %)			Final Composition (vol%)			
	B_4C	SiC	Diamond	B_4C	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

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]:

$$\sigma_{Si} = -250\ (\Delta w)\{\mathrm{MPa}\} \tag{1}$$

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).

2.4. 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 × 3.4 × 5.0 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 5×10^{-4} 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.