Mechanical Properties and Residual Stresses in ZrB₂-SiC Spark Plasma Sintered Ceramic Composites

R. Stadelmann¹, M. Lugovy², N. Orlovskaya^{1*}, P. Mchaffey³, M. Radovic³, V. M. Sglavo⁴, S. Grasso⁵, M. J. Reece⁵

1. University of Central Florida, Department of Mechanical, Materials & Aerospace Engineering, Orlando, FL USA

2. Institute for Problems of Materials Science, Kiev, Ukraine

3. Texas A & M University, Mechanical Engineering, College Station, TX USA

4. University of Trento, Department of Materials Engineering and Industrial Technologies, Trento, Italy

5. Queen Mary University of London, School of Engineering and Material Science, London, UK

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*Corresponding Author: Dr. Nina Orlovskaya
University of Central Floirda
4000 Central Florida Blvd.
Orlando, FL 32816
Phone number: (407) 823-5770
Fax number: (407) 823-0208
Email address: Nina.orlovskaya@ucf.edu

Abstract

ZrB₂-17vol%SiC, ZrB₂-32vol%SiC, and ZrB₂-45vol%SiC ultra-high temperature particulate ceramic composites were sintered using Spark Plasma Sintering (SPS). The mechanical performance of the ZrB₂-SiC composites was investigated using 4-point bending to determine their instantaneous flexural strength and fracture toughness. Resonant Ultrasound Spectroscopy was used to determine the Young's, shear, and bulk moduli as well as Poisson's ratio of all examined composites. The distribution of thermal residual stresses and the effect of applied external load on their re-distribution was studied using micro-Raman spectroscopy. Piezospectroscopic coefficients were determined for all three ZrB₂-SiC ceramic composites and their experimentally obtained values were compared with the piezospectroscopic coefficients

both published in the literature and calculated theoretically. Finally an attempt was made to evaluate the redistribution of thermal residual stresses under external applied stress in order to estimate their contribution to the mechanical behavior of the material.

Introduction:

The leading edges and nose cones of hypersonic vehicles experience aerodynamic heating loads resulting in a very high temperature gradient within the short distance from the surface to the center of the edge or nose cone [1, 2]. The surface temperature in the stagnation region of sharp leading edges can potentially exceed 2000°C (3632°F). Few materials can survive extended periods of time at these temperatures and retain their dimensional structural integrity in an aggressive oxidizing environments [3, 4]. ZrB₂ based Ultra High Temperature Ceramics (UHTCs) with high melting temperatures and large thermal conductivities are very promising candidates for the protection of sharp edges and are capable of maintaining their sleek shapes without significant deformation or melting. Based on their unique combination of properties, ZrB₂ based ceramics are prime candidates for use in the extreme environments associated with hypersonic flight, atmosphere re-entry, and rocket propulsion. In order to improve the oxidation resistance of ZrB₂, SiC is added as a second phase which forms a silica film which is stable in oxidizing environments on the surface of the composites to protect it from further oxidation.

While ZrB₂-SiC ceramic composites exhibit superior properties for ultra-high temperature applications, the brittleness of the composites is a significant drawback in applications where a sufficiently high mechanical performance and reliability is required. One of the feasible ways to increase the composite's toughness in the temperature range lower than sintering temperature is to design an optimum distribution of thermal residual stresses, which originate due to mismatch of coefficients of thermal expansion (CTE) and Young's moduli

between ZrB_2 and SiC phases. Residual stresses that results from thermal manufacturing processes are unavoidable in processed ceramics and arise due to anisotropy in their thermo-mechanical properties and different thermal expansion of the constituents. Thus, better control of the mechanical behavior and reliability of ZrB_2 -SiC ceramics can be obtained through design and measurements of residual stresses and their redistribution during thermal cycling.

For successful design of a composite with respect to the residual stress distribution understanding the evolution of these stresses in the composites is a prime requirement. To control the mechanical behavior and reliability of components made out of ZrB_2 -SiC composites, redistribution of the residual stresses also needs to be characterized and understood. Therefore, the evolution of residual stresses, their redistribution as a function of applied stress, as well as the characterization of the residual stresses itself are critical issues in the design and operation of ZrB_2 -SiC composites. The appearance of residual microstresses in the as-processed ZrB_2 -SiC composite is explained by the mismatch in Young's moduli (E) and CTE (α) between ZrB_2 ($E=520$ GPa, $\alpha= 7.49 \times 10^{-6} \text{ K}^{-1}$) [6, 7] and 6H-SiC ($E= 410$ GPa, $\alpha=5.07 \times 10^{-6} \text{ K}^{-1}$)[5, 6], as well as the difference between room temperature (20°C) and the sintering temperature (typically at $\sim 1950^\circ\text{C}$) of the composite [8]. The cooling of the composite from the sintering temperature will induce a uniform compressive stress within the SiC grains and the radial and tangential stresses within ZrB_2 -SiC interface [9]. When modeling multiphase particle reinforced composites, residual microstresses in the matrix and inclusions (different phases) can be a-priori estimated. However, experimental determination of these microstresses as a function of microstructural parameters would allow not only a better assessment of stress state in a particular composite to be better, but also allow design of the composites with specific properties to suit target applications.

Raman spectroscopy is a powerful tool for study of various vibrational modes, electronic transitions, and residual stresses in solids [10, 11]. In recent years the method to analyze stresses in ceramics using piezospectroscopy techniques, has been developed. It is based on the fact that in crystalline materials the atomic vibrational frequencies depend on the interatomic force constant [12]. In strain-free (stress-free) crystalline materials, interatomic force constants as well as the vibrational frequencies correspond to the equilibrium atomic spacing. Residual stress causes a residual strain, which in turn changes the equilibrium atomic spacing within a material and thus the interatomic force constants, bond length; and the force constants either increase or decrease compared to the equilibrium values. As a results, Raman scattering wavenumbers from solids are perturbed by elastic strain and this fact can be used as a tool for the non-destructive analysis of stress and strain. The optics of the Raman microprobe define both the lateral spatial resolution of the piezospectroscopic measurements and the depth in the material from which the spectra are collected. The depth of resolution strongly depends on the depth of field of the optics and the details of optical scattering within the probed volume of the sample [13, 14]. Both lateral resolution and penetration depth of the laser beam are strongly wavelength-dependent [15-17] and determine the analyzed volume of the subsurface material within which the residual stresses varies. Depending on the laser wavelength and the type of material studied, the penetration depth can vary from tens of nanometers to several millimeters [18] and therefore, if the penetration depth is significant, the larger volume of the strained structure that can be sampled [19]. Techniques have been developed to enable the calibration of the penetration depth, thus allowing the probed volume both as a function of laser wavenumber used in the measurements and the properties of the material to be varied [20, 21]. The piezospectroscopy technique was

successfully applied to carbon [22, 23], Si [24, 25], Si₃N₄ [26, 27], SiC [28, 29], Al₂O₃ [30], LaCoO₃ [10], LaGaO₃ [31], ZrO₂ [32-34], GaN [35] and other ceramic materials.

The goal of this paper is to perform the measurements, and study the distribution and re-distribution of residual stresses in SiC grains as well as their effect on the mechanical properties of ZrB₂-17, 32, and 45 vol% SiC ceramic composites using micro-Raman piezospectroscopy. By knowing the localized stress distribution in the SiC, it might be possible to calculate the components of thermal residual stresses and their redistribution in the ZrB₂ matrix phase of the composites. The paper consists of the following sections: 1) Sintering of ZrB₂-SiC ceramic composites by SPS; 2) Determination of piezospectroscopic coefficients for the 966cm⁻¹ FLO Raman active peak of 6H-SiC by *in-situ* bending technique; 3) Estimation of statistical distribution of thermal residual stresses in SiC grains of three ZrB₂-17, 32, and 45 vol% SiC ceramic composites; and 4) Evaluation of mechanical properties of ZrB₂-SiC ceramic composites.

Experimental procedure

1. Ceramic processing

Spark Plasma Sintering (SPS) was used to process the ZrB₂- 17, 32, 45 vol% SiC composites. Three batches were prepared by weighing the ZrB₂ powder (H.C. Starck-ZrB₂ Grade B) and the SiC powder (H.C. Starck- Alpha -SiC Grade UF-10) in appropriate proportions, and mixing them together in a plastic bottle, using ZrO₂-Y₂O₃ balls and acetone as a milling media. After 48 hours of milling, the batches were dried up and sieved to break up the agglomerates. The sieved powders were loaded in the graphite die, using the graphite foil as an intermediate

layer between the die and powder. The ZrB_2 -17, 32, and 45 vol% SiC samples were sintered (using a SPS machine FCT HPD 25; FCT Systeme GmbH, Rauenstein, Germany), at 1950°C, 50 MPa, 100°C/min heating and cooling rate, and dwell time of 15 minutes. After grinding/removal the graphite foil from the surface of the sintered samples, the density of the samples was determined using the liquid immersion technique.

2. Microstructural and Fractography analysis

Scanning electron microscope (Zeiss-SEM) was used for the analysis of fracture surfaces of the ZrB_2 -17, 32, and 45 vol% SiC bars after mechanical testing. Backscattered SEM images (Using a Tescan Vega SEM), were used to determine the near-neighbor distance between SiC grains. This was done by analyzing the micrographs using the Adobe Photoshop software; 100 measurements were made to obtain a statistical data set.

3. Micro-Raman spectroscopy

3.1 Micro-Raman spectrometer set-up: A Renishaw in-Via micro-Raman spectrometer system was used to study the vibrational spectra of the SiC, ZrB_2 -SiC (17, 32, and 45 vol%) ceramic composites. The Raman microscope system comprises a laser (532 nm silicon laser) to excite the sample, a single spectrograph fitted with an edge filter, and an optical microscope (a Leica microscope with a motorized XYZ mapping stage) rigidly mounted and optically coupled to the spectrometer [36]. The maximum power of the laser is 100mW, and 50% and 100% laser powers was used for measurements [37]. The average collection time for a single spectrum was 200s per

point. The incident and scattered beams were focused with a microscope using a 100x objective lens, which produced a laser spot diameter as low as 1–2 μm [37]. Spectral resolution of Renishaw in-Via micro-Raman spectrometer system is $\sim 0.1\text{ cm}^{-1}$. Such high resolution allows to determine peak position with required accuracy. All measurements were performed at room temperature. Before the measurements, the spectrometer was calibrated with a Si standard calibration source and using the Si band position at 520.3 cm^{-1} . The stage has high resolution positioning of 100 nm in X, Y, and Z directions.

3.2 Determination of laser penetration depth: To estimate the laser penetration depth, wedge samples were produced using 4mmx1.5mmx20mm bar samples of both pure SiC, and ZrB₂-17, 32, and 45 vol% SiC ceramic composites. The bar was mounted in an epoxy mold at a 5° angle (Figure 1), then covered with epoxy. Once hardened, the bar was ground to create a wedge sample as shown in Figure 1. To ensure that the tip of wedge was as thin as possible the sample length was measured in 30 minute interval while using 75, 45, and 30 μm diamond discs for grinding. Once the sample length began to decrease, it was assumed that, the thinnest possible wedge tip had been reached. The wedge sample surface was then further polished using 9, 3, and 1 μm diamond suspensions. The measurements of the laser penetration depth in the samples were performed using the following experimental set up of the Renishaw Raman spectrometer system: 100x objective lens were used to focus the laser beam of 50 or 100% available laser power during 15 to 60 secs exposure time. Spectra were acquired starting from the wedge tip, where the thickness of the sample was minimal, along the central line of the sample. In the first 500 μm from the wedge tip the spectra were acquired every 20 μm . After 500 μm , the step was changed to 50 μm . After the spectra were collected, the samples were removed from the epoxy and the

thickness versus distance from the wedge tip was measured using optical microscopy. It was determined that the thinnest section of the samples varied in the range of 20 μm from one side and increased to 1,500 μm on the other side. The normalized area of the Raman peaks were plotted as a function of sample thickness in order to determine the thickness of the wedge sample where the intensity of the Raman peak reached the maximum value, as this is an indication of the laser penetration depth of that material. In our experiments, the thinnest portion of the sample at the wedge tip was $\sim 20\mu\text{m}$ and for the spectrometer set up no difference in the intensity of the collected Raman peak as a function of sample's thickness was observed. Thus, it was concluded that the laser penetration depth was less than $20\mu\text{m}$ and could not be explicitly determined.

3.3 *In-situ* 3-point bending device: A miniature 3 point bending stage fitted below the objective lens of the optical microscope was used to apply load to the specimens [38]. The stage was designed so that the surface of the sample's under tension was exposed to the laser beam and, therefore, the Raman spectra were collected from the surface under tension. Optical axis of objective lenses on the optical microscope coincides with longitudinal axis of pushing bar of *in-situ* 3-point bending device. Therefore, measurement locations always lie on the line of maximum stress. The maximum tensile stress exist on the surface under tension and it linearly decreases toward the neutral axis of the bent sample. As the Raman spectra were collected from the subsurface volume of the sample within a finite depth, the position of the collected Raman peak is, in fact, an average peak position for the volume because of the stress distribution inside the volume. Therefore the volume of the probed material should be estimated by measuring the laser penetration depth. From measurements of the penetration depth in our experiments we can only conclude that it was less than $20\mu\text{m}$, however since the overall thickness of the samples used in *in-situ* bending experiments was 1.5mm with neutral axis location at $750\mu\text{m}$ away from

the tensile surface, one can conclude that any variations in tensile stresses within the depth of probed volume can be neglected.

3.4 Determination of piezospectroscopic coefficients: The internal/thermal residual stresses in the material was determined from Raman piezospectroscopy data using the linear expression below [33, 39, 40]:

$$\Delta\nu = \Pi < \sigma > \quad (1)$$

where $\Delta\nu$ is the difference in Raman active peak positions of the stressed material and the stress-free material, Π is the average piezospectroscopic coefficient for the material, and $<\sigma>$ is the mean or average stress in the material. A predetermined stress was applied using the *in-situ* 3-point bending device and the corresponding shift, $\Delta\nu$, of the Raman peak was measured. Then, the average piezospectroscopic coefficient was calculated using Eqn (2):

$$\Pi = 3 \frac{\partial(\Delta\nu)}{\partial\sigma} \quad (2)$$

where the derivative $\frac{\partial(\Delta\nu)}{\partial\sigma}$ is the slope of the change in Raman peak position as a function of applied stress. As the data collected from the surface under uniaxial tension was used for the calculation of piezospectroscopic coefficients, a factor 3 was used in the Eqn. (2), since the piezospectroscopic coefficient is typically calculated for hydrostatic stress state.

The average piezospectroscopic coefficients were determined from calibration measurements made separately for pure SiC, ZrB₂-17, 32, and 45 vol% SiC ceramic composites using 5X and 50X objective lenses on the optical microscope. The first set of measurements, labelled 5X, were collected using a Leica 5X lens, with a 15mm working distance and a laser spot diameter of ~20 μ m. The Raman spectra were collected using static scan setting, 50% laser

power, and 50 second exposure time. To find the piezospectroscopic coefficient a 3-point bending device was used to apply loads to the specimens, as described by Fitt [38]. The measurements were made by keeping the selected spot constant throughout the entire loading of the sample. Stresses were applied between 0-300MPa at 50MPa intervals, with collection of Raman spectra at each step. To gather statistically representative results, 10 separate loadings were conducted, and then for each stress the average peak position was determined. The second set of measurements, labelled 50X, were collected using a Leica 50x lens, with a 13mm working distance and laser spot diameter of $\sim 2\mu\text{m}$. The Raman spectra were collected using a static scan setting, 50% laser power, and 50 second exposure time. The same 3-point bending device was used to apply a load to the sample. The applied stresses were 0-300MPa with a 100MPa step size. For each applied stress 100 different random spots were selected to collect the Raman spectra from.

4. Mechanical properties

The Young's, bulk, and shear moduli along with the Poisson's ratio of the materials were measured at room temperature using a Resonant Ultrasound Spectroscopy (RUS). RUS is a highly accurate method for determining the elastic properties from the resonant spectra of a sample of known mass, geometry, and dimensions [41-44]. The composite pellets of 20 mm in diameter and 2-3 mm thick were placed on 3 transducers of which one of them was sending out an ultrasonic waves at sweeping frequency and the other two transducers recorded the natural frequencies at which the sample was vibrating. For determining the elastic moduli of the examined materials from resonant spectra, it was assumed that the composite pellets were isotropic, and thus, only two elastic constants, i.e., C_{11} and C_{44} are required. From the known sample dimensions, density, and a set of "guessed" elastic constants C_{11} , and C_{44} , the first 40

resonant frequencies were calculated for each sample. A multidimensional software Quasar RuSpec (Magnaflux Quasar Systems, Albuquerque, NM) that iteratively minimizes error between the measured and calculated resonant frequencies by changing the initially “guessed” elastic constants, was used to determine elastic constants for the set of measured resonant frequencies of the sample. The elastic constants C_{11} and C_{44} were further used to calculate Young’s, shear and bulk moduli and Poisson’s ratio of the composite samples. It is worth noting here that the fitting error, i.e. the root-mean-square (RMS) error between the measured and calculated resonant frequencies, never exceeded 0.3% for all of the tested samples.

Bars with dimensions of 2x2.5x25mm were machined out of the SPS samples by Prematech Advanced Ceramics, MA. Flexure strength was measured using a four-point test technique in accordance with the EN843-1 standard. Five samples were used for room temperature testing for each composition. The crosshead speed was set to 0.5mm/min.

Fracture toughness was measured using the Single Edge V Notch Beam (SEVNB) technique in accordance with the CEN/TS 14425-5 standard. A single notch was made on the 2 mm side of the 2x2.5x25mm bar as near to the center as possible with a depth between 20 to 40 % of the total depth of the bar, since it was shown that within this range the depth of the notch has no influence on the measured K_{Ic} values [45]. A diamond saw was used to make the initial 0.5 mm depth notch, after that the final 1 to 1.5 mm depth notch with $\sim 45\mu\text{m}$ tip radius was produced by manually cutting using the razor blade with 15 and then 3 μm diamond paste deposited. Five samples were tested at room temperature with the crosshead speed of 0.5mm/min.

Results & discussion

1. Shrinkage of ZrB₂-SiC ceramics during SPS and resulting microstructure

Figure 2 shows the shrinkage of the ZrB₂-SiC ceramics during spark plasma sintering together with the pressure profile and temperature profiles, as a function of sintering time. The sample was heated from 400°C to the sintering temperature of 1950°C in 15 min, then dwelled at 1950°C for 15 min, and then cooled down back to 400°C in 15 min. A pressure of 50MPa was applied during the heating, when the temperature was at 1000°C, held constant after that for the remainder of the run until the temperature during cooling reached 1000°C, then the pressure was gradually removed. The highest shrinkage rate was at 1500°C. All three ZrB₂-17, 32, and 45 vol% SiC composites showed the same shrinkage behavior. The two plots for ZrB₂-32 and 45 vol% SiC compositions were completely coincided and can not be distinguished on Figure 2, but the ZrB₂-17vol% SiC showed slightly different behavior. The difference might be due to different weight of powder placed in the graphite die for sintering.

The microstructure of three ZrB₂-SiC ceramic composites is shown in Figure 3. The SiC grains are homogeneously distributed in the ZrB₂. The sintered ceramic composites have a porosity of less than 4% [8]. The measured grain sizes of the SiC are $\sim 1.48 \pm 1.0 \mu\text{m}$, $1.83 \pm 1.4 \mu\text{m}$, and $2.12 \pm 1.48 \mu\text{m}$ for ZrB₂-17vol%SiC, ZrB₂-32vol%SiC, and ZrB₂-45vol%SiC ceramic composites respectively [8]. While the size of ZrB₂ grains is about 5-7 μm for ZrB₂-17vol%SiC ceramics(Figure 3A). The ZrB₂ grain size decreased to 2-3 μm for the ZrB₂-32vol%SiC and for ZrB₂-45vol%SiC composites.

2. Determination of piezospectroscopic coefficients of 6H-SiC using *in-situ* Raman 3-point bending

In order to calculate the piezospectroscopic coefficients for both pure SiC and for ZrB₂-17, 32, and 45vol%SiC ceramic composites the measurements of the FLO 6H-SiC peak position as a function of applied uniaxial stress were performed using an *in-situ* 3-point bending device as shown in Figure 4 and described in more details in the experimental section. The peak shifts to lower wavenumbers as the applied stress increases to 300 MPa, indicating the presence of tensile stresses in the SiC grains on the surface of the samples. While the position of the FLO SiC peak is a function of the ceramic compositions, the calculated slope for all four materials are similar. The slopes of the four plots are equal to the derivative $\frac{\partial(\Delta\nu)}{\partial\sigma}$, where $\Delta\nu = \nu - \nu_0$, where ν_0 is the peak position for zero applied stress and ν is the peak position for applied stress. The piezospectroscopic coefficients measured using the four different ceramic compositions are presented in Table 1.

Once the piezospectroscopic coefficients are known, the average thermal residual stresses, σ_r in SiC grains of ceramic composites can easily be calculated by using the following:

$$\sigma_r = \frac{\Delta\nu}{\Pi} \quad (3)$$

For comparison, the theoretical values of the average thermal residual stresses were calculated using Eqn.(4) [39], and the elastic properties of pure ZrB₂ and pure SiC reported in [6]:

$$\sigma_r = -3f_m K^* (\alpha_m - \alpha_p) \Delta T \quad (4)$$

where f_m is the volume fraction of matrix phase in the composite, K^* is the effective bulk modulus defined in Eqn. (5), α is the CTE, ΔT is the temperature change between the sintering temperature and room temperature ($\Delta T = -1930^\circ\text{C}$). The equation for the effective bulk modulus is expressed below:

$$K^* = \frac{K_m K_p}{K_p f_p + K_p f_p n_m + K_p n_m + K_m f_m n_m} \quad (5)$$

where K^* is the effective bulk modulus, K is the bulk modulus of the phases, and f_m and f_p are the volume fractions of the matrix and strengthening phases in the composite, respectively, n_m is defined in Eqn. (6):

$$n_m = \frac{2(1 - 2v_m)}{1 + v_m} \quad (6)$$

Where v_m is the Poisson's ratio of the matrix phase. For experimental values of average thermal residual stresses in ZrB₂-17, 32, and 45vol%SiC the four different piezospectroscopic coefficients were used. The results of such calculations are shown in Table 2. The best fit between experimental results and theoretically calculated values exists for the case when the piezospectroscopic coefficient of the specific composition was used to determine the experimental value of thermal residual stresses. It means that $\Pi_{ZrB_2-17vol\%SiC}$ coefficient was used to determine the experimental value of thermal residual stresses in ZrB₂-17vol%SiC, $\Pi_{ZrB_2-32vol\%SiC}$ was used for ZrB₂-32vol%SiC, and $\Pi_{ZrB_2-45vol\%SiC}$ was used for ZrB₂-45vol%SiC. The corresponding experimental and theoretical values of thermal residual stresses along with their distribution are shown in Figure 5. For the determination of the statistical distribution of thermal residual stresses, the Raman spectra were collected from 100 randomly chosen single SiC grains. As the SiC grain size was on the average about 2μm, a laser spot of about 2μm (50X objective lens) used. The statistical distribution of the stresses is shown in Figure 5B, where the absolute values were taken to make the thermal residual stresses positive. The plots are presented as a normal distribution with the average values and standard deviations being equal to our experimental values (Figure 5A), with the absolute average values of the

thermal residual stresses being the highest for ZrB₂-17vol%SiC and the lowest one for ZrB₂-45vol%SiC.

Figure 6 shows 2D and line maps of the thermal residual stresses for selected areas at the surface of the ZrB₂-SiC ceramic composites. The zero-stress 966cm⁻¹ FLO SiC peak position and the measured peak position of each point were used in the map creation. For each composition the piezospectroscopic coefficient obtained for this composition was used to calculate the thermal residual stresses. As the volume percentage of SiC phase increases in the ZrB₂-SiC composites the average values of the thermal residual stresses decreases.

3. Statistical distribution of thermal residual stress in SiC grains under applied load

In addition to measurements of thermal residual stresses where no external load was applied, experiments were performed to determine if and how an applied stress affects the statistical distribution of thermal residual stresses in ZrB₂-SiC composites. In order to be able to estimate the effect of external stress, the ZrB₂-SiC ceramic composites were loaded to 200 MPa and further to 300 MPa using 3-point bending and, while under constant stress, Raman spectra were collected from 100 randomly chosen SiC grains. The stresses were calculated using corresponding piezospectroscopic coefficients for each of the three ZrB₂-17, 32, and 45 vol% SiC composites. The calculated stresses from the shift of the Raman peak contains two stress components – one contribution from the thermal residual stresses and other from the applied external load. Therefore, to determine the distribution of thermal residual stresses both as a

function of the composition of ceramic and as a function of applied stress, the corresponding values of applied stress were subtracted from the stress calculated by Raman piezospectroscopy. The corresponding distributions of thermal residual stresses both under no stress and under 200 MPa and 300 MPa applied stress for three ZrB₂-SiC ceramic composites are shown in Figure 7 and Table 3, no noticeable difference can be found between the distributions of stresses in each composite at different applied stresses. Thus the conclusion can be made that there is no redistribution of thermal residual stresses under applied load for each composition, when the applied stress is up to 300 MPa in tension.

4. Mechanical properties of ZrB₂-SiC ceramics

The elastic properties of ZrB₂-17, 32, and 45vol%SiC ceramic composites, measured Resonant Ultrasonic Spectroscopy (RUS) are shown in Figure 8. The Young's modulus decreases with increasing content of SiC phase as shown in Figure 8A. This decrease is consistent with the rule of mixture as, for example, the Young's Modulus of ZrB₂ larger (520 GPa [6]) than that of the 6H-SiC phase (410 GPa [6]). At the same time, the Poisson's ratio increases slightly with increasing the SiC content, because of increasing amount of the more compliant SiC phase in the particulate composite shown in Figure 8A. The bulk and shear moduli as a function of volume percent of SiC is shown in Figure 8B. It shows that as the volume percent of SiC increases, the bulk and shear moduli values decrease. The measured properties correspond well with the previously reported data on similar composites [46-53].

The instantaneous strength and fracture toughness of ZrB₂-SiC ceramic composites are shown in Figure 9. The 4-point bending strength values are shown in Figure 9A as a function of the composites' composition. The strength of the ZrB₂-17vol%SiC and ZrB₂-32vol%SiC

composites are equal to 585 ± 88 MPa, and 552 ± 59 MPa, respectively, whereas the ZrB₂-45vol%SiC composite shows a significant improvement in strength, as the measured values are equal to 751 ± 81 MPa. The fracture toughness of ZrB₂-SiC ceramic composites is shown in Figure 9B as a function of composition, and the measured values are equal to 2.54 ± 0.29 MPa*m^{1/2}, 2.64 ± 0.27 MPa*m^{1/2}, and 2.90 ± 0.34 MPa*m^{1/2} for ZrB₂-17, 32, and 45vol%SiC respectively. Thus, a slight increase in fracture toughness is observed when the SiC phase content is increased. As ZrB₂-SiC ceramic composites are brittle materials, the strength of ZrB₂-SiC could be described by the following well known equation:

$$\sigma_s = \frac{K_{IC}}{\psi\sqrt{a}} \quad (7)$$

where K_{IC} is the fracture toughness of the material; ψ is the geometrical coefficient dependent on the shape of the critical defect when $\psi=1.264$ for the assumed to be semi- circular surface defect; and a is a radius of the critical surface defect that serves as the fracture origin of failure. The size of the critical defect a could be both evaluated using Eqn. (7), or it could be directly measured using the size of the fracture origin identified from the fracture surface by SEM. The calculated values were equal to 12 μ m, 14 μ m, and 9 μ m using Eqn. (7), while measured values using fractography results (Figure 10) were equal to 9.62 μ m, 11.44 μ m, and 9.75 μ m (Figure 10B, D, and F) for ZrB₂-17, 32, and 45vol%SiC respectively, thus showing the excellent agreement between the estimated size of critical defect in ZrB₂-SiC ceramic composites and measured values. It was established in [30, 54] that when a crack propagates in two phase composites, an increase or decrease in fracture toughness could be achieved depending on the values of thermal effective residual stresses acting in the material [30, 54] . In our work we use the following Eqn:

$$\Delta K_{1c} = 2\sigma_{eff} \sqrt{\left(\frac{2(\Delta - d)}{\pi}\right)} \quad (8)$$

where $\Delta K_{1c} = K_{1c} - K_0$ (K_0 is the fracture toughness of the hypothetical matrix material when no residual stress is present, and K_{1c} is the fracture toughness of the particulate composite), σ_{eff} is an effective residual compressive stress components in the ZrB_2 matrix phase (while the average thermal residual stress state in the ZrB_2 matrix is still tensile), Δ is an average near-neighbor distance between SiC grains, and d is the size of SiC grains. The average effective residual stress σ_{eff} in the matrix could be expressed by the following equation:

$$\sigma_{eff} = \sigma_r \left(\frac{\Delta}{d}\right)^{-3} \quad (9)$$

as the compressive component of residual stress in ZrB_2 matrix phase decreases with the third power of the distance from the center of the grain [30]. Thus the Eqn. (8) can be rewritten as:

$$\Delta K_{1c} = 2\sigma_r \left(\frac{\Delta}{d}\right)^{-3} \sqrt{\left(\frac{2(\Delta - d)}{\pi}\right)} \quad (10)$$

and than, the fracture toughness of ZrB_2 -SiC ceramic composites can be represented by:

$$K_{1c} = K_0 + 2\sigma_r \left(\frac{\Delta}{d}\right)^{-3} \sqrt{\left(\frac{2(\Delta - d)}{\pi}\right)} \quad (11)$$

Using Eqn. (11), the fracture toughness of ZrB_2 -SiC ceramic composites can be evaluated and the calculated K_{1c} values can be compared with experimentally measured values in order to validate the proposed model. As most of the parameters in Eqn. (11) can be determined experimentally and unknown K_0 can be found by fitting the data, this model can be used to evaluate the increase in fracture toughness of ZrB_2 -SiC ceramic composite due to presence of thermal residual stresses. Note that σ_r , Δ , and d are all known parameters in Eqn (11) as their values for all three ZrB_2 -SiC compositions were measured and K_0 was determined by fitting the

calculated values of fracture toughness to the fracture toughness measured experimentally. The least-squares method was used to obtain the best fit, where the sum of squared residuals was minimized and the residual is the difference between the measured and calculated (Eqn. (11)) K_{IC} values. The values of Δ , d , and K_0 are listed in Table 4. The calculated K_{IC} values obtained using Egn (11) are shown in Figure 9B. As both σ_r , Δ , and d all have a statistical distribution of their values, as do the experimentally measured K_{IC} values, it is important to perform an error propagation or uncertainty analysis to determine the uncertainty in the calculated K_{IC} values. The standard deviation of calculated K_{IC} value could be determined using the following expression [55]:

$$StDev(K_{IC}) = \sqrt{\left[\frac{\partial K_{IC}}{\partial \sigma_r} * StDev(\sigma_r)\right]^2 + \left[\frac{\partial K_{IC}}{\partial \Delta} * StDev(\Delta)\right]^2 + \left[\frac{\partial K_{IC}}{\partial d} * StDev(d)\right]^2} \quad (12)$$

where $\frac{\partial K_{IC}}{\partial \sigma_r}$, $\frac{\partial K_{IC}}{\partial \Delta}$, and $\frac{\partial K_{IC}}{\partial d}$ are the partial derivatives of K_{IC} (11) with respect to σ_r , Δ , and d , respectively. By calculating the standard deviation of the variables in the parentheses of Egn (12), the uncertainty of the K_{IC} values are shown in Figure 9B using the data for σ_r , Δ , d , and K_0 from Table 4. An excellent match between the measured and calculated fracture toughness of ZrB₂-SiC ceramic composites was found for all examined composite samples, Figure 8B.

Furthermore, the results in Figure 9B and Table 4 were used to evaluate strength of the ZrB₂-SiC ceramic composite using Eqn. (7) and estimate the surface critical defect size, which was assumed to be a constant for each composition. The calculated strength values are shown in Figure 9A. The uncertainty of strength values are also shown in Figure 9A as dotted lines, when the strength is calculated using Egn (7) and uncertainty is determined using the following Eqn. (13) [55]:

$$StDev(\sigma) = \sqrt{\left[\frac{\partial \sigma}{\partial K_{1C}} * StDev(K_{1C}) \right]^2} \quad (13)$$

As one can see from Figure 9A, there is good correlation between the calculated and experimental strength values can be found.

Conclusion

In this study an attempt was made to evaluate the possible redistribution of thermal residual stresses in ZrB₂-SiC ceramic composites under applied bending stress for the first time. For this evaluation, *in-situ* micro-Raman spectroscopy was used to calculate the piezospectroscopic coefficients to estimate the values and distribution of thermal residual stresses as well as to estimate the influence of applied stress on to the distribution of thermal residual stresses in ZrB₂-17, 32, and 45 vol% SiC ceramic composites. A simple model was used to calculate the effect of thermal residual stresses on both the fracture toughness and fracture strength of the ceramic composites. The calculated values of K_{1C} and σ showed very good correlation with experimentally measured values, thus verifying the accuracy of the proposed model.

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Figure 1: Wedge sample schematic (A), anticipated penetration depth (B), optical micrographs of produced wedge samples for ZrB_2 -17vol%SiC (C), ZrB_2 -32vol%SiC (D), and ZrB_2 -45vol%SiC (E) ceramic composites

Figure 2: The pressure, temperature, and shrinkage plots showing the sintering parameters of three ZrB₂-17, 32, and 45vol%SiC ceramic composites by SPS

Figure 3: SEM backscattered micrographs of ZrB_2 -17vol%SiC (A), ZrB_2 -32vol%SiC (B), and ZrB_2 -45vol%SiC (C) ceramic composites, respectively. Dark grains belong to SiC phase, and the light grains belong to ZrB_2 matrix phase

Figure 4: 6H-SiC FLO peak position as a function of applied stress for pure SiC and ZrB₂-17, 32, and 45vol%SiC ceramic composites

Figure 5: Comparison of experimental and calculated average thermal residual stresses (A), and distribution of thermal residual stresses of ZrB₂-17, 32, and 45vol%SiC at 0 MPa applied load (B)

Figure 6: Optical micrographs of ZrB_2 -17vol%SiC (A), ZrB_2 -32vol%SiC (B), and ZrB_2 -45vol%SiC (C), the 2D maps of thermal residual stress in ZrB_2 -17vol%SiC (D), ZrB_2 -32vol%SiC (E), and ZrB_2 -45vol%SiC (F), and line maps along X-Y line of 2D maps for ZrB_2 -17vol%SiC (G), ZrB_2 -32vol%SiC (H), and ZrB_2 -45vol%SiC (I)

Figure 7: Experimentally measured re-distribution of thermal residual stresses as a function of applied tensile stress for (A) ZrB_2 -17vol%SiC, (B) ZrB_2 -32vol%SiC, (C) ZrB_2 -45vol%SiC ceramic composites

Figure 8: Elastic properties: (A) Young's modulus and Poisson's ratio; (B) shear and bulk moduli of ZrB_2 -17, 32, and 45vol%SiC ceramic composites.

Figure 9: 4-point bending strength (A) and fracture toughness (B) of ZrB₂-17, 32, and 45vol%SiC ceramic composites. ●—measured values, ○—estimated values accounting the effect of the thermal residual stresses in SiC grains, the dotted lines are the upper and lower bounds of uncertainty for the calculated values of fracture strength and fracture toughness.

Figure 10: Fractography of ZrB₂-SiC ceramic composites. SEM micrographs of the whole fracture surfaces with areas indicated for locations of possible fracture origins (A, C, E) and the micrographs of the fracture origins (B, D, F) of the ZrB₂-17vol%SiC (A, B); ZrB₂-32vol%SiC (C, D); ZrB₂-45vol%SiC (E, F) tested in 4-point bending.

Anticipated Penetration Experimental Results

1: ZrB₂-17vol%SiC 2: ZrB₂-32vol%SiC 3: ZrB₂-17vol%SiC

A

10μm

B

10μm

C

10μm

● Pure SiC ▲ ZrB2-17vol%SiC ■ ZrB2-32vol%SiC ◆ ZrB2-45vol%SiC

Table 1: Piezospectroscopy coefficients Π of SiC phase measured in pure SiC and three ZrB₂-SiC ceramic composites

#	Composition	Π (GPa ⁻¹ *cm ⁻¹)
1	Pure SiC	-5.94±3.3
2	ZrB ₂ -17vol%SiC	-5.7±3.0
3	ZrB ₂ -32vol%SiC	-6.39±3.5
4	ZrB ₂ -45vol%SiC	-6.06±3.1

Table 2: Calculated values of thermal residual stresses in SiC grains of three ZrB₂-SiC ceramic composites using piezospectroscopic coefficients Π from Table 1 without external applied load

Composition	Thermal Residual Stresses (MPa)					
	Model [39]	Using Π from Table 1				#2,3,4 Composition Dependent
		#1 SiC	#2 ZrB ₂ -17vol%SiC	#3 ZrB ₂ -32vol%SiC	#4 ZrB ₂ -45vol%SiC	
ZrB ₂ -17vol%SiC	956	859±310	895±323	798±288	842±304	895±323
ZrB ₂ -32vol%SiC	748	850±256	885±267	790±238	833±251	790±238
ZrB ₂ -45vol%SiC	582	751±219	783±228	698±204	736±215	736±215

Table 3: Calculated thermal residual stresses in SiC grains of three ZrB₂-SiC ceramic composites as a function of applied bending stress

Composition	Thermal Residual Stress (MPa)		
	$\sigma_{\text{appl}} = 0\text{MPa}$	$\sigma_{\text{appl}} = 200\text{MPa}$	$\sigma_{\text{appl}} = 300\text{MPa}$
ZrB ₂ -17vol%SiC	895±323	872±314	889±274
ZrB ₂ -32vol%SiC	790±238	763±260	865±251
ZrB ₂ -45vol%SiC	736±215	706±225	765±233

Table 4: The summary of the parameters used for the calculation of K_{IC} (Eqn. 11)

Composition	K_{IC}^* (MPa*m ^{1/2})	$d^\dagger$ (μm)	$\Delta^\ddagger$ (μm)	$K_0^\times$ (MPa*m ^{1/2})
ZrB ₂ - 17vol%SiC	2.54±0.29	1.48±1.0	5.36±2.85	2.48
ZrB ₂ - 32vol%SiC	2.64±0.27	1.83±1.4	3.93±1.64	
ZrB ₂ - 45vol%SiC	2.9±0.34	2.12±1.48	3.49±1.54	

* The K_{IC} is an experimentally measured fracture toughness

† d is an average size of SiC grains

‡ Δ is an average distance between SiC grains in ZrB₂-SiC ceramic composites

× K_0 is a fracture toughness of an ideal ZrB₂ matrix material without residual stresses and σ_r values used in the K_{IC} calculation are taken from Table 3 corresponding to the data when $\sigma_{appl}=0$ MPa.