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Mechanical properties of ZrB$_2$ ceramics determined by two laboratories

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Abstract

The mechanical properties for zirconium diboride (ZrB$_2$) were measured at two laboratories and compared. Two billets of ZrB$_2$ were prepared by hot-pressing commercial powder. The relative densities of the billets were >99% and with an average grain size of 5.9 $\pm$ 4.5 μm. Both laboratories prepared American Society for Testing and Materials (ASTM) C1161 B-bars for strength and ASTM C1421 bars with notch configuration A for fracture toughness. Specimens were machined by diamond grinding at the Army Research Laboratory (ARL) and electrical discharge machining (EDM) at Missouri S&T. Strength bars tested at Missouri S&T were polished to a .25 μm finish while the bars were tested as-ground at ARL. Strengths were 473 $\pm$ 79 MPa for the Missouri S&T bars and 438 $\pm$ 68 for the ARL bars while the fracture toughness values were 3.9 $\pm$ .7 MPa•m$^{1/2}$ for the Missouri S&T bars and 4.4 $\pm$ .6 MPa•m$^{1/2}$ for the ARL bars. Vickers hardness was measured by both laboratories over a range of indentation loads. The resulting hardness values were on the low end of previously reported values and were quite different from each other especially at indentation loads ≤20N. The study demonstrated that the properties of materials tested to ASTM standards at different laboratories can be compared directly. In addition, strength and fracture toughness were nearly identical for bars prepared by conventional diamond grinding or EDM.

KEYWORDS
fracture mechanics/toughness, hardness, mechanical properties, strength

1 | INTRODUCTION

The desire to develop vehicles and projectiles that travel at the speed of sound and beyond has been increasing.[1] Materials with melting temperatures of 2000°C and higher, ceramics based on silicon carbide (SiC),[2] and silicon nitride (Si$_3$N$_4$)[3] as well as carbon-carbon (C-C) composites[4] were developed and investigated to handle the aerothermal heating experienced at these velocities. The desire to push velocities into the hypersonic regime now requires the development of materials with

the required oxidation resistance and thermomechanical properties that can handle the higher levels of aerothermal heating (above 2000°C) experienced during hypersonic flight.[5–7] The temperature requirement alone severely limits the available materials. Ultrahigh temperature ceramics (UHTCs) consisting of the carbides and/or borides of hafnium (Hf), zirconium (Zr), titanium (Ti), tantalum (Ta), and niobium (Nb) fall into this category as do composites based on these materials.[8] High-entropy ceramics that are multicomponent ceramic oxides, carbides, nitrides, and borides in solid solution with homogeneous crystalline

phases are also considered potential candidates.[9,10] Many of these materials have been fabricated and examined over the past several decades to determine their potential for use in the extreme environments encountered during hypersonic flight.

Unlike many conventional advanced ceramics that require the use of traditional diamond grinding methods to create test specimens or components many UHTCs conduct electricity at a sufficient level to enable specimens to be fabricated using electrical discharge machining (EDM).[11–13] The purpose of this effort was to determine if the strength and fracture toughness of specimens fabricated using EDM were different than those prepared using conventional diamond grinding methods. Hardness was also measured by both Missouri S&T and Army Research Laboratory (ARL) following the appropriate American Society for Testing and Materials (ASTM) standards.

1.1 | Experimental procedures

Two zirconium diboride (ZrB_2) plates were simultaneously fabricated at Missouri S&T for this effort. Zirconium diboride powders (Grade B, H.C. Starck[*]) were mixed with 1 weight percent each of B_4C (Grade HS, H.C. Starck) and C (phenolic resin, Georgia Pacific Chemicals[†]) and ball milled for 4 h in acetone using ZrB_2 milling media. The powder was rotary evaporated at 70°C then sieved through a 140-mesh sieve. Two billets were fabricated using the powder by hot-pressing (HP50, Thermal Technology) at 2100°C in helium with a pressure of 32 MPa resulting in plates with relative densities greater than 99%. Samples were held at temperature until ram travel stopped, indicating densification had ceased, ∼30 min. The resulting billets were nominally 65-mm square and ground flat with a surface grinder to a thickness of approximately 8 mm. One plate remained at Missouri S&T for specimen preparation, testing, and analysis while the second one was sent to ARL.

Specimens nominally 3 × 4 × 45 mm in size were machined from both billets for flexure strength and chevron notch fracture toughness testing according to ASTM C1161[‡] and ASTM C1421[§], respectively. Conventional diamond grinding, following the procedures for specimen preparation in C1161 and C1421, was used to produce specimens from the ARL billet. The final surface finish on all of these specimens was 400-grit. Specimens

were machined at Missouri S&T using wire EDM (HSS-150, Agie[**]) followed by surface grinding with a 600-grit diamond wheel. One 4 mm surface was then polished to a .25 μm finish using successively finer diamond abrasives. The polished surface was the tensile surface for flexure strength testing.

The flexure strength was determined in four-point flexure on a load frame using a fully articulating fixture having load and support spans of 20 and 40 mm respectively following the procedures in ASTM C1161. The displacement rate for these tests was .5 mm/min. Fracture toughness was determined using the chevron notch configuration "A" according to ASTM C1421. Diamond grinding was used to produce the notch in the specimens from both billets.

Vickers and Knoop hardness values were determined over a range of indentation loads between .1 kg and 10 kg following the procedures in ASTM C1327[††] and C1326[‡‡], respectively. Optical fractography was used to locate and identify the strength-limiting feature in the flexure strength specimens (ASTM C1322[§§]) and to analyze the fracture process in the fracture toughness tests. Scanning electron microscopy (SEM) was also used in the fracture analysis as well as the microstructural analysis.

Grain size measurements were performed on the polished faces of flexure bar pieces after flexure testing. Samples were chemically etched using a 50:50 by volume mixture of potassium hydroxide and sodium hydroxide. The mixture was heated to ∼200°C to form a liquid. Polished samples were pre-heated to the same temperature, dipped into the molten salt mixture, and then immediately moved to boiling water to remove the salt and stop the etching process. Images were taken with a scanning electron microscope (eLine plus, Raith[***]). Grain boundaries were outlined in black, and then image processing software (ImageJ, National Institutes of Health) was used to measure the grain size. Grain size was approximated by fitting each grain to an ellipse with the long axis of the ellipse taken as the grain size.

2 | RESULTS AND DISCUSSION

The microstructure of the hot-pressed ZrB_2 examined is shown in Figure 1. In general, the microstructure had a

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[*] H.C. Stark, Goslar, Germany.

[†] Georgia Pacific Chemicals, Atlanta, GA, U.S.A.

[‡] ASTM C1161 "Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature," ASTM International, West Conshohocken, PA 19428-2959.

[§] ASTM C1421 "Standard Test Methods for Determination of Fracture Toughness of Advanced Ceramics at Ambient Temperature," ASTM International, West Conshohocken, PA 19428-2959.

[**] Lincolnshire, IL, U.S.A.

[††] ASTM C1327 "Standard Test Method for Vickers Indentation Hardness of Advanced Ceramics," ASTM International, West Conshohocken, PA 19428-2959.

[‡‡] ASTM C1326 "Standard Test Method for Knoop Indentation Hardness of Advanced Ceramics," ASTM International, West Conshohocken, PA 19428-2959.

[§§] ASTM C1322 "Standard Practice for Fractography and Characterization of Fracture Origins in Advanced Ceramics," ASTM International, West Conshohocken, PA 19428-2959.
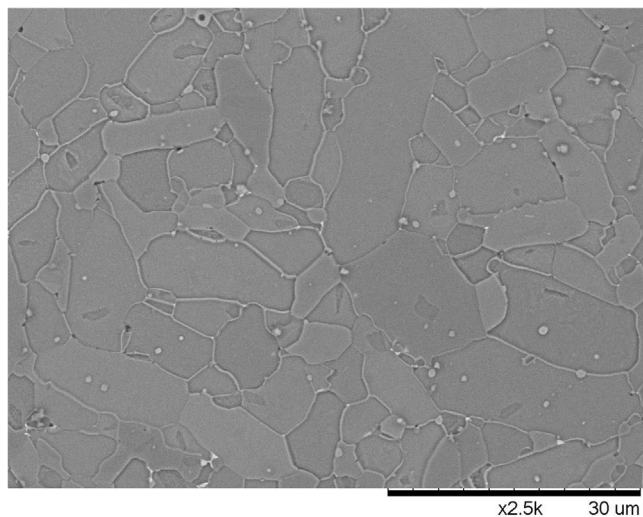
[***] Dortmund, Germany.

FIGURE 1 Representative microstructure of ZrB2 examined in this study.

mixture of equiaxed and elongated grains with a skewed size distribution. The equiaxed grains were typically less than 10 μm in size while the elongated grains had a major axis that was 50%–60% longer than the minor axis. As a result, the overall average grain size was 5.9 $\pm$ 4.5 μm with $d_{10} = 1.6$ μm and $d_{90} = 12.1$ μm.

Figure 2 shows essentially no difference in the surface finish of the specimens prepared by EDM and conventional diamond grinding. The only noticeable difference was on the tensile surface where the ARL specimens had a diamond ground finish while Missouri S&T polished the surface after EDM, Figure 2. EDM enabled more specimens to be cut from the same size plate than conventional diamond grinding. Fifteen specimens (10 flexure and 5 chevron notch) were obtained when EDM was used while only 13 specimens (8 flexure and 5 chevron notch) were able to be machined out of the same size billet using diamond grinding. The difference is the result of the larger kerf associated with the diamond grinding wheels compared to that associated with the wire used in EDM.

The density of both plates was measured independently by both laboratories. The measured densities were essentially the same with the average being 6.08 g/cm^3. Based on the theoretical density of ZrB$_2$ of 6.10 g/cm^3 reported on powder diffraction file card 01 - 075–0964, both billets had >99% relative density. ARL determined the elastic properties of the plate it received using an ultrasound method. The measured elastic modulus was 529 $\pm$ 17 GPa, the shear modulus 231 $\pm$ 7 GPa, and Poisson's ratio .14. The elastic property values are in excellent agreement with previously published values for hot-pressed ZrB$_2$.[14–18]

The average flexure strength and fracture toughness values obtained by the two laboratories along with the pooled data from both sets are shown in Table 1. A Weibull analy-

sis[†††] was performed on the individual strength data sets. The average strengths were 438 $\pm$ 68 MPa for the ARL bars and 473 $\pm$ 79 for the Missouri S&T bars. The slightly higher average strength of the Missouri S&T specimens is most likely due to the tensile surface of these specimens being polished. Because the flexure strengths obtained by both labs were essentially the same, a pooled Weibull analysis was also performed, see Figure 3. The location of the fracture origin was quite distinct when viewed optically and under the SEM, Figure 4. The primary fracture origin in the ARL tested specimens was machining damage from the specimen preparation process. A series of small machining cracks (red arrows in Figure 4B) are apparent on the fracture surface. These cracks linked up to form the critical flaw strength-limiting flaw. An estimated flaw size range of 70–150 μm was calculated for the ARL strength values using fracture mechanics: $a = (\sigma/K_{Ic}Y)^2$ where a is the flaw size; σ is the fracture strength; K_{Ic} the fracture toughness, and Y is the stress intensity shape factor = 1.2. (A Y value of 1.2 was chosen since the flaws tended to have a semicircular shape.[19]). This range of flaw sizes is in excellent agreement with the measured sizes of these critical flaws.

When pooled, the average strength across both sets of strength bars was 458 $\pm$ 77 MPa, which is about 15% higher than previously published values for a hot-pressed ZrB$_2$ that were obtained using the same specimen size and loading configuration.[14,15] Strengths for ZrB$_2$ of 480 MPa,[16] 508 MPa[18], and 565 MPa[17] have been reported, but these values were obtained using the smaller "A" size flexure bar (1.5 $\times$ 2 $\times$ 25 mm) and associated 4-point loading configuration outlined in ASTM C1161. Strength size-scaling, according to ASTM C1683[‡‡‡], of the pooled average flexure strength and Weibull modulus from this study to the smaller specimen dimensions yields a value of 560 MPa. This confirms that some of the previously reported higher strength values[17] were likely due to the testing of a smaller specimens and differences in the loading configuration. Another study on a ZrB$_2$ fabricated by spark plasma sintering also used the smaller "A" size flexure bar, but tests were performed in 3-point loading.[20] These tests yielded a strength value of 450 MPa. While this is comparable to the average pooled strength value in the present study in addition to the smaller specimen size and 3-point loading configuration the material only had a density around 5.8 g/cm^3.
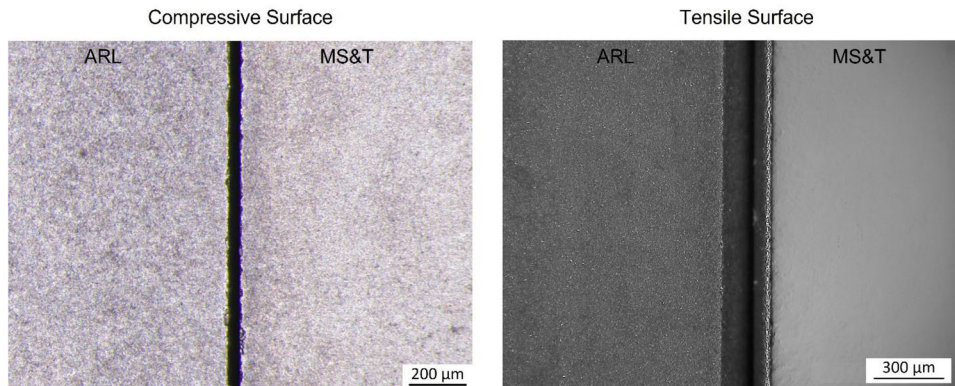
FIGURE 2 Representative images of the compressive and tensile surfaces of the flexure specimens examined.

TABLE 1 Summary of mechanical properties measured

	ARL	MS&T	Pooled
Density (g/cm3)	6.08	6.07	6.08
Flexure Strength (MPa)	438 ± 68 (8)	473 ± 79 (10)	458 ± 77 (18)
Fracture Toughness (MPa√m)	4.4 ± .6 (4)	3.9 ± .7 (6)	4.1 ± .7 (10)

Strength and fracture toughness values are shown with standard deviation, and the number in parentheses is the number of specimens tested.
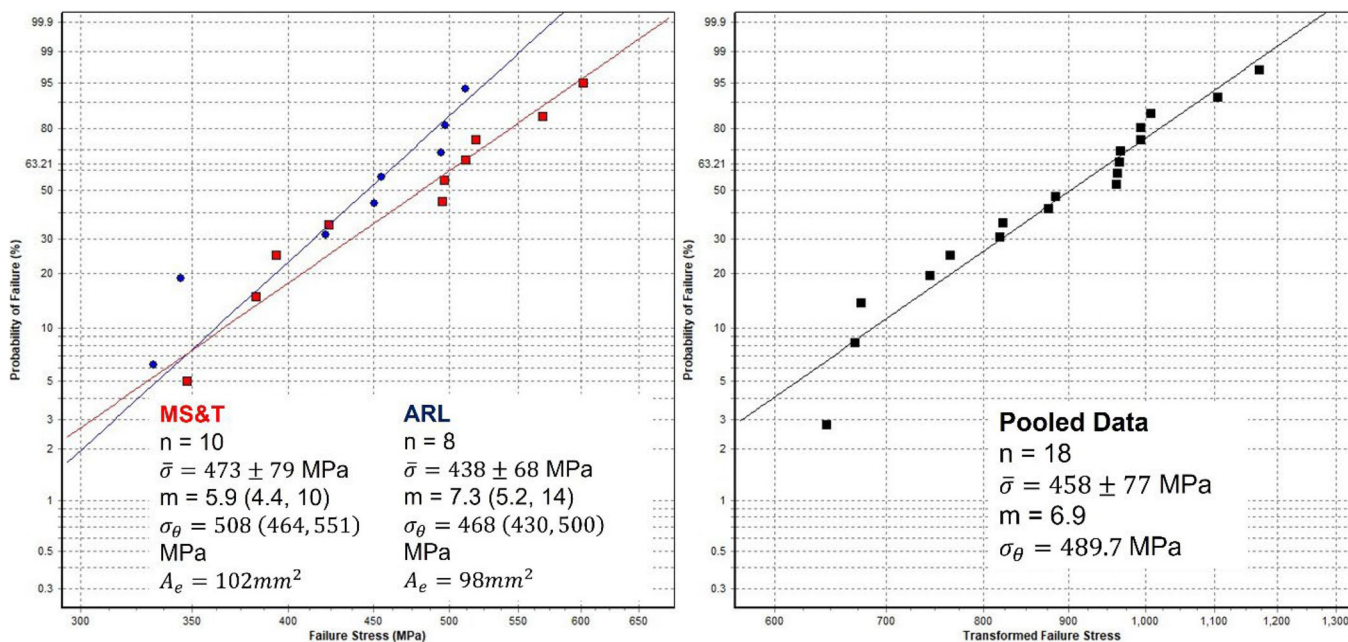

FIGURE 3 Weibull analysis of the individual data sets (left) and the pooled data set (right).

The fracture toughness values were $3.9 \pm .7$ MPa•m$^{1/2}$ at Missouri S&T and $4.4 \pm .6$ MPa•m$^{1/2}$ at ARL, which resulted in a pooled average of $4.1 \pm .7$ MPa•m$^{1/2}$. The fracture toughness of ZrB_2 has been reported to be between 2.6 and 3.8 MPa√m.[15,17,18] The average fracture toughness values from both laboratories are in excellent agreement with each other and are at or slightly above the high end of the previously reported values. This difference may be due to the use of a modified chevron notch method,[2] an indentation fracture strength method[4] and the indentation/crack length method[5] that were respectively used in the previous studies.

The Vickers and Knoop hardness were measured by ARL at loads between .98N (.1 kg) and 98N (10 kg) while

FIGURE 4 (A) Optical image of both halves of the fracture surface. It is very easy to see the location of fracture initiation. (B) Scanning electron microscopy (SEM) image of a typical flaw in the Army Research Laboratory (ARL) specimens prepared using conventional diamond machining. Red arrows highlight multiple machining cracks at the surface which linked up to form the strength-limiting flaw. The red lines outline the general shape of the flaw that has a depth (a) of ~70 μm and width (2c) of ~250 μm. Strength of this specimen was 511 MPa.
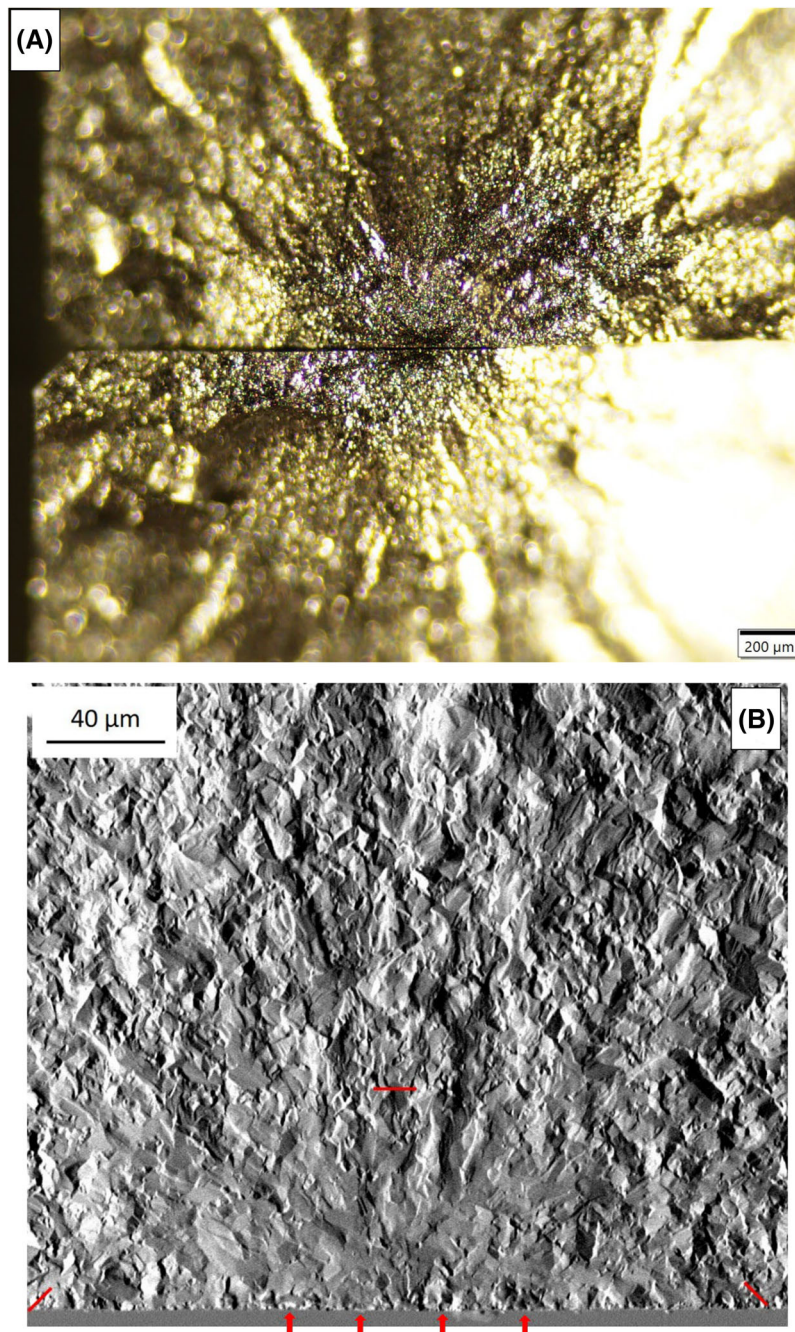
MS&T measured the Vickers hardness between .98N and 19.8N (2 kg). A clear indentation size effect (ISE) was observed in all three sets of hardness data, Figure 5. Although both laboratories obtained similar ISE curve for the Vickers data the MS&T hardness values were consistently higher than the ARL values especially at loads of 20N and lower. Vickers hardness obtained at 9.8N (1 kg) is commonly reported for ZrB_2 with values ranging from 14.6 to 23 GPa. Both of the HV1 values (Missouri S&T: 15.3 ± .5 GPa and ARL: 14.2 ± .2 GPa) are on the lower end of this hardness range. Some of the reasons for the differences between the two laboratories could be: speed of indentation, accuracy of loading, vibrations, indenter shape deviations or even simply differences associated with the operators who performed the measurements. It is unclear why both of these values are on the lower end of the previously reported hardness values, but this could be due to microstructural differences.

Since the flexure strength and fracture toughness values were the essentially the same for both laboratories, it indicates that both machining processes, EDM and conventional diamond machining, can be used with
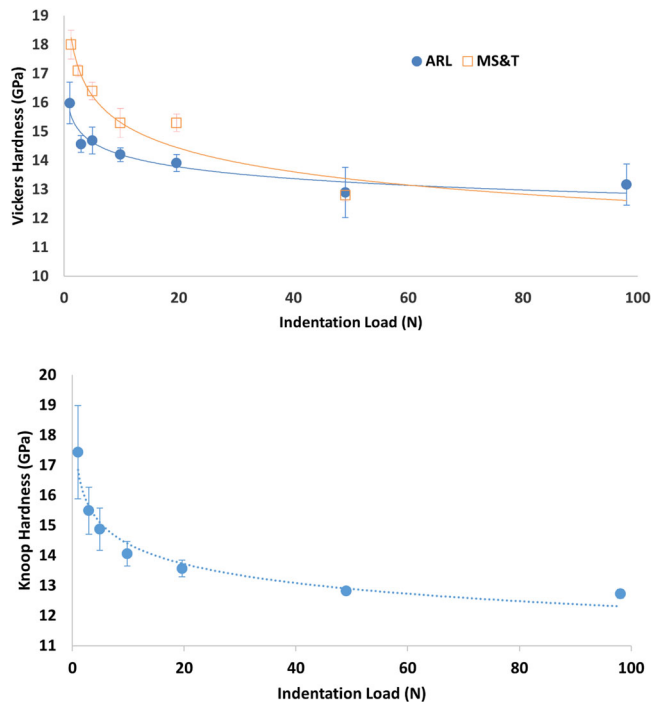
FIGURE 5 Top–Vickers hardness measured by both laboratories. Bottom–Knoop hardness measured.

confidence. In addition, the results indicated that testing to the ASTM standards enables direct comparison of strength and fracture toughness values among different laboratories. In addition, testing to ASTM standards for strength and fracture toughness should provide values that can be used to compare the strengths and fracture toughness values for materials prepared by different processes or from different starting materials.

3 | CONCLUSIONS

A comparative study was conducted by two laboratories (Missouri S&T and ARL) to evaluate a hot-pressed ZrB_2. Specimens were prepared by both wire EDM and conventional diamond machining. The flexure strength was tested to ASTM C1161 resulting in strengths of 473 MPa at Missouri S&T and 438 MPa at ARL with a pooled average of 458 MPa. Fracture toughness determined with chevron notched bars according at ASTM 1421 were 3.9 MPa•m$^{1/2}$ at Missouri S&T and 4.4 MPa•m$^{1/2}$ at ARL for a pooled average of 4.1 MPa•m$^{1/2}$. The resulting strength and fracture toughness values from each a laboratory were comparable based on standard deviations of the average property values indicating that both machining methods are acceptable means of preparing specimens for mechanical property testing and that results from different laboratories can be directly compared when testing

to appropriate standards. On the other hand, the Vickers hardness measured by both laboratories was considerably different at indentation loads of 20N and lower. There is no clear explanation for this difference.

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