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Mechanical behavior of zirconium diboride–silicon carbide ceramics at elevated temperature in air

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Abstract

The mechanical properties of zirconium diboride–silicon carbide (ZrB_2–SiC) ceramics were characterized from room temperature up to 1600 °C in air. ZrB_2 containing nominally 30 vol% SiC was hot pressed to full density at 1950 °C using B_4C as a sintering aid. After hot pressing, the composition was determined to be 68.5 vol% ZrB_2, 29.5 vol% SiC, and 2.0 vol% B_4C using image analysis. The average ZrB_2 grain size was 1.9 μm. The average SiC particles size was 1.2 μm, but the SiC particles formed larger clusters. The room temperature flexural strength was 680 MPa and strength increased to 750 MPa at 800 °C. Strength decreased to ∼360 MPa at 1500 °C and 1600 °C. The elastic modulus at room temperature was 510 GPa. Modulus decreased nearly linearly with temperature to 210 GPa at 1500 °C, with a more rapid decrease to 110 GPa at 1600 °C. The fracture toughness was 3.6 MPa·m$^{1/2}$ at room temperature, increased to 4.8 MPa·m$^{1/2}$ at 800 °C, and then decreased linearly to 3.3 MPa·m$^{1/2}$ at 1600 °C. The strength was controlled by the SiC cluster size up to 1000 °C, and oxidation damage above 1200 °C.

Keywords: Zirconium diboride; Silicon carbide; Hot pressing; Mechanical properties; Failure analysis

1. Introduction

Zirconium diboride (ZrB_2), a transition metal boride compound, is part of a class of materials known as ultra-high temperature ceramics (UHTCs). This family of compounds is characterized by melting points in excess of 3000 °C.[1] The borides generally exhibit higher thermal conductivities (60–125 W (m K)$^{-1}$) and lower electrical resistivities (7.8–22 μΩ cm) at room temperature than carbide or nitride ceramics.[2,3] Borides are also resistant to chemical attack.[4] These properties have made borides candidates for applications including molten metal crucibles,[5,6] furnace electrodes,[5] cutting tools,[4,7] and wing leading edges on future hypersonic aerospace vehicles.[8,9] Additionally, ZrB_2 based particulate composites, especially those with silicon carbide (SiC) additives, have displayed enhanced properties. ZrB_2–SiC composites exhibit room temperature strengths in excess of 1000 MPa,[10–12] fracture toughness values as high as 5.5 MPa·m$^{1/2}$,[10,11,13] and hardness values exceeding 22 GPa.[8,10,12] Chamberlain et al. showed that the room temperature strength increased from 565 MPa for nominally pure ZrB_2 to over 1000 MPa with the addition of 20 or 30 vol% SiC.[10] Similarly, the fracture toughness increased from 3.5 MPa·m$^{1/2}$ for nominally pure ZrB_2 to 4.4 MPa·m$^{1/2}$ for the addition of 20 vol% SiC and 5.3 MPa·m$^{1/2}$ for 30 vol% SiC. Zhang et al. showed that the hardness of pressureless sintered ZrB_2–SiC ceramics increased with increasing SiC content, from 15.3 GPa for 10 vol% SiC to 22.4 GPa for 30 vol% SiC,[14] while Chamberlain et al. found the hardness to be ∼23–24 GPa for ZrB_2 with up to 30 vol% additions of SiC. Chamberlain also found the modulus of hot pressed, nominally pure ZrB_2 was 489 GPa, which decreased to 466 GPa for 20 vol% and 484 GPa for 30 vol% SiC.[10] For pressureless sintered ZrB_2–SiC, Zhang et al. found that the modulus increased from 404 GPa for 10 vol% SiC to 492 GPa for 30 vol%. These studies showed that the addition of SiC not only increased strength, fracture toughness, and hardness, but also influenced the oxidation rate of ZrB_2 by forming a silica rich oxide layer on the surface, slowing the rate of oxidation of the underlying material.[15–17] This combination of properties has resulted in ZrB_2–SiC composites being

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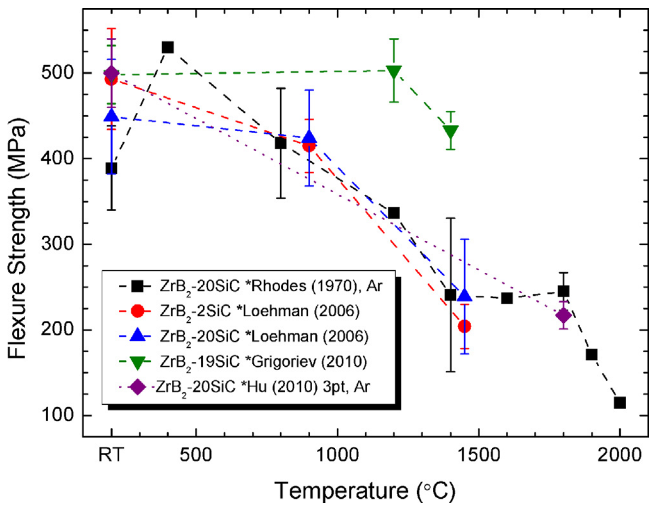

Fig. 1. Summary of the strength of ZrB_2–SiC ceramics at elevated temperature from selected studies.[18,23,25,54] Tests were performed using 4-pt flexure in air unless noted.

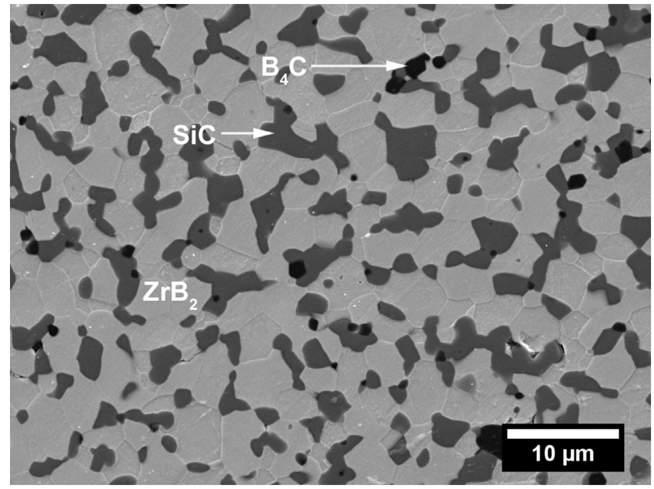

Fig. 2. SEM image of a polished and chemically etched cross-section of ZrB_2–30SiC.

studied for aerospace applications related to hypersonic flight. For the present study, ZrB_2 containing nominally 30 vol% SiC was selected based on its combination of room temperature mechanical properties and oxidation resistance.

While several studies have reported the elevated temperature mechanical properties of ZrB_2 ceramics, most of the studies have reported a single property (i.e., strength) for a limited number of temperatures and have not provided a systematic evaluation of the effects of temperature on mechanical behavior. Previous studies have shown that the strength of ZrB_2 composites generally decreases above about ~800 °C.[18–23] Fig. 1 summarizes previous studies of the strength of ZrB_2–SiC ceramics at elevated temperatures. Rhodes et al. reported the strengths in argon for hot pressed ZrB_2 up to 2200 °C and ZrB_2–20 vol% SiC up to 2000 °C in argon in 1970.[18] They reported the strength of ZrB_2–20 vol% SiC to be 390 MPa at room temperature, which decreased to ~240 MPa at 1400 °C to 1800 °C, and then decreased again to 115 MPa at 2000 °C. Rhodes et al. also produced ZrB_2–SiC–C composites with strengths between 220 and 350 MPa at 1400 °C and 1800 °C in an argon atmosphere.[18] More recent studies have reported the elevated temperature strengths of ZrB_2[19,24] and ZrB_2–SiC[22,23,25] ceramics up to 1500 °C in air. While these studies used ceramics with higher room temperature strengths that are more representative of current UHTCs, the ceramics included nitride or disilicide additives as sintering aids. For example, Monteverde et al. reported that a 4 wt% addition of Si_3N_4 to ZrB_2–20 vol%SiC could produce a ceramic with a room temperature strength of 730 MPa, but the strength dropped to 250 MPa at 1200 °C.[22] For ZrB_2–15 vol% SiC, Monteverde et al. reported a room temperature strength of 887 MPa that dropped to 255 MPa at 1500 °C. Loehman et al. examined ZrB_2–20 vol% SiC with a room temperature strength of 450 MPa that decreased to 240 MPa at 1450 °C.[23] Disilicide additions can improve the elevated temperature strength of ZrB_2 ceramics.[20,21,26] Sciti et al. measured strengths of 330 and 370 MPa at 1500 °C for ZrB_2 with 15 vol% additions $MoSi_2$ or $TaSi_2$.[20,21] Silvestroni et al. reported strengths for ZrB_2 with 5 vol% $MoSi_2$ to be 570 MPa at room temperature and 490 MPa at 1500 °C.[26] Since the Rhodes studies, most studies have only reported strength at one or two elevated temperatures.

Studies of other elevated temperature mechanical properties of ZrB_2 ceramics such as elastic modulus and fracture toughness have been limited. Rhodes et al. measured the elastic modulus in argon up to 2100 °C for ZrB_2 and up to 2000 °C for ZrB_2–20 vol% SiC.[18] Zhu measured the modulus of ZrB_2 and ZrB_2 with B_4C and C additions up to 1500 °C in air.[19] Rhodes reported a modulus of ~520 GPa for ZrB_2–20 vol% SiC at room temperature, which decreased to 445 GPa at 1400 °C, and to 106 GPa at 1600 °C. Based on these recent studies, strength data for ZrB_2 based ceramics have not been measured systematically at regular temperature intervals. In addition, no recent studies report the elevated temperature fracture toughness of these materials. Most studies report strength at room temperature and 1200 °C with either 1400 °C or 1500 °C as the highest reported test temperature.

As with other brittle materials, the strength of ZrB_2–SiC ceramics is controlled by the largest flaws present in the microstructure. Previous research has identified the size of the SiC inclusions as the critical flaw in dense, fine grained ZrB_2–SiC.[11–13] At some critical level of thermal expansion mismatch and cluster size, spontaneous microcracking of the matrix can occur, which has been studied by a number of authors.[12,27,28] The CTE mismatch between ZrB_2 (~5.2 ppm/K at 298 K),[1,29] SiC (~3.3 ppm/K at 298 K)[29] and B_4C (~5.7 ppm/K from 300–1970 K)[30] results in residual compressive stress in the SiC and tensile stresses in the ZrB_2 matrix and B_4C reinforcing phase. Watts et al. showed that a decrease in hardness (21 to 18 GPa) occurred at a maximum SiC particle size of 11.5 μm due to stress induced microcracking.[12] Watts et al. directly measured the residual stresses that accumulate in ZrB_2–30 vol% SiC upon cooling, finding a compressive stress of 880 MPa in the SiC phase and a tensile stress of 450 MPa in the ZrB_2 phase prior to the onset of microcracking.[31,32] Additionally, they found that the residual stresses begin to accumulate at ~1400 °C upon cooling and that the maximum stress was at the ZrB_2–SiC interface with