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Creep behavior of a zirconium diboride–silicon carbide composite

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Abstract

Flexural creep studies of ZrB_2–20 vol% SiC ultra-high temperature ceramic were conducted over the range of 1400–1820 °C in an argon shielded testing apparatus. A two decade increase in creep rate, between 1500 and 1600 °C, suggests a clear transition between two distinct creep mechanisms. Low temperature deformation (1400–1500 °C) is dominated by ZrB_2 grain or ZrB_2–SiC interphase boundary and ZrB_2 lattice diffusion having an activation energy of 364 ± 93 kJ/mol and a stress exponent of unity. At high temperatures (>1600 °C) the rate-controlling processes include ZrB_2–ZrB_2 and/or ZrB_2–SiC boundary sliding with an activation energy of 639 ± 1 kJ/mol and stress exponents of $1.7 < n < 2.2$. In addition, cavitation is found in all specimens above 1600 °C where strain-rate contributions agree with a stress exponent of $n = 2.2$. Microstructure observations show cavitation may partially accommodate grain boundary sliding, but of most significance, we find evidence of approximately 5% contribution to the accumulated creep strain.

Keywords: Creep; Deformation; Cavitation; Diborides; UHTC

1. Introduction

Ultra-high temperature ceramics (UHTC's) are designed for service at temperatures greater than 1500 °C. ZrB_2 and HfB_2 are primary candidates because of their high melting points (~3000 °C), thermal together with other desireable levels of electrical and mechanical properties and chemical stability at the intended application temperatures. An extensive review of these diborides and other refractory materials appears in Fahrenholtz et al.[1] Primary applications for UHTC's include hypersonic flight, atmospheric re-entry vehicles, refractory linings, electrodes, microelectronics and cutting tools.[1–9] Most notably, the sharp leading edges of hypersonic and atmospheric re-entry vehicle designs require improved material performance under the ultra-high stagnation point temperatures, convective heating and extreme oxidation conditions. Composites of ZrB_2 and HfB_2 are often processed with SiC, typically in quantities of 10–30% by volume SiC.[1–9]

ZrB_2 based UHTC composites are a focus of current ceramics research including their processing, oxidation and physical and mechanical properties. Mechanical behavior studies have been limited to high temperature MOR and fracture characterization with upper temperature limits through 1600 °C.[8,10,11] One exception is a ZrB_2–30%SiC composite MOR study, at 1800 °C, where reported viscoelastic material response under constant displacement conditions.[12] The MOR behavior at 1600 C of a ZrB_2–ZrC composite showed extensive non-linearity.[11] Additionally, Bird et al.[10] showed strain-rate sensitivity at 1600 °C during fracture experiments and a nonlinear load–displacement threshold temperature of ~1200 °C. However, few conventional creep experiments have been conducted for ZrB_2 based UHTC composites and the rate controlling creep mechanisms are not understood. UHTC target applications include the potential for considerable creep deformation.

Early atmospheric creep investigations include those conducted by Kats[13] and Spivak[14] on ZrC–ZrB_2 and ZrB_2–ZrN composites, respectively. ZrB_2–ZrC investigations[13] included low stress (5–30 MPa) compressive creep characterization and composition dependence on creep rate, between 1700 °C and

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2420 °C. Creep rates were reported to range between $\sim 10^{-6}$ and $10^{-4}\ s^{-1}$ with corresponding stress exponent of unity and activation energy of 270 ± 29 kJ/mol for all stress and temperature combinations. Activation energy and stress dependency on creep rate, $\dot{\varepsilon}$, are typically assessed by using the classical Norton equation[15]

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp\left(-\frac{Q}{RT}\sigma^n\right) \quad (1)$$

where Q is activation energy, R is the gas constant, T is absolute temperature, σ is applied stress, and $\dot{\varepsilon}_0$ and n are empirical constants. Kats et al.[13] found a strong ZrC composition dependency on creep rate with a maximum occurring at 50 vol% ZrC. Diffusion accommodated deformation limited by carbon diffusion through ZrC ($Q = 272$ kJ/mol) was the rate-controlling creep mechanism. Spivek et al.[14] conducted a similar investigation on flexure creep rate and ZrN composition influences. The grain sizes were significantly larger than those of Ref. [13] and hence considerable creep rate reduction was realized. However, the creep rate–ZrN composition dependencies were identical to those of ZrB_2–ZrC system with a maximum creep rate occurring at 50% ZrN. The reported large accumulated creep strains and microstructure continuity are characteristic of structural superplasticity or grain boundary sliding.

Recent ZrB_2 based atmospheric creep investigations show similar impacts of the compositional variations on the creep rates with the overall strains attributed to grain boundary sliding.[16] Talmy et al.[16] studied the SiC content and grain size effect on creep rate of up to 50% SiC content and SiC grain sizes of 2 and 10 μm, and test conditions between 1200 °C and 1500 °C with stresses through 180 MPa. They found the creep rate to increase with increasing SiC composition, stress and temperature. The creep rate was found to decrease with increasing SiC grain size. An apparent maximum in creep rate was realized at 50% SiC, consistent with Refs. [14,13]. The evaluated Norton stress exponent and activation energy were reported as $n = 1$ and $n = 2$ for 0–25% SiC and 50% SiC compositions, associated with activation energies of 130 and 511 kJ/mol for 0% and 50% SiC, respectively. The reported dominant creep mechanisms included diffusion accommodated by deformation and grain boundary sliding for the 0–25% SiC and 50% SiC composites, respectively.

Passive oxidation of UHTC's is well known for ZrB_2–SiC composites above 1500 °C. However, under passive conditions, oxygen diffusion through a glass filled porous ZrO_2 structure under extended high temperature exposure times is expected to complicate the creep problem.[5,17–20] In ZrB_2–SiC particulate composites, SiC vol% > ~25 is assumed to exceed the percolation threshold leading to an interconnected network of SiC from specimen surface inward.[16,21] Severe oxidation may have a marked influence on measured creep rate as inward oxygen diffusion and glass formation,[16,20] at grain boundaries, may accelerate creep.[8,16,21] Talmy et al.[16] report "fibrillation" of SiC phase in ZrB_2–50% SiC composite extending an appreciable distance inward from the tensile face. Additionally, they showed the apparent oxidation rate increase with tensile stress. To circumvent this problem, an inert or protective atmosphere is required. However, inherent difficulties maintaining a protective environment, beyond 1500 °C exist, rendering real-time displacement measurements difficult to obtain. Guo et al.[22] conducted a limited number of inert atmosphere flexure creep experiments on ZrB_2–30% SiC composite at 1500 °C and 1600 °C at 19 MPa. Displacement measurements were completed by beam curvature measurements and hence a discontinuous testing scheme was employed. However, their extended creep times and temperature revealed cavity nucleation at ZrB_2/SiC triple points. An apparent increase in cavity number density and size was observed with temperature, where cavitation sites were predominately ZrB_2–SiC grain junctions. Other methods for conducting inert or protective polycrystalline creep experiments include a non-contact flexure creep apparatus using specimen Joule heating and induced Lorentz forces for applicable creep temperature and stress, respectively. The details of this method are reported elsewhere.[23] Such an apparatus and testing approach still require validation against existing creep data. It is apparent, that most existing UHTC creep data is restricted to temperatures below 1500 °C.

The present study seeks to provide a characterization of temperature and stress dependent creep behavior for ZrB_2–20% SiC UHTC through 1820 °C. Protected atmosphere flexure creep experiments were conducted to determine the predominate temperature and stress dependent deformation mechanisms, based on experimental Norton constants, known creep models and microstructure.

2. Experimental methods

2.1. Material and processing

ZrB_2–20 vol% SiC billets were produced by Missouri University of Science and Technology (MST). MST billets were hot pressed in a similar manner to that described in Chamberlain et al.[3] ZrB_2 powder (Grade B, H.C. Starck, Newton, MA) was >99% pure with average particle size of 2 μm. SiC powder (Grade UF-10, H.C. Starck) was predominantly α-SiC with purity of 98.5% and particle size of 0.7 μm. B_4C/ZrB_2 powder (Grade HD-20, H.C. Starck) was also added to billets at 2 wt% to reduce SiC/ZrB_2 particle oxide surface films improving densification during pressing. Powders were ball milled with WC-6Co media, resulting in approximately 2.2–2.4 wt% WC-6Co impurity concentrations based on true and theoretical density differences. Confirmation of impurity concentration by XPS analytical technique is reported elsewhere.[10] A maximum hot pressing temperature and pressure of 1950 °C and 32 MPa, respectively, with heating rates of 30 °C/min up to 1650 °C and 90 °C/min up to 1950 °C were employed. All billets received were machined to test specimen dimensions with metal bonded diamond wafering blades.

2.2. Characterization

Microstructure observations were completed using scanning electron microscopy (LEO 1525 FE SEM) and Orientation