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Grain rotation and translation contribute substantially to creep of a zirconium diboride silicon carbide composite

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Abstract—Electron back scatter diffraction (EBSD) techniques as well as a novel microstructure mapping technique for the direct measurement of local grain-to-grain movements, provided the tools necessary for the assessment of creep deformation mechanisms of a ZrB_2–20% SiC composite. Flexure creep behavior determined here draws upon our previous research conducted at 1800 °C and 16 through 97 MPa for the same composite and within the context of existing creep theory.

We found ZrB_2 grain deformation scaled with the macroscopic creep strains. To this end, our novel indentation mapping method clearly defined the local ZrB_2 grain boundary sliding event, with deformation components of 80% grain translations and rotations, with the remainder attributed to cavitation and other deformations. EBSD kernel average misorientation methods indicated dislocation flow as the local deformation mechanism confined within the ZrB_2 near-grain boundary zones, serving solely to accommodate the grain rotation and translation events. Based upon this, we propose a modified grain boundary sliding model accounting for near-grain boundary deformation by dislocation glide and climb, operating in sequence with cavitation.

Texture analysis from acquired EBSD pole figures confirmed minimal contribution from SiC grain deformation to the tensile bending component, in contrast with a more significant contribution along the compression zone. We find evidence of <5% and <20% SiC grain deformation, contributing to the macroscopic creep strain, for tension and compression bending fibers, respectively. Cavitation accounts for no more than 5% of the macroscopic creep strain, agreeing with our previous estimates and the balance attributed to ZrB_2 grain boundary sliding.

Keywords: Creep; Diboride; EBSD; UHTC; Dislocations

1. Introduction

Structures exposed to extreme temperature environments ($T > 1500$ °C) require metals or metal compounds with melting points greater than $T > 3000$ °C [1,2]. A survey of existing candidate materials satisfying this single requirement limits the search to precious refractory metals, oxide, boride, carbide and nitride systems. Group IV borides, select group IV and V carbides and nitrides meet the high melting point criteria for such extreme environments [1–3]. Selected ultra-high temperature composite (UHTC) applications include hypersonic flight, winged atmospheric re-entry and low earth orbiting vehicles, refractory linings, electrodes, microelectronics and cutting tools [1–7]. Most notably, the aerodynamic surfaces of hypersonic and winged atmospheric re-entry vehicles, and structural propulsion components require improved material performance under these ultra-high temperatures, convective heating and extreme oxidation conditions [7,8]. From this list, the metal boride compounds offer a unique combination of high melting points, high thermal conductivity and thermodynamic stability, advancing the candidacy of this class for ultra-high temperature oxidizing environments. In particular, the oxidation and vapor pressure research by MANLABS, Inc. identified HfB_2 and ZrB_2 monoliths as the most suitable diboride compounds for high temperature applications requiring oxidation resistance [1,3,5].

These high application temperatures (1500–2200 °C) may promote mechanical behaviors ranging from, predominately, linear elastic to viscoplastic. Opeka et al. reported an onset of permanent deformation at 1200 °C under Modulus of Rupture (MOR) loading of HfB_2 [9]. Bird et al. [10] reported similar behavior transitions in the ZrB_2–20% SiC system, for both MOR and fracture conditions, both near 1200 °C. This composite also displayed a behavioral transition between 1400 and 1800 °C under creep flexure conditions. Below 1500 °C diffusion creep dominates, while grain boundary sliding persists beyond 1600 °C, associated with increasing steady state strain rates of 10^{-9}–10^{-5} s^{-1} [11]. Unlike many structural ceramics, only a minor contribution from cavitation was found. The behavior follows the Norton creep equation [12] of:

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

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where Q is activation energy, R is the gas constant, T is absolute temperature, σ is applied stress, and $\dot{\varepsilon}$ and n are empirical constants. Accelerated creep rates of four decades over 400 °C increase in temperature were measured.

Langdon proposed grain boundary sliding as an independently operating creep mechanism, while maintaining a constant grain shape [13,14]. Rachinger [15] was the first to prove this behavior for aluminum using a soap bubble analogy. Later, the superplastic literature considered large creep deformations for fine-grained materials, preserving equiaxed grain structures and microstructural continuity during grain boundary sliding and grain neighbor re-arrangement [16–21]. Ashby and Verrall [19] proposed grain boundary sliding in the context of combined diffusion and dislocation mechanism contributions [13,17–19,21].

The pioneering work of Rachinger [15] and, later, Langdon developed direct measurement techniques for quantifying grain boundary sliding strain contributions. Rachinger's [15] unique experiments measured the grain deformation behavior during plastic flow of Aluminum to 50% strain. Using transverse and parallel markings relative to the stress axis, he tracked local grain deformations and translations with the macroscopic creep strains associated with initial equiaxed grain structures [15]. Similar grain marking experiments have been conducted on various ceramics and metals to quantify grain boundary sliding contributions to strain [16,22]. Moreover, scribe experiments have resolved microstructure mechanisms involving grain shape change [23]. Approaching high temperatures, the grain boundary markers exhibited offset discontinuities associated with sliding grain boundaries [14,16]. Langdon [13,14,24] later showed such marker line offsets are expected for grain translations for both the Lifshitz [25,26] and Rachinger [15,26] type, while grain deformation should not produce such offsets. All materials supporting these referenced studies exhibited excellent oxidation resistance at testing temperatures and were coarse-grained microstructures (60–80 μm) [16]. In consideration of the present study, this deformation mapping method suffers inherent difficulties when the grain size approaches the scribe dimensions. Additionally, mapping ZrB_2 materials with chemically unstable surfaces at testing temperatures raises inherent difficulties for post mortem interpretation.

The present work expands on our earlier flexure creep research [11], also conducted at 1800 °C for $ZrB_2$20% SiC. The microstructures alone, however, provided no conclusive clues to fully understand the deformation mechanisms accounting for the observed creep strains. Unlike many other structural ceramics referenced in the creep literature, the level of cavitation found accounted for less than 10% of the strain, leaving the post-creep microstructure appearance very similar to its initial state. We probed the microstructure through three independent methods. To consider the global question of how the microstructure accommodates the strain, we first examined at the optical scale, in particular, comparing grain boundary intercepts with bend radius traces near the tensile surface to those along the compressive surface. When combined with grain aspect ratio data, these data helped us predict any possible grain structure rearrangement. Second, deformation mapping using electron back scatter diffraction (EBSD) methods characterized the micro-deformation. Finally, we introduce our version of the earlier scribe experiments, using nano indentations as fiducial markers for tracking relative grain movements and assessing the micro-scale deformation. These micro-scale measurements allow us to propose revised creep deformation models that expand upon our findings in Ref. [11] within the context of existing creep theories.

2. Experimental methods

2.1. Materials and processing

ZrB_2–20 vol% SiC billets were produced by Missouri University of Science and Technology (MST) in a similar manner to that described in Chamberlain et al. [27]. ZrB_2 powder (Grade B, H.C. Starck, Newton, MA) was >99% pure with an average particle size of 2 μm. SiC powder (Grade UF-10, H.C. Starck) was predominantly α-SiC with a purity of 98.5% and particle size of 0.7 μm. B_4C/ZrB_2 powder (Grade HD-20, H.C. Starck) additions of 2 wt% reduced SiC/ZrB_2 particle oxide surface films, thereby improving densification. Powders were ball milled with WC-6Co media, resulting in approximately 2.2 to 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.

2.2. Characterization

Microstructure observations were completed using optical light microscopy (Keyence VH-Z500R Zoom lens equipped with the VHX-S15 motorized stage and the VHX-H2M software), scanning electron microscopy (LEO 1525 FE SEM SE Detector and FEI Quanta 400 SEM BSE and SE Detector) and electron backscatter diffraction (EBSD) using a Hikari camera and Octane Energy Dispersive Spectroscopy (EDS) detector mounted on a SEM (Philips XL-30 FEG SEM). Quantitative particle and grain spacing statistics were collected using the linear intercept method, detailed in [28], on two vacuum crept and un-crept specimens, for a total of four specimens, from the same billet, utilizing gray-scale binary threshold imaging (Nikon Nis-Elements Documentation V3.22.00). Sampled areas used for all specimens, both optical and SEM, encompassed approximately 6000 and 1000 grains, respectively. Outer-fiber strains and approximate neutral axis positions, after creep, were optically determined on three vacuum specimens using the radius of curvature method outlined in [11]. Cavity volume fractions were measured on fracture surfaces according to procedures outlined in [11]. Orientation Imaging Microscopy (OIM) was implemented for acquiring two-dimensional crystallographic orientations of crept and uncrept composite microstructures from EBSD – generated Kikuchi patterns. OIM data collection and analysis of ZrB_2 and 2-H α-SiC Kikuchi patterns used the TSL OIM Data Collection/Analysis V5.3 suite (EDAX Inc.) with a survey window of approximately 100 μm × 100 μm at a 0.2 μm step size, surveying approximately 1500 ZrB_2 grains, and 4×4 binning for the coarse scans on a single vacuum crept and uncrept specimen. Patterns were collected for both tensile and compressive deformation states, taken from 0.08 ± 0.03 and 0.92 ± 0.03 normalized bar heights, respectively. Fine scans