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ScienceDirect
Journal of the European Ceramic Society 31 (2011) 1345–1352
www.elsevier.com/locate/jeurceramsoc

Compressive strength degradation in ZrB_2-based ultra-high temperature ceramic composites

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Available online 19 June 2010

Abstract

The high temperature compressive strength behavior of zirconium diboride (ZrB_2)–silicon carbide (SiC) particulate composites containing either carbon powder or SCS-9a silicon carbide fibers was evaluated in air. Constant strain rate compression tests have been performed on these materials at room temperature, 1400, and 1550 °C. The degradation of the mechanical properties as a result of atmospheric air exposure at high temperatures has also been studied as a function of exposure time. The ZrB_2–SiC material shows excellent strength of 3.1 ± 0.2 GPa at room temperature and 0.9 ± 0.1 GPa at 1400 °C when external defects are eliminated by surface finishing. The presence of C is detrimental to the compressive strength of the ZrB_2–SiC–C material, as carbon burns out at high temperatures in air. As-fabricated SCS-9a SiC fiber reinforced ZrB_2–SiC composites contain significant matrix microcracking due to residual thermal stresses, and show poor mechanical properties and oxidation resistance. After exposure to air at high temperatures an external SiO_2 layer is formed, beneath which ZrB_2 oxidizes to ZrO_2. A significant reduction in room temperature strength occurs after 16–24 h of exposure to air at 1400 °C for the ZrB_2–SiC material, while for the ZrB_2–SiC–C composition this reduction is observed after less than 16 h. The thickness of the oxide layer was measured as a function of exposure time and temperatures and the details of oxidation process has been discussed.

Keywords: Composites; Borides; Carbides; Strength; Structural applications

1. Introduction

The high melting point of refractory metal diborides coupled with their ability to form refractory oxide scales give these materials the capacity to withstand temperatures in the 1900–2500 °C range. These ultra-high temperature ceramics (UHTCs) were developed in the 1960s.[1] Fenter[2] provided a comprehensive review of the work accomplished in the 1960s and early 1970s. These materials are almost never used in pure form. Instead, additions of silicon carbide are used to enhance oxidation resistance and limit diboride grain growth.[3–6] Carbon is also sometimes used as an additive to enhance thermal stress resistance.[7–9] These materials offer a good combination of properties that make them candidates for airframe leading edges on sharp bodied re-entry vehicles.[10] UHTCs have potential to perform well in such applications' environment, i.e. air at low pressure. Some interest has also been shown in these materials for single use propulsion applications.[11]

Major improvements in the manufacturing and characterization of ZrB_2 materials and composites have been put forward in recent years, and now several important aspects of their properties and processing are well understood.[4,12–21] However, the study of high temperature properties has been mostly limited to oxidation behavior, an area which is also well understood.[8,21–28] Very few studies of high temperature mechanical properties exist.[7,11,29]

In this workIn this work, we investigated the mechanical behavior of ZrB_2–SiC composites, with and without added C and SCS-9a fibers. Samples were studied in compression at room temperature, 1400, and 1550 °C, in atmospheric air. The degradation of the mechanical properties as a result of atmospheric air exposure at high temperatures were also studied as a function of exposure time.

2. Experimental procedures

Samples of ZrB_2–SiC composites were fabricated by uniaxial hot pressing by Materials and Machines, Inc., Tucson, AZ. ZrB_2 and α-SiC powders were obtained from H. C. Starck and had

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doi:10.1016/j.jeurceramsoc.2010.05.020

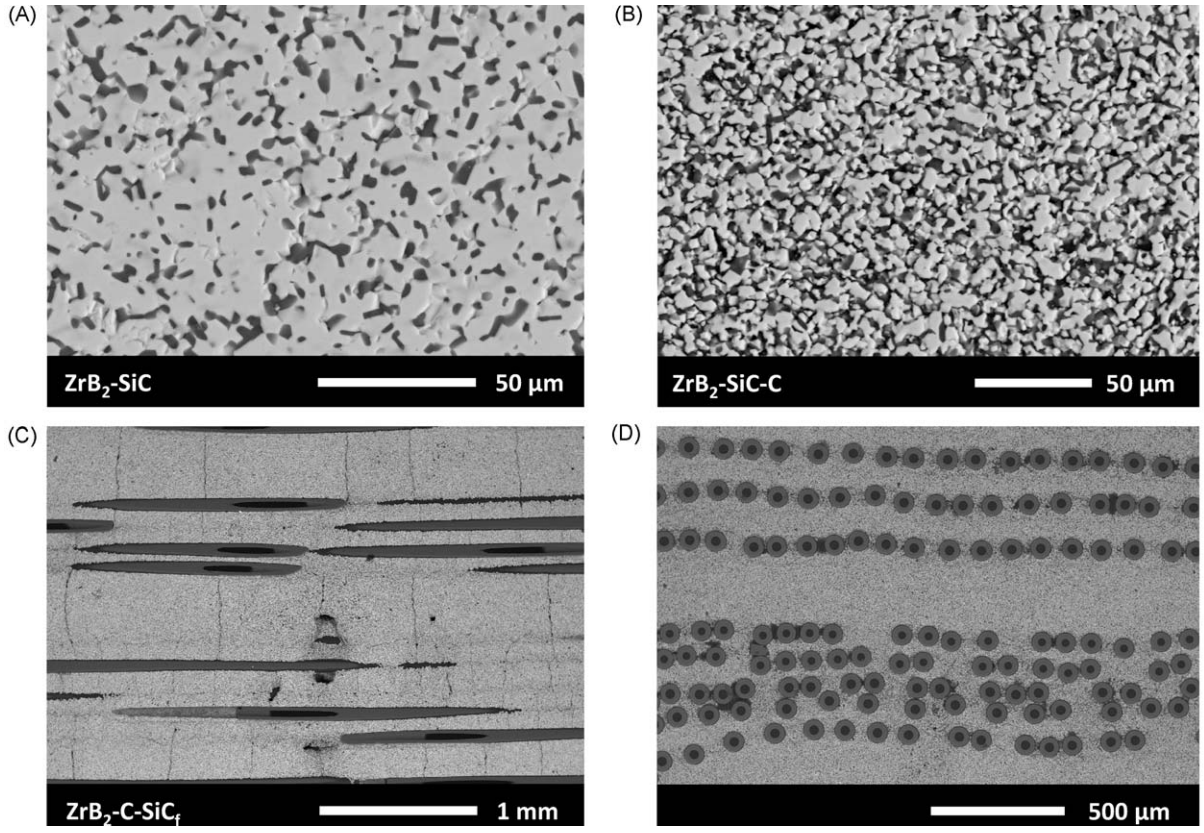

Fig. 1. Microstructure of the as-received materials (BSE contrast). (A) ZrB_2–20 vol.% SiC (ZS). (B) ZrB_2–30 vol.% C–14 vol.% SiC (ZSC). (C and D) Longitudinal and traversal section of ZrB_2–20 vol.% SiC–35 vol.% SCS fibers (ZSS).

nominal sizes of d_{50} = 3–5 μm and d_{50} = 1.4 μm, respectively. C powders were obtained from Asbury Graphite Mills. SiC fibers were obtained from Textron Specialty Materials (SCS-9a fibers). Two particulate composites were studied, one containing ZrB_2 plus 20 vol.% SiC (ZS), and the other containing ZrB_2 plus 14 vol.% SiC and 30 vol.% C (ZSC). The specimen densities obtained were 5.57 g/cm^3 (99.9% of theoretical density) for ZS and 4.50 g/cm^3 (99.0% of theoretical density) for ZSC. The composite panel was prepared by the filament winding and slurry deposition technique followed by hot pressing in a graphite die. The composite density obtained was 3.47 g/cm^3, while the theoretical density is 4.60 g/cm^3 for 35 vol.% fiber loading.

Compression tests were carried out on an electromechanical universal testing machine with a furnace attached to its frame, at constant cross-head displacement rate (strain rates of 2×10^{-5} s^{-1} and 2×10^{-4} s^{-1}). Load was applied using alumina rods with SiC pads. Samples were cut into parallelepiped shape using a low speed diamond saw. Nominal sample dimensions were 3 mm × 3 mm × 5 mm, and the load was applied to the longest dimension. Some samples were finely polished (up to 0.5 μm) to further study the strength dependence with surface defects. Mechanical tests were conducted at room temperature, 1400, and 1550 °C. Several samples were exposed to oxidation by annealing at 1400 °C in atmospheric air in a tube furnace, and exposure times ranged from 6 to 48 h. The room temperature strength was measured after oxidation, to study the degradation of the mechanical properties after exposure to an oxidizing environment. At least three samples were studied at each temperature or exposure time at 1400 °C. Error bars throughout this paper represent one standard deviation.

Microstructural studies were carried out using SEM and EDS techniques, on both as-fabricated and tested specimens. Samples were prepared for SEM observation using conventional metallographic techniques which involved cutting, grinding, and lapping. A conductive coating of either carbon or gold was applied to the specimens prior to microscopic observation.

3. Results and discussion

3.1. Microstructure of as-received specimens

Fig. 1 shows the as-fabricated microstructures of three types of composites studied. The ZS composite appears to be fully dense, while the ZSC suffered from significant grain pullout during sample preparation. This is attributed to the weak bonding of C to the ZrB_2 and SiC phases, which results in removal of the C phase during polishing. In ZS, ZrB_2 grains (gray phase) are equiaxed with reported grain size in the 6–12 μm range, while the SiC grains (dark phase) are elongated with sizes of approximately 1.5–3 μm thick by 3–11 μm wide/long.[7] In ZSC, the grain pullout during polishing made the estimation of grain size difficult, although it can be seen from Fig. 1 that ZrB_2 grain size is smaller in ZSC than in ZS. It should be noted that, at least for the ZS composite, the grain size is close to the critical grain size