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Short communication

Mechanical properties of individual phases of ZrB_2-ZrC eutectic composite measured by nanoindentation

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ABSTRACT

Zr-based ceramics are of interest for applications in aerospace propulsion, owing to their high hardness and stability. Application of these ceramics requires better understanding of their mechanical behavior in small scales and at elevated temperatures. Here, we prepared a ZrB_2-ZrC ceramic eutectic composite, consisting of self-assembled ZrC rods grown within a single-crystalline ZrB_2 matrix, and studied the mechanical properties of the individual eutectic phases using nanoindentation at both room and elevated-temperatures. The Vickers hardness of the eutectic composite was measured at room temperature. These data provide insight into the understanding of the mechanical behavior of the individual phases of non-oxide ceramic eutectic composites for high-temperature applications.

1. Introduction

Recent development in hypersonic flights and new aircraft engines has renewed the interest in high-temperature ceramics, especially transition-metal based diborides and carbides, owing to their intrinsic stability and exceptional thermal, electrical and mechanical properties [1–3]. For example, ZrB_2 and ZrC are among the very few compounds with melting temperatures >3000 °C: 3245 °C and 3445 °C for ZrB_2 and ZrC, respectively [4]. However, the relatively low fracture toughness of diborides and carbides prevents their wide-spread applications. As a self-assembled in-situ composite, the eutectic architecture has one continuous reinforcing phase embedded in another matrix phase. This could offer superior mechanical properties (e.g., higher fracture toughness) to either constituent alone, because of the strong constraining effects from the interlocking microstructures [5,6].

In the past several decades, attention was mainly focused on metallic or oxide eutectics, e.g., Al_2O_3-YSZ (Yttria-stabilized ZrO_2) [7]. One main reason is that oxide eutectics have excellent resistance to oxidation at elevated temperatures [7]. For instance, Al_2O_3-$Y_3Al_5O_{12}$ eutectics are thermally stable in air up to 1650 °C [8]. In contrast, thermal gravimetric analysis (TGA) shows that ZrB_2 is only thermally stable below 700 °C. However, additives, such as SiC, can effectively reduce the oxidation rate of ZrB_2 above 1100 °C by forming a protective silica-rich layer [1]. Another barrier to the application of non-oxide ceramics is their extremely high melting temperatures, which make them difficult to process by conventional sintering [9]. ZrB_2-ZrC eutectic composite was first reported by Orand'yan and Unrod in 1975 [10]. Since then, few studies have been conducted on this quasi-binary eutectic system [11,12]. Moreover, the mechanical properties of the individual eutectic phases have never been studied, probably because conventional mechanical tests are not valid for testing the individual eutectic phases that exist at the micron-scale. Here, we produced a ZrB_2-ZrC rod-like eutectic composite through arc-melting mixed powders of micron-sized ZrB_2 and ZrC in Ar and measured the hardness and Young's modulus of the individual eutectic phases using nanoindentation at both room and elevated temperatures. Vickers hardness of the entire rod-like eutectic composite was measured in room temperature. These data will be useful for understanding the mechanical behavior of individual phases of non-oxide ceramic eutectic composites at elevated temperatures.

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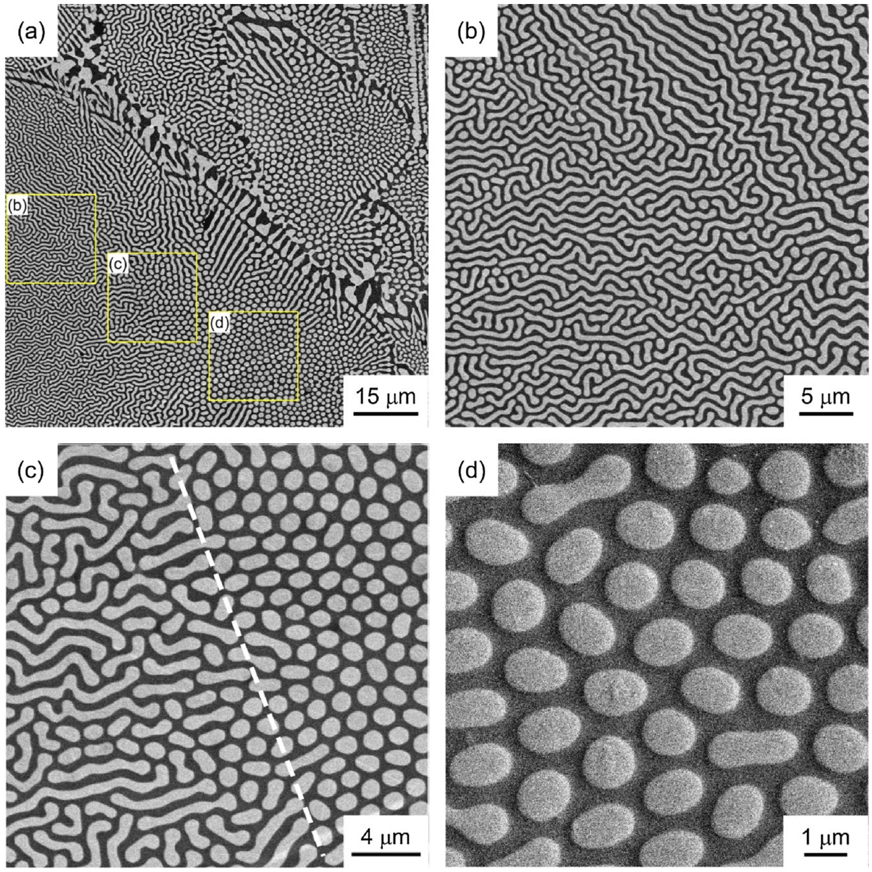

Fig. 1. SEM micrographs of the ZrB_2-ZrC eutectic composite (a) coexistence of the rod-like and labyrinth eutectic structures (the boxed areas of (b), (c) and (d) in Fig. 1(a) generally correspond to Figs. 1(b), (c) and (d), respectively), (b) labyrinth eutectic structure, (c) transition region between the rod-like and labyrinth eutectic structures, (d) rod-like eutectic structure.

2. Experiment

The starting materials were ZrB_2 powder (C < 0.5, O < 1.5, N < 0.5 (wt%), 1.5–2.5 μm, Kojundo Chemical Laboratory, Japan) and ZrC powder (95%, 2.5 μm, Kojundo Chemical Laboratory, Japan). ZrB_2 and ZrC powders (mole ratio: 55/45) were wet-milled in ethanol for 4 h using ZrO_2 balls as milling media. The mixed powders were dried and cold pressed into disks (10 mm in diameter and 3 mm thick). The disks were melted twice by arc-melting in Ar and solidified on a water-cooled copper hearth. The specimens were polished with final polishing using 1 μm diamond slurry. Scanning electron microscopy (SEM)/Focused ion beam (FIB) milling/Electron backscatter diffraction (EBSD) were performed on a Dual-beam SEM/FIB microscope (FEI Helios Nano-lab 650). Transmission electron microscopy (TEM) was conducted using a JEOL 2010F TEM (200 kV) and a JEOL 2100 Cs-corrected analytical STEM (200 kV). Nanoindentation was carried out on a Hysitron Ti 950 Triboindenter (Minneapolis, MN, USA) loaded with a high temperature xSol Berkovich probe. Berkovich hardness (H_B) of ZrB_2 and ZrC were measured from at least 5 indentation measurements with a peak load of 2.5 mN at room temperature, 300 °C and after cooling to room temperature. Elastic modulus (E) was determined through the load-displacement curves using the Oliver-Pharr method [13]:

$$\frac{1}{E_r} = \frac{1-\upsilon^2}{E} + \frac{1-\upsilon_i^2}{E_i} \quad (1)$$

where E and υ are Young's modulus and Poisson's ratio for the specimen, respectively, and E_i and υ_i are the same parameters for the Berkovich indenter. The Poisson's ratios (υ) of ZrB_2, ZrC, and the diamond indenter (elastic modulus: 1140 GPa) were 0.13, 0.18 and 0.07, respectively [13–16]. The Vickers hardness (H_v) of the entire eutectic composite was determined from 5 indentation measurements at room temperature with an applied load of 2 N using Eq. (2):

$$H_V = \frac{1.854P}{d^2} \quad (2)$$

where P is the peak indentation load (newtons) and d (micrometers) is the average length of the indentation diagonal. Average grain size and the indentation size were estimated from SEM and in-situ atomic force microscopy (AFM) micrographs, respectively, using ImageJ software [17].

3. Results and discussions

An SEM micrograph of the ZrB_2-ZrC eutectic composite is shown in Fig. 1(a), where both rod-like and labyrinth eutectic structures are observed. In the labyrinth structure (enlarged in Fig. 1(b)), the wavy lamellae (bright contrast) are ZrC, grown in a ZrB_2 matrix (dark contrast). A transition region between the rod-like and labyrinth eutectic structures (Fig. 1(c)) is indicated by a dashed-line. Within the labyrinth structure, both isolated and merged ZrC rods were observed. It was likely that each wavy ZrC lamella was formed by merging a group of ZrC rods. The rod-like structure is highlighted in Fig. 1(d), where highly densified ZrC rods are round-shaped. In general, boride and carbide eutectics will show rod-like morphologies at the volume fractions of the minor phases less than 30%; otherwise, lamellar morphologies will occur [2]. For example, Sorrell *et al.* prepared a 48ZrB_2-52ZrC (mol%) eutectic composite with a lamellar structure using a floating-zone technique [11]. However,