Journal of the European Ceramic Society 36 (2016) 239–242

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Short communication

Nanohardness and elastic anisotropy of ZrB_2 crystals

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ARTICLE INFO

Article history:
Received 21 May 2015
Received in revised form 8 September 2015
Accepted 12 September 2015
Available online 28 September 2015

Keywords:
ZrB_2 crystal
Nanoindentation
Hardness
Indentation modulus
Elastic anisotropy

ABSTRACT

Room temperature instrumented nano-indentation with a Berkovich tip was carried out on polycrystalline ZrB_2. The orientation of the individual grains was mapped using electron backscattered diffraction. The anisotropy in properties was ~20% and ~7% for nanohardness and indentation modulus, respectively. The nanohardness decreased from basal towards prismatic orientation with a minimum at ~50–60° and the indentation modulus increased with a maximum at ~70–80°. The indentation modulus anisotropy, calculated by Vlassak-Nix model, shows similar tendency as the experimental values.

1. Introduction

Ultra-high temperature ceramics (UHTC) are a family of materials that are chemically and physically stable at very high temperatures. They are usually based on the refractory borides, carbides, nitrides and oxides of early transition metals [1,2]. Zirconium diboride (ZrB_2) is an important member of the UHTCs family due to its high melting point (>3000 °C), high oxidation resistance above 1500 °C and excellent thermal and electrical conductivity. These properties make ZrB_2 an ideal candidate to withstand extreme chemical and thermal environments, including hypersonic flight [3].

Zirconium diboride is a non-oxide ceramic with hexagonal structure, (space group P6/mmm, No. 191) with lattice parameters of $a = 3.170$ Å and $c = 3.53$ Å, respectively [4]. The individual grains within the polycrystalline ZrB_2 are essentially single crystals with orientation-dependent mechanical properties. It is necessary to understanding this orientation dependence in order to optimize microstructures containing grains with desired orientations to design composites having enhanced combinations of hardness, toughness and wear resistance [5]. The mechanical properties of ZrB_2 crystals, similarly to other materials, are not absolutely the same at micro or nano levels compared with their macroscopic counterparts due to the different internal defect structure (dislocations, impurities, etc.). Thus, direct measurements are necessary to be performed on the grains in that condition as they are in presence in polycrystalline ZrB_2 instead of on properly oriented single crystals.

In the past, several investigations focused on the understanding of the orientation dependence of microhardness and the possible deformation mechanisms at room and elevated temperatures in ZrB_2 single crystals [6–9]. Xuan et al. [6] performed Vickers microhardness measurements on ZrB_2 single crystals, on basal (0001), and the prismatic $(10\bar{1}0)$ and $(11\bar{2}0)$ planes at room and elevated temperatures up to 1000 °C. According to their results, the hardness was very similar on both types of prismatic planes and lower than on the basal plane. A similar result was reported in the work of Nakano et al. [7] who used Knoop indentation testing. They reported a slight hardness anisotropy (~15%) for ZrB_2 single crystal, which was explained by activation of the $\left\{10\bar{1}0\right\}\langle11\bar{2}0\rangle$ slip system based on the critical shear stress analysis of Daniels and Dunn [8]. Later TEM investigations clearly identified $\left\{10\bar{1}0\right\}\langle11\bar{2}0\rangle$ type slip, which is typical for hexagonal crystals, as the only responsible mechanism for room-temperature plastic deformation in single crystal ZrB_2, [9].

Recent scratch [10–12] and indentation [13,14] investigations on polycrystalline ZrB_2 and ZrB_2–SiC composites have also revealed readily detectable plastic deformation features in the form of slip-lines. Ghosh et al. inferred $\left\{10\bar{1}0\right\}\langle11\bar{2}0\rangle$ type slip activation by TEM observation and reported for the first time a [0001] type Bugers vector in ZrB_2 grains, which possibly corresponds to the $\left\{10\bar{1}0\right\}$ [0001] system, [11]. Performing low-load indentation,

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http://dx.doi.org/10.1016/j.jeurceramsoc.2015.09.012
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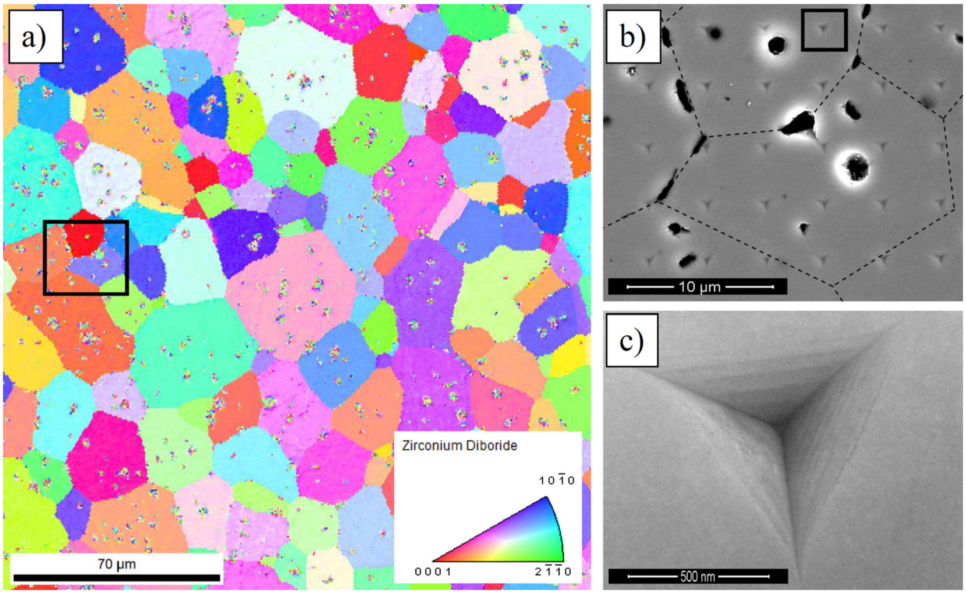

Fig. 1. Characteristic maps of polycrystalline ZrB_2 made by (a) EBSD prior to indentation; (b) SEM on a particular part of the indented surface (grain boundaries are marked) together with; (c) a selected indent located in grain close to basal orientation.

Guicciardi et al. [14] observed pop-in phenomena in ZrB_2–SiC composite when indents were placed inside ZrB_2 grains.

While the mechanisms of plastic deformation of ZrB_2 have been widely studied in single crystals and also in polycrystalline ZrB_2 ceramics, the orientation dependence (anisotropy) of hardness and elastic properties of single crystals or polycrystalline ZrB_2 have not been reported.

The aim of the present work was to study the influence of grain orientation on the nanohardness and indentation modulus of polycrystalline ZrB_2 ceramic to reveal the anisotropy of the elastic and plastic properties.

2. Experimental

The experimental material was a spark plasma sintered (SPS) ZrB_2 sample prepared by two steps SPS process. The starting material was a ZrB_2 powder with average grain size of 2.4 µm (Starck, Germany) containing impurities of C 0.13; O 0.8; N 0.21; Hf 1.77 wt%. All of the experiments were carried out using an SPS furnace (FCT HPD 25; FCT Systeme GmbH) under vacuum (5 Pa). In the first step, the cold pressed material (10 MPa for 1 min) was subjected to pressure-less sintering at 1900 °C for 20 min and cooled down at 100 °C/min. In the second step, the sample was heated up to 1700 °C (heating rate of 100 °C/min) under constant pressure of 16 MPa, which followed by an additional heating up to 2100 °C (heating rate of 50 °C/min) under a linearly increasing pressure up to 60 MPa. The sample was dwelled for 20 min and then cooled to room temperature at 100 °C/min.

The microstructure parameters were determined using standard ceramographic procedures (cutting, grinding, polishing, etching), SEM observation (FEI Quanta 3D and JEOL JSM 7000F) and statistical analyses [15]. Before nanoindentation the ZrB_2 sample was subjected to EBSD investigation on a FEI Quanta 3D to determine the crystal orientation of the individual ZrB_2 grains.

Nanoindentation tests were carried out at room temperature on an Agilent G200 Nano Indenter operating in continuous stiffness measurement (CSM) mode using a brand new diamond Berkovich tip. The tip was calibrated prior to the measurements using a fused silica sample. Nanoindentation was performed with a maximum penetration depth of 200 nm and strain rate of $0.05\ s^{-1}$. The indentation depth was selected to be as small as possible but be in possession of a well developed plastic zone close to the tip with a surrounding elastic region. According to the general rule of nanoindentation, the distance between the indents should be cca. triple of their diameter (d), which is $d \sim 1.3$ µm in the present case, to avoid the interaction of their stress fields. Thus, indents were positioned on the previously EBSD mapped surface area, in a 30 × 30 array with distance of 4 µm between the indents. The hardness and indentation modulus was calculated according to the Oliver Pharr method [16] using Poisson ratio and Young's modulus values of $\nu_{ZrB2} = 0.26$, $\nu_i = 0.07$ and $E_i = 1140$ GPa for ZrB_2 and diamond indenter tip, respectively. The measured hardness and modulus values were almost constants in the depth region of 50–200 nm which confirmed the selection of 200 nm.

The crystal orientations of the indented ZrB_2 grains were determined on the basis of the measured EBSD map using the OIM software, which defines the crystal orientations in terms of Euler angles (φ_1,Φ,φ_2) relative to the sample coordinate system [17]. Only those indents that were located inside the grains farther than 2 µm from the grain boundaries, inclusions and pores observed by SEM were taken into account. The averaged hardness and modulus values, deriving from the depth range of 150–200 nm, were paired with the corresponding grain orientation as a function of the relevant Euler angles Φ and φ_2, due to the assumed rotational symmetry of nanoindentation [17].

3. Results and discussion

The characteristic microstructure of the investigated ZrB_2 is shown in Fig. 1a,b. Fig. 1a is an EBSD image of the particular surface area where the indentation testing was carried out. It shows a wide range of grain orientations, which provided a suitable area for the orientation dependence analysis. The majority of the ZrB_2 grain diameters fall into the range of 10–40 µm. Fig. 1b shows the microstructure of the ZrB_2 ceramics along with the indentation impressions. There are micro-pores at the triple point, grain boundaries and also located within the grains with diameters up to several micrometers. From Fig. 1b, which the selected area marked in Fig. 1a, it is evident that the grains size is large enough to guarantee statistically low probability of interaction between the indents