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Textured HfB_2-based ultrahigh-temperature ceramics with anisotropic oxidation behavior

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Based on recent preliminary results of textured ZrB_2-based ceramics, *c*-axis oriented HfB_2-based ultrahigh-temperature ceramics with a Lotgering orientation factor as high as 0.91 were prepared by slip casting in a strong magnetic field alignment, followed by spark plasma sintering. The textured sample displays significantly anisotropic properties. Compared with textured ZrB_2-based ceramics, the HfB_2-based material shows much better oxidation resistance.

Keywords: Hafnium diboride; Slip casting; Strong magnetic field alignment (SMFA); Texture; Anisotropy

Transition metal borides, mainly hafnium diboride (HfB_2) and zirconium diboride (ZrB_2), belonging to the class of ultrahigh-temperature ceramics (UHTCs), are currently expected to be a potential candidate material for aerospace applications because of their high melting points (>3000 °C) and excellent chemical stability. The introduction of SiC improves the properties, especially the oxidation resistance, of these diborides [1,2]. Despite their potential, their widescale use still presents a challenge, due, in part, to limitations in their high-temperature properties and oxidation resistance. To improve their performance, most research has focused on composition design of existing materials – i.e. selecting different additives to change the material composition to improve the performance of materials [3–5]. However, grain boundary phases deriving from the additions often drastically deteriorate the strength and other mechanical properties at elevated temperature [6,7].

The controlled development of microstructures has recently become an important topic in ceramic processing because it allows improvement in mechanical, thermal, electrical and other properties. As a common method for microstructure tailoring, texture development offers the unique opportunity to optimize the performance of ceramics, and has been widely used in the materials field [8–10]. "Templated grain growth" (TGG) and "hot-working" methods [8,11] are two major methods for texture development. However, to the knowledge of the authors, virtually nothing has been published in the open literature discussing the texture development of UHTCs, partly due to the difficulty of preparing templated grains. Recently, strong magnetic field alignment (SMFA) has been successfully utilized to texture "non-magnetic" ceramics (e.g. Al_2O_3, TiO_2, AlN and Si_3N_4); this technique involves the alignment of particles in a strong magnetic field, typically $\geqslant 10$ T, during slurry consolidation, followed by sintering [12–15]. The alignment is achieved with the axis showing the highest magnetic susceptibility parallel to the magnetic field. In this novel method, the primary requirement is that the target material should be non-cubic (or anisotropically magnetic) and the suspension should be well dispersed with low viscosity. Compared with the conventional methods for texture development, SMFA has the attraction that it is not limited by particle morphology.

Using the SMFA method, we recently successfully prepared *c*-axis highly textured ZrB_2-based ceramics,

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which showed anisotropic properties [16]. As another important candidate material for aerospace applications, HfB_2-based composites appear more promising compared to ZrB_2-based composites; the Hf materials have higher melting point, hardness and thermal conductivity, etc. [17]. HfB_2 has the same hexagonal structure as ZrB_2; accordingly, the SMFA method should be effective for texturing HfB_2-based ceramics as well. This paper describes the texture development of HfB_2-based ceramics via SMFA and discussion is focused on the anisotropic oxidation behavior.

Commercially available SiC ($D_{50} = 0.45$ μm, purity: 98%) and synthesized HfB_2 were used as starting materials; HfB_2 powder was synthesized via modified carbothermal/borothermal reduction of HfO_2 at a relatively low temperature (1600 °C) [18]. In this study, HfB_2, HfB_2–5 vol.% SiC and HfB_2–20 vol.% SiC composites were prepared, and are designated as HB, HS5 and HS20, respectively. Distilled water was used as a dispersing medium and 1.5 wt.% (based on the total weight of the powders) polyethylenimine (PEI, $\overline{M_w} = 10{,}000$, Wako Pure Chemical Industries Ltd., Tokyo, Japan) was chosen as a dispersant. First, the synthesized HfB_2 powder was planetary milled for 8 h in a Si_3N_4 jar with Si_3N_4 balls to break up the agglomerates. Slurries with solid loading of 30 vol.% were then prepared by ball milling for 24 h in a plastic bottle with Si_3N_4 balls. After degassing, slip casting was performed using a glass case set on a plaster block with a 0.2 μm membrane filter in a 12 T magnetic field. The direction of the magnetic field was perpendicular to the direction of slip casting. After consolidation, the drying was performed in an oven at 50 °C for 24 h, followed by cold isostatic pressing at 392 MPa. The green bodies were calcined at 700 °C for 0.5 h in vacuum to burn out the polymer dispersant before sintering. The sintering was conducted in a spark plasma sintering (SPS) furnace at 1900 °C under a pressure of 50 MPa in vacuum. The final density was measured using the Archimedes method.

The crystallographic orientation and phase compositions were evaluated by X-ray diffraction (XRD, JDX 3500, Rigaku Co., Japan) using CuK_α radiation ($\lambda = 1.54178$ Å) and a scanning rate of 2 min^{-1} on different surfaces of the samples. The Lotgering orientation factor, $f(0\,0\,l)$, was used to evaluate the degree of texture in the green and sintered samples [16]. The hardness and fracture toughness were measured by the indentation method [19] using a load of 5 kg for 10 s on a polished surface and the reported value was an average of three measurements. After grinding to a 3 μm surface finish, the oxidation behavior of HS20 was studied in a box furnace. The sample was placed on a zirconia plate with minimal contact area and the two surfaces of SS and TS (defined below) were kept under the same environmental conditions. The furnace was heated at ~10 °C min^{-1} to 1600 °C and held for 10 min–10 h in stagnant air. The microstructures were observed by scanning electron microscopy (SEM, JSM-6500, Hitachi Co., Tokyo, Japan) along with energy-dispersive spectroscopy (EDS) for chemical analysis.

After planetary milling, the HfB_2 powder was well-dispersed and had an average particle size of 0.67 μm. The rheological behavior analysis showed that the 30 vol.% HfB_2 aqueous slurries almost maintained a constant viscosity of ~20 mPa s as the shear rate increased from 25 to 400 rpm and no shear thinning behavior appeared. Thus, the results confirmed that 1.5 wt.% PEI could stabilize the HfB_2 aqueous suspension efficiently.

The green bodies prepared by slip casting in the magnetic field showed obvious c-axis orientation, as revealed by the XRD patterns collected from the top and side surfaces of the green bodies (Fig. 1). The top and side surfaces, which are parallel and perpendicular to the magnetic direction, are denoted as TS

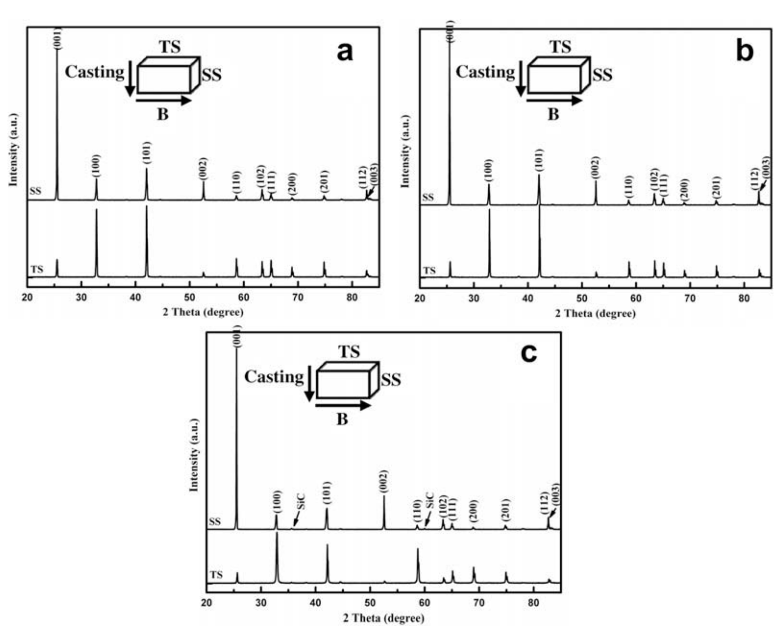

Figure 1. XRD patterns collected on the TS and SS surfaces of the green bodies: (a) HB; (b) HS5; (c) HS20.