

Spark-plasma sintering of ZrB_2 ultra-high-temperature ceramics at lower temperature via nanoscale crystal refinement

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Abstract

We have explored the feasibility of reducing the spark-plasma-sintering (SPS) temperature of additive-free ZrB_2 ultra-high-temperature ceramics (UHTCs) via crystal size refinement of the starting powder down to the low nanoscale. We found that under otherwise the same SPS conditions (75 MPa pressure, and 100 °C/min heating ramp) nanoscale ZrB_2 can be densified at temperatures about 450 °C lower than for the typical micrometre and submicrometre ZrB_2 powders, and at least 250 °C below the ultra-fine powder temperature. Furthermore, the nanoscale crystal refinement also promotes the production of fine-grained ZrB_2 UHTCs. We also found that elimination of the B_2O_3 impurities plays an important role in the complete densification. The unequalled sinterability of the nanoscale ZrB_2 powders highlights the need to use high-energy ball-milling for the comminution of the typical commercially available ZrB_2 powders.

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1. Introduction

Zirconium diboride (ZrB_2) is one of the few compounds that can be classed as ultra-high-temperature ceramics (UHTC).¹ Its favourable set of properties (among others, melting point 3250 °C, hardness 23 GPa, elastic modulus >500 GPa, electrical resistivity $\sim 10^{-5} \Omega \text{ cm}$, and thermal conductivity $>60 \text{ W m}^{-1} \text{ K}^{-1}$) makes ZrB_2 a very attractive candidate material in the world of extreme environment engineering for such applications as hypersonic flight, scramjet and rocket propulsion, atmospheric re-entry, refractory crucibles, and plasma-arc electrodes, to cite just some.^{2,3}

It is widely recognized by the ceramics community that one of the greatest obstacles to the successful development and implementation of ZrB_2 UHTCs is their poor sinterability, to which various intrinsic and extrinsic factors contribute. The former include the strong covalent bonding, the low self-diffusion coefficients, and the large particle sizes that together impose

severe kinetic restrictions on the diffusion,^{2–5} and among the latter is contamination by surface oxides that favours coarsening over densification.^{2,3,5} The strategy typically adopted to tackle the problem of ZrB_2 's poor sinterability is to introduce sintering additives (either liquid phase formers, or reactive agents) together with the refinement of the starting powders by ball milling (normally in the form of wet attrition milling) down to the submicrometre scale.^{2,3} Regarding this latter point, in a recent study we investigated in detail the spark-plasma sintering (SPS) kinetics of ZrB_2 without additives as a function of the crystal size from a couple of micrometres down to a few nanometres (achieved by high-energy ball-milling), and concluded that the breakthrough needed to obtain ZrB_2 powders with unmatched sintering behaviour requires going beyond the simple refinement to the submicrometre scale, and that it is nanoscale crystal refinement which offers an unprecedented opportunity to significantly reduce the sintering temperature of ZrB_2 .⁶ This latter expectation, which until now has not been confirmed experimentally, arises from the observation that only nanoscale crystal refinement promotes considerably greater grain-boundary diffusion at much lower temperatures in ZrB_2 ,⁶ and this is the mass transport mechanism responsible for the material's densification. Elucidating this pending issue of the role of the crystal refinement

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scale in reducing the sintering temperature of ZrB_2 is thus a fundamental question requiring a prompt experimental response not only because lower-temperature sintering is one of the long sought for objectives in the field of UHTCs, but also because, if confirmed, it could have important implications regarding the comminution practices employed by the UHTC community.

With this in mind, the objective of the present work is to extend the previous kinetics study by conducting the first extensive set of SPS experimental measurements explicitly designed to explore by means of a detailed densification study the question of the crystal refinement scale in reducing the sintering temperature of ZrB_2 . For this proof-of-concept study, we spark-plasma sintered six ZrB_2 powders with varied crystal sizes in the micrometre, submicrometre, and nanometre scales, without the introduction of sintering additives to thus investigate crystal-size effects without this interference. The details of the experiments and the major findings are described below.

2. Experimental procedure

The six ZrB_2 powders used in the present study were taken from the broader set of ZrB_2 powders utilized in the previous SPS kinetics study.⁶ We shall thus here only summarize their preparation protocol. Briefly, the coarse powder with an average crystal size of 2 μm was obtained from a commercial source (Grade B, H.C. Starck, Germany). The powders with submicrometre and ultra-fine crystals (~ 500 and 160 nm, respectively), and the three powders with nanometre crystals (~ 70 , 25, and 10 nm) were prepared by subjecting the commercial ZrB_2 powder to high-energy ball-milling in air in a shaker mill (Spex D8000, Spex CertiPrep, USA) for different times as required to reach the desired average crystal size,⁶ using WC balls as milling media with a ball-to-powder weight ratio of 4:1. More details of the preparation and characteristics of these ZrB_2 powders can be found elsewhere.^{6–9} However, it is also important to mention here that to prevent the powder contamination during high-energy ball-milling, a first milling cycle was carried out with the objective of depositing a thin film of ZrB_2 on the surface of the container and of the balls, and the resulting powder was thrown away. Then, the milling cycle was repeated utilizing the same container and balls, using the resulting powder for this study. With this milling procedure, (i) WC contamination was only detected in the powder ball-milled for 180 min, but not in the rest of powders, and in a minimal amount of ~ 0.9 vol% according to the Rietveld analysis of the X-ray diffraction (XRD) pattern collected with a high-resolution diffractometer, and (ii) no Fe contamination was detected in any of the ball-milled powders.⁹ The direct measurement carried out here through the weight loss of the balls indicates however that the contamination by WC is indeed lower than 0.5 vol%. This WC contamination degree is about 4–6 times lower than that introduced typically with other common milling procedures, which is due to the combination of many factors such as the two-milling protocol adopted here, the low charge ratio (i.e., the ball-to-powder weight ratio) of 4 used in this study, and the more than likely differences in other milling parameters (for example size, density, and surface roughness of the WC balls, wettability of the ZrB_2 powder towards the WC

balls at the milling condition, extent of filling of the container, and milling atmosphere and environment, to name a few), as well as to the fact that the shaker mills operate with compressive forces whereas the attritors and the conventional mills function with a combination of shear and compressive forces.

The different ZrB_2 powders were individually loaded into 12-mm diameter graphite dies lined with graphite foil and surrounded by a 1 cm thick graphite blanket to minimize heat loss, and were then spark-plasma sintered (Dr. Sinter SPS-2050, Sumitomo Coal Mining Co., Japan) in a dynamic vacuum atmosphere (i.e., 6 Pa). The graphite die has a wall thickness of 9 mm, and has a hole machined in its central region of 2.5 mm depth. Two types of SPS cycles were implemented: (i) heating at 100 °C/min up to the target temperature under 75 MPa pressure, and soaking at these conditions of temperature and pressure for a certain time (henceforth termed the simple SPS cycle), and (ii) heating at 100 °C/min up to the target temperature under 20 MPa pressure, followed by soaking at the target temperature under 75 MPa pressure for a certain time (henceforth termed the complex SPS cycle). Details of another SPS cycle used only sporadically will be given along with the corresponding results. For each ZrB_2 powder, the target temperature (measured by an optical pyrometer focused on the interior of hole of the graphite die^c) was considered as a variable, setting its values in accordance with the reference of its transition temperature from surface diffusion to grain-boundary diffusion (T_{GBD}) determined in the previous kinetics study⁶ (i.e., ~ 1550 , 1650, 1740, 1765, 1785, and 1810 °C for the crystal sizes of 10, 25, 70, 160, 500, and 2000 nm, respectively). After the completion of the SPS cycle, the load was released and the electrical power was shut off to allow rapid cooling (in 1–2 min) to room temperature. The SPS furnace is equipped with a dilatometer of resolution better than 0.001 mm, connected to a computer to log the shrinkage curves. These curves were corrected for the expansion of the graphite parts (i.e., die, punches, and spacers) to give the real shrinkage curves of the powders themselves, and were then converted to densification curves by considering the relative densities of the sintered samples. The sintered materials were examined by scanning electron microscopy (FE-SEM; S4800-II, Hitachi, Japan) to validate the porosity data, and also to observe their microstructure. The SEM observations were done on fracture surfaces, at 5 kV without metal coating.

3. Results and discussion

The T_{GBD} data obtained in the previous SPS kinetics study⁶ suggested that the ZrB_2 nano-powder with 10-nm crystals would exhibit the lowest sintering temperature of all the powders to be

^c It is a well-known fact in SPS that the actual temperature inside the specimen is greater than the temperature measured by the optical pyrometer. However, a previous SPS study on HfB_2 and HfC ¹⁰, which have both thermal and electrical conductivities similar to ZrB_2 , has shown that for the same graphite die and experimental configuration than used here the temperature mismatch is in the range 100–125 °C at 1700 °C and around 250 °C at 2200 °C. With this information, the temperature mismatch up to 1625 °C is estimated to be not greater than 50–75 °C.

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