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Preparation of nano-size ZrB_2 powder by self-propagating high-temperature synthesis

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Abstract

Preparation of nano-size ZrB_2 powder by SHS has been investigated. Zr and B elemental powders were mixed with 10–50 wt.% NaCl, and prepared pellets were reacted under argon. Adiabatic temperatures were calculated by HSC software. Increasing NaCl content led to a continuous decrease in adiabatic temperatures and reaction wave velocity. Products were subjected to XRD, SEM and FESEM analyses. Average crystallite size of ZrB_2, which was 303 nm without NaCl, decreased to 32 nm with 40% NaCl addition. Distinct decrease in ZrB_2 particle size was also observed from SEM analyses. 30% NaCl addition was found to be optimum for ensuring a stable SHS reaction and providing the formation of nano-size ZrB_2 particles. It was revealed from particle size distribution measurements that ZrB_2 powder obtained by 30 wt.% NaCl addition contained particles mostly finer than 200 nm. A mechanism, similar to solution-precipitation was proposed for the particle size refining effect of NaCl.

Keywords: Powders-chemical preparation; Grain size; Borides; Refractories; SHS

1. Introduction

Zirconium diboride (ZrB_2) is one of the most stable borides.[1] It is in ultrahigh-temperature ceramics class with a melting point of as high as 3050 °C. It has outstanding wear and corrosion resistance, high heat and electrical conductivity, and high hardness.[2] Possible applications of ZrB_2 bearing ceramics involve cutting tools, crucibles for molten metal handling, high-temperature electrodes and high-temperature spray nozzles.[1–3] ZrB_2 has been produced through various methods starting from elemental Zr or its oxide, ZrO_2. Reaction between Zr and B elemental powders, metallothermic reduction of ZrO_2 and B_2O_3 by magnesium or boron,[4,5] fused salt electrolysis,[6] mechanochemical synthesis and combustion synthesis[7] are some of the methods.

In the last decade, there has been a growing appeal on the production of ceramic powder having ultrafine or nano-sized particles and nano-grained sintered particles. Exceptional properties such as excellent sinterability of nano-powder and improved mechanical properties of the formed nano-grained particles are the motivation for this appeal.[8,9] In this respect SHS is quite challenging due to the high temperatures involved that lead to considerable grain coarsening in the product. Formation of nano-sized powder through SHS has been investigated by various groups.[10–13] For this purpose, effect of addition of diluents into the reactants, which are mostly preformed powder of the same kind as the expected products, has been investigated.[13] However, the simple use of the product as a diluent did not provide sufficient grain refinement and the formation of submicron size particles is not achieved in most cases.[12] The use of volatile species as diluent has been recently suggested as an alternative method. Specifically, in the case of the SHS leading to the formation of borides and carbides, NaCl has been employed.[10–12] Nanometric TiB_2 powder was reported to be produced through SHS using H_3BO_3, Mg and TiO_2, and NaCl as the diluent.[11] Grain refinement, due to addition of NaCl, has also been reported in the combustion synthesis of TiC from Ti and C powders.[12] Starting powder mixtures containing H_3BO_3, ZrO_2 and Mg have

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been used for the synthesis of ZrB_2 by SHS and it was stated that addition of NaCl resulted in a decrease in the particle size of the formed ZrB_2.[10] However, utilization of oxide starting materials not only results in formation of side products like magnesium borates that require further removal steps such as acid leaching; but also decrease the efficiency of the reactions.[7,14] Additionally, residual ZrO_2 remains in the products in spite of the precautions including utilization of sub-stoichiometric amount of ZrO_2 in the starting mixture.[15] Unreacted ZrO_2 in the products cannot be removed from ZrB_2 due to its insolubility in acid solutions.[7,15] Consequently, starting from elemental Zr and B powders was found to be more advantageous and is the topic of the present study.

In the present study, SHS preparation of nano-size ZrB_2 powder has been investigated from Zr and B elemental starting powders with NaCl additions. Increased surface area of the nano-size powder obtained by this technique is expected to provide sintering at lower temperatures and also bring about better mechanical properties of the sintered parts, as compared to micron-scale powder.[8]

2. Experimental procedure

Preparation of ZrB_2 from mixtures of elemental Zr (Alfa Aesar, 95%), elemental amorphous B (Alfa Aesar, 90%) and NaCl (Merck Chemicals) through SHS has been investigated. According to SEM observations Zr powder was composed of particles having 1–3 μm size and B particles were smaller than 1 μm.[16] Starting materials in powder form were weighed in stoichiometric proportions according to reaction (1) then dry mixed and ground thoroughly in an agate mortar and pestle. NaCl (Merck Chemicals) was added to Zr–B mixtures in 10–50% weight ratio with 10 wt.% increments. The powder mixtures were pressed in the form of 10 mm high cylindrical pellet with a diameter of 8 mm and % theoretical density of 50–55.

Two reasons were considered for the utilization of NaCl as a diluent. First, NaCl does not react with the starting materials and it is believed to have the possibility to develop a layer among forming ZrB_2 crystals thereby preventing their growth by separating them from each other. Second reason is the ease in separation of NaCl from the products, due to its high solubility in water.[12]

Adiabatic temperatures of the mixtures containing increasing amounts of NaCl according to reaction (1) were calculated by the HSC software.[17]

$$Zr + 2B + (x)NaCl = ZrB_2 + (x)NaCl \quad (1)$$

The reacting pellets were placed inside a stainless steel reactor and the SHS process was ignited by an electrically heated tungsten coil placed at a distance of 1.0 mm from the top surface of the pellet. All experiments were conducted in a high purity argon (99.998%) atmosphere. Video recordings of the reaction were used to measure the reaction velocity.

Products obtained after SHS reactions were subjected to X-ray powder diffraction (XRPD) analyses (Bruker D8 Advance) with Cu Kα radiation. Average crystallite size of ZrB_2 crystals obtained by using various amounts of NaCl was calculated according to Scherrer formulae, making use of the widths of the peaks on XRPD patterns.[18] In these calculations, the measured peak widths were corrected by removing the instrumental line broadening, which was obtained by utilizing a BaF_2 reference sample.[18] Particle size and morphology of the products were examined by scanning electron microscope (SEM, Cambridge Stereoscan 200). In order to remove the NaCl from ZrB_2 particles, product pellets were crushed and ground in an agate mortar and pestle. NaCl in the obtained powder was dissolved in distilled water at room temperature and the slurry was centrifuged at 3000 rpm (Misral 2000) for 3 min to separate the fine ZrB_2 particles by sedimentation. Filtering could not be utilized for solid–liquid separation because of the possibility of loosing fine particles, which pass through the filter. After decantation, the residue containing sediment ZrB_2 particles were dried. They were subjected to further SEM (Zeiss Leo 1430), field emission scanning electron microscope (FESEM, JEOL 6335F), and particle size distribution analyses (Malvern Instruments, Zetasizer Nano-ZS).

3. Results and discussion

Adiabatic temperatures of the Zr–B mixtures containing 0–50 wt.% NaCl according to reaction (1) were calculated by HSC software, and they are presented in Fig. 1. The calculated adiabatic temperature for the undiluted reaction (1) is equal to the ZrB_2 melting point (3050 °C). The adiabatic temperature was not lowered for NaCl additions up to 10 wt.% although a decrease in the fraction of molten ZrB_2 in the product should occur as well as a decrease in the actual 'real temperature' which is predictably lower than the adiabatic value due to heat losses and therefore not thermodynamically bound to the melting point

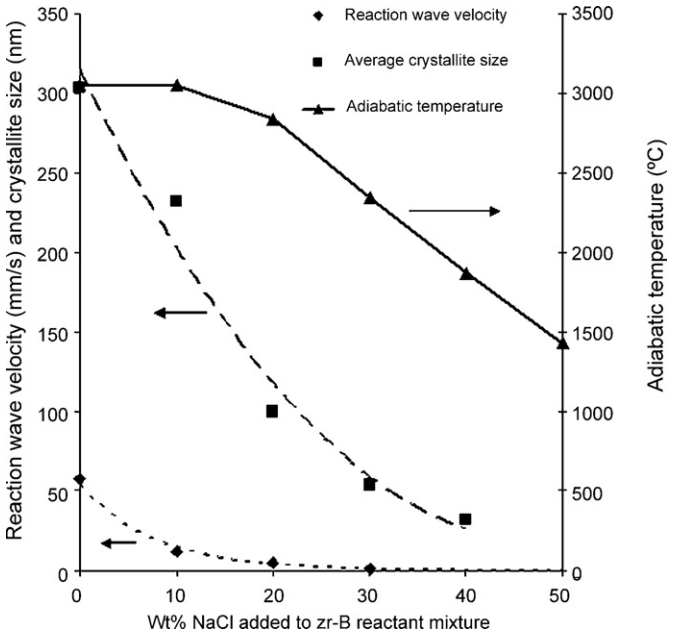

Fig. 1. Adiabatic temperatures, propagation velocity of the reaction wave, and average crystallite size of the formed ZrB_2.