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Titanium diboride ceramics for solar thermal absorbers

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ABSTRACT

Titanium diboride (TiB_2) is a low-density refractory material belonging to the family of ultra-high temperature ceramics (UHTCs). This paper reports on the production and microstructural and optical characterization of nearly fully dense TiB_2, with particular interest to its potential utilization as novel thermal solar absorber. Monolithic bulk samples are produced starting from elemental reactants by a two-step method consisting of the Self-propagating High-temperature Synthesis (SHS) followed by the Spark Plasma Sintering (SPS) of the resulting powders. The surface of obtained samples has-been characterized from the microstructural and topological points of view. The hemispherical reflectance spectrum has been measured from 0.3 to 15 μm wavelength, to evaluate the potential of this material as solar absorber for future concentrating solar plants.

1. Introduction

Solar thermal technology is recognized among the most promising renewable energy sources in the future. However, physics states that the efficiency of thermal cycles increases with temperature. For Concentrating Solar Power (CSP) plants, temperatures are usually limited to 800 K or lower values [1,2], because of criticalities of the sunlight receiver element. For this reason, the main challenge for CSP technology advance is to find a receiver material able to withstand to operating temperatures higher than those allowed by current systems, while showing a high sunlight absorption as well as low re-radiation losses.

Recently, the use of carbide and boride materials belonging to the class of ultra-high temperature ceramics (UHTCs) was proposed for novel solar receivers operating at higher temperature than standard systems [3–11]. In fact, it was demonstrated that this material family shows intrinsic spectral selectivity which makes them appealing for sunlight absorption up to very high temperatures with reduced thermal losses [3–11]. Moreover, these materials also have well known characteristics such as ultra-refractoriness, good chemical stability at high temperature, good thermal conductivity, hardness and superior mechanical properties [12–15], which have implied their successful use for aerospace, military and, in general, for all applications where high temperatures conjugate extremely demanding performances [12–18].

In this regard, titanium diboride (TiB_2) has been studied in the literature for its high hardness, low density, high melting point exceeding 3000 °C, high wear resistance, high thermal and electrical conductivity and low thermal expansion coefficient [19,20]. All these properties made this system attractive for ballistic armors, wear parts, cutting tools, etc. [21]. TiB_2 is also widely used in combination with other oxide and non-oxide ceramics, to increase strength and fracture toughness of the matrix [22–26].

Bulk monolithic TiB_2 materials are typically obtained by classical Hot-Pressing (HP) either starting from commercially available [27–34] or lab-made powders [32,35–40].

In general, regardless the method used to synthesize the powders to be sintered, temperature levels equal or exceeding 1800 °C and processing times on the order of hours are needed when using the HP approach to achieve densities levels above 95% of the theoretical value.

This holds also true when the TiB_2 powders to be hot-pressed were prepared by Self-propagating High-temperature Synthesis (SHS) [35]. Indeed, relative densities of 98% or more were reached only when operating at temperatures equal or higher than 1800 °C. The only exception is represented by the study conducted by Peters et al. (2009) [32], where 98.6% and 98.9% dense products were obtained by HP at 1500 °C (106 MPa, 1 h) when starting from commercial TiB_2 powders mechanically treated for 30 min or using elemental reactants milled for 6 h, respectively. However, iron contamination from milling media, i.e.

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0.86 and 1.55 wt%, respectively, was found in the milled powders.

Alternative sintering methods such as Hot Isostatic Pressing (HIP) [41], high-pressure sintering [42], high-pressure self-combustion synthesis [42], microwave sintering [43] and Spark Plasma Sintering (SPS) [44–50] have been also recently proposed for the fabrication of dense TiB_2 materials.

In this context the SPS technique, also referred to as Pulsed Electric Current Sintering (PECS), where the powders undergoing consolidation are rapidly heated by an electric pulsed current flowing through the conductive die and a mechanical load is simultaneously applied along the axial direction, was demonstrated to be particularly promising [51]. The various studies conducted so far clearly evidenced the capability of the latter technology to lead to highly dense TiB_2 products under relatively milder sintering conditions, with respect to the other consolidation methods previously mentioned.

Despite the high interest in TiB_2, its optical properties are, to the best of our knowledge, totally unexplored, as far as bulk materials are concerned. Indeed, the only literature source is limited to the spectral range from 0.4 to 1.0 μm and is referred to thin films [52].

The present investigation is first aimed to the optimization of the SPS conditions for the full densification of additive free TiB_2 powders synthesized by SHS. In this regard, it should be noted that the combination of the SHS and the SPS techniques was recently exploited for the fabrication of other UHTC systems, both in monolithic [11,53,54] and composite forms [55–59].

Subsequently, in the present work we report on microstructure, topological characterization, and hemispherical reflectance spectra in the wavelength range 0.3–15 μm of TiB_2 produced by the two-steps SHS-SPS technique, with the aim to evaluate the material potential for solar absorber applications.

2. Experimental

Commercially available titanium (Sigma-Aldrich, St. Louis, Mo, USA, < 45 μm, 99.98% purity), and amorphous boron (Sigma-Aldrich, St. Louis, Mo, USA, < 1 μm, ≥95% purity) were used as starting powders for the synthesis of $TiB_2$by SHS according to the following stoichiometry:

$$Ti + 2B \rightarrow TiB_2 \quad (1)$$

Reactants mixing was carried out in a SPEX 8000 (SPEX CertiPrep, USA) shaker mill for 20 min using plastic vials and six zirconia balls with 2 mm diameter. Approximately 8 g of the obtained mixture was subsequently cold-pressed to obtain cylindrical pellets with a diameter of 10 mm and height of 30 mm, to be reacted by SHS under Ar atmosphere inside a closed stainless steel vessel. The reaction was activated at one pellet end using an electrically heated tungsten coil. A two-color pyrometer (Ircon Mirage OR 15-990, USA) was used for measuring the combustion temperature during SHS. The resulting porous material was reduced in powder form by milling about 4 g of it for 20 min using the SPEX 8000 device with a ball-to-powder weight ratio of 2. A laser light scattering analyser (CILAS 1180, France) was utilized to determine particle size of obtained powders. Surface area was obtained through BET measurements performed using a Micromeritics ASAP 2020 equipment (Micromeritics, Georgia, USA).

Consolidation of SHS powders to produce TiB_2 cylindrical disks (about 14.7 mm diameter, and 3 mm thickness) for optical characterization was carried out by Spark Plasma Sintering (SPS 515S model, Fuji Electronic Industrial Co., Ltd., Kanagawa, Japan). This apparatus consists of a uniaxial press, able to provide up to 50 kN loads, combined with a DC pulsed current generator (10 V, 1500 A, 300 Hz). A sequence of 12 ON pulses followed by 2 OFF pulses is adopted, with the characteristic time of single pulse equal to about 3.3 ms.

About 3 g of powder mixture were placed inside the graphite mould (outside diameter, 30 mm; inside diameter, 15 mm; height, 30 mm). Commercial TiB_2 powders (Sigma-Aldrich, St. Louis, Mo, USA, cod. 33628-9, < 10 μm) were also processed by SPS for the sake of comparison. A graphite foil (99.8% pure, 0.13 mm thick, Alfa Aesar, Karlsruhe, Germany) was inserted between the internal surfaces of the die and the top and bottom surface of the sample and the plungers, to facilitate sample release at the end of the SPS process. Both die and plungers were made of AT101 graphite (Atal Srl., Italy). In addition, with the aim of minimizing heat losses by thermal radiation, the die was covered with a layer of graphite felt. The die was then placed inside the reaction chamber of the SPS apparatus and the system was evacuated down to 10–20 Pa.

During SPS experiments, the current was increased from zero at a constant rate up to a maximum intensity value (I_M) in 10 min. The latter level was maintained for a given holding time (t_D). The effects of I_M and t_D on powders densification were investigated in the ranges 800–1100 A and 0–20 min, respectively. The mechanical pressure (P) was kept constant to 60 MPa during the entire sintering process. The temperature of the external surface of the graphite mould was measured by an infrared pyrometer (Ircon Mirage OR 15-990, USA) focused on the lateral surface of the die. Each SPS run was repeated at least twice.

The relative density of the polished sintered samples was determined by the Archimede's method, using high purity distilled water as buoyant, at 20 °C. Weighting of the specimen was carried out taking advantage of a Ohaus Explorer Pro (Ohaus Corporation, NJ, USA) analytical balance (± 0.0005 g precision), using the theoretical value of 4.5 g/cm^3 as reference for TiB_2 [19].

Phase identification was performed using a X-rays diffractometer (Philips PW 1830, Almelo, The Netherlands)with Cu Kα radiation (λ = 1.5405 Å) and a Ni filter. A Rietveld analytical procedure was employed to estimate the relative amount of the phases present in SHS-obtained powders [60].

The microstructure of end products was examined by High-Resolution Scanning Electron Microscopy (HRSEM, mod. S4000, Hitachi, Tokyo, Japan), coupled with energy dispersive X-rays spectroscopy (EDS) (Thermo Fisher Scientific, Waltham, MA, USA). A ZEISS EVO LS 15 apparatus (Carl Zeiss Microscopy GmbH, Jena, Germany) equipped with a LaB_6 filament as electron source was also used for microstructural characterization.

The surface texture characterization was carried out with a non-contact 3D profilometer (Taylor-Hobson CCI MP, Leicester, UK) equipped with a 20X magnification objective lens. For each samples, two distinct areas (0.08 × 1 cm^2) were scanned along two orthogonal directions and the obtained 3D data were processed with the software Talymap 6.2 (Taylor-Hobson, Leicester, UK). In this work, the texture characterization was performed in terms of areal field parameters, as 3D parameters can provide a more comprehensive information about surface texture with respect to 2Dones. Thus, the evaluation of 3D texture parameters [61] was carried out on the two datasets collected for each sample, after denoising (median filter 5 × 5), form removing, S-filtering and after applying an areal robust gaussian L-filter (L-filter = 0.8 mm).

Hemispherical reflectance was measured using a double-beam spectrophotometer (Perkin Elmer Lambda900) equipped with a Spectralon®-coated integration sphere for the 0.25–2.5 μm wavelength region and a Fourier Transform spectrophotometer (Bio-Rad "Excalibur") provided with a gold-coated integrating sphere and a liquid nitrogen-cooled detector for the range 2.5–15.0 μm.

3. Results and discussion

3.1. Powders synthesis and characterization

A recent study addressed to the formation and simultaneous consolidation of ZrB_2 by reactive SPS evidenced the possible problems arising when the synthesis reaction of strongly exothermic systems takes place under the combustion regime inside a closed graphite