Titanium diboride ceramics for solar thermal absorbers

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Abstract

Titanium diboride (TiB₂) 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 TiB₂, 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.

Keywords: Optical properties; solar absorbers; borides; TiB₂; Self-propagating High-temperature Synthesis (SHS); Spark Plasma Sintering (SPS).

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, 1h) when starting from commercial TiB$_2$ powders mechanically treated for 30 min or using elemental reactants milled for 6h, respectively. However, iron contamination from milling media, i.e. 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 1.0μm 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 TiB₂ by SHS according to the following stoichiometry:

\[ \text{Ti} + 2 \text{B} \rightarrow \text{TiB}_2 \] (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 TiB₂ 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 TiB₂ 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 (I₀) in 10 min. The latter level was maintained for a given holding time (t₀). The effects of I₀ and t₀ 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/cm³ as reference for TiB₂ [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 LaB₆ 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 x 1 cm²) 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 5x5), 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 2.5-15.0μm.

3. Results and discussion

3.1. Powders synthesis and characterization

A recent study addressed to the formation and simultaneous consolidation of ZrB₂ 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 mould [62]. This feature holds also true when considering titanium diboride, which is characterized by a very high formation enthalpy, i.e. (−ΔH_f^0) = 323.8 kJ/mol [63]. To overcome such drawbacks, in the present work synthesis and consolidation of TiB₂ are carried out in two separate steps, the first one consisting in obtaining the boride phase by SHS according to reaction (1).

Upon ignition, the generated combustion front exhibited a self-sustaining character with a measured maximum temperature of about 2200°C. As shown in Figure 1a, where the XRD pattern of the resulting product is reported, during SHS the elemental reactants are almost completely transformed into hexagonal TiB₂. Small amounts of cubic and orthorhombic TiB were also detected by the XRD analysis, whereas no residual titanium was found. More specifically, the Rietveld analysis provided that the relative amount of TiB₂ in the SHS-obtained product was above 96 wt.%. As recently reported in the literature to justify the presence of unreacted Hf and Zr, respectively, in HfB₂ [59] and ZrB₂ [58] ceramics obtained by SHS, the formation of TiB is likely due to some deficiency of B in the reaction environment. This could be caused by some expulsion of the latter reactant during the evolution of the SHS reaction and/or by their partial consumption to reduce some oxides often present on the starting powders surface. Irrespective of the specific motivation, the
reactants proportion required to produce TiB₂ according to Eq. (1) is not fulfilled, so that the following reactions might also take place [64]:

\[
\begin{align*}
\text{Ti} + \text{B} & \rightarrow \text{TiB} \quad (2) \\
\text{Ti} + \text{TiB}_2 & \rightarrow 2\text{TiB} \quad (3)
\end{align*}
\]

In this regard, it should be noted that the use of some extra boron, i.e. the boron-to-metal B/Me (Me=Hf, Zr) atomic ratio in the range 2.1-2.2, was found beneficial to decrease the amounts of residual reactants and secondary phases in HfB₂ [59] and ZrB₂ [58] products. On the other hand, all the attempt made along the same direction did not determine an improvement of the composition of the TiB₂-based ceramic synthesized in this work. Nonetheless, the reasonably high purity level achieved with an initial B/Ti molar ratio equal to 2 was considered satisfactory for the scope of the present investigation.

The obtained SHS products were characterized, after being pulverized and before their consolidation, by laser light scattering analysis, SEM and BET measurements. Granulometry data indicated that particles size was less than 20 μm, with an average value of 7.56±0.05 μm. Such result is consistent with SEM observations (cf. Figure 1b), which confirmed that each individual particle is generally smaller than 10 μm and most of them are few microns in size. In addition, BET analysis provides a surface area of 1.28 m²/g for TiB₂ powders produced in the present work. The latter value is slightly higher compared to those of ZrB₂ and TaB₂ powders recently synthesized following the same processing route, i.e. 1.09 and 1.16 m²/g, respectively [58].
Figure 1. XRD pattern (a) and SEM micrograph (b) of TiB$_2$ powders obtained by SHS after 20 min ball milling.

3.2. Sintering optimization and microstructure of dense samples

The identification of the optimal SPS conditions for complete consolidation of TiB$_2$ powders produced by SHS was obtained investigating the effect of current intensity and holding time, while maintaining the applied pressure constant to 60 MPa. The obtained data are plotted in Figure 2a and Figure 2b, respectively.

Figure 2. Effect of (a) mean current intensity ($t_D$ = 20 min, $P$=60 MPa) and (b) dwell time ($I_M$= 950 A, $P$=60 MPa) on the density of TiB$_2$ bulk products obtained by SPS.

As shown in Figure 2a, an increase of the current intensity in the range of 800-950 A, which corresponds to a temperature rise approximately from 1400 to 1530°C, produces a significant
improvement in powder densification. In particular, sintered products with relative densities of 99.45% (average value) were obtained when \( I_m = 950 \) A was applied for 20 min. A further increase of the applied current to 1000 A or higher levels \((T\geq1575^\circ C)\) leads to full consolidation.

As far as the study of the influence of holding time is concerned, the obtained results (Figure 2b) evidenced that the major effect is shown when processing powders are maintained at the highest current level for the first 5 min, where the relative density correspondingly increased from 76% to above 95% of the theoretical value. This effect proceeds, but at a lower rate, as sintering time was prolonged to 20 min. Based on the obtained results, the selected SPS conditions to produce nearly fully dense TiB\(_2\) samples for optical measurements are \( I_m = 950 \) A, \( t_0 = 20 \) min, and \( P = 60 \) MPa. Correspondingly, the maximum temperature level measured during the sintering process was 1530±20°C. For the sake of comparison, the latter condition was also applied to process by SPS commercially available TiB\(_2\) powders. The resulting sintered samples were highly porous, i.e. relative density of 80±3%, which is consistent with similar results reported in the literature for such system when operating with sintering temperature of about 1500°C [44]. It should be noted that the condition adopted in this work is relatively milder, not only with respect to those required when considering the classical HP approach, as mentioned in the Introduction, but also when the comparison is extended to previous studies involving SPS-like apparatuses for the fabrication of dense titanium diboride. For instance, 97.6% dense samples were obtained from commercial TiB\(_2\) powders sintered by SPS at 1800°C for 5 min [44]. Even lower density levels, i.e. slightly higher than 80% [47] and 96% [50], were achieved at 1800°C and 2000°C, respectively, in similar studies. The characteristics of the starting powders apparently affect in a significant manner their sintering ability as well as the characteristics of resulting bulk product. A peculiar behavior was recently observed during the SPS process of TiB\(_2\) powders previously synthesized by borothermal reduction of TiO\(_2\) [46]. Indeed, in the cited reference it was unexpectedly observed that the relative density of sintered materials was lowered from 97.8 to 96.1% as the sintering temperature was increased from 1400 to 1500°C. It was postulated that this feature could be associated to the formation of a second phase (TiB) during SPS, which consumes TiB\(_2\) thus leading to void formation. In contrast, as clearly shown in Figure 2a, an increase of the applied current above 950 A does not correspond in the present study to a decrease of the product density, as observed by Mukhopadhyay et al. [46].

As far as favourable densification conditions required in the present work are concerned, they can be ascribed not only to the use of the efficient SPS technique but also to the characteristics of SHS powders, which apparently display a high sintering ability. The latter characteristic was clearly evidenced for the TiB\(_2\) system by Khanra et al. (2005) [65], who compared the sintering behavior displayed by SHS-treated powders obtained from TiO\(_2\), boric acid and Mg, with respect to that of commercially available products. In particular, about 97 and 86% dense materials were respectively obtained when the two kind of powders were processed for 30 min at 1950°C in a furnace. This outcome is consistent with the results more recently reported in other studies involving the consolidation by SPS of other borides-based UHTCs [56, 62]. Such characteristics in the powders can be associated to the high defect concentration generated by the severe heating and cooling rate conditions (up to on the order of \(10^5\) K/min) encountered during the evolution of the SHS process [66]. In addition, it is also likely that the small amount of TiB present in the powders synthesized in this work (cf. Figure 1a) might also help to promote their consolidation.

The microstructures of polished and fractured surfaces of dense products were first examined by SEM and two representative micrographs are shown in Figure 3(a) and 3(b), respectively.

Surprisingly, in spite of the rather high relative density achieved, the material surface (Figure 3(a)) appears to contain a not negligible amount of residual porosity (black areas). Nonetheless, the
fracture surface reported in Figure 3(b) provides a completely different picture, as the bulk of the sample is almost fully dense with only few isolated pores. The most likely explanation for justifying the presence of observed surface voids is that a certain amount of small TiB$_2$ grains was removed during the polishing step. The latter statement is in agreement with the motivation recently provided by Sabahi Namini et al. (2015) [67] to explain the presence of pores on the surface of highly dense SiC-reinforced TiB$_2$ samples produced by hot-pressing.

The XRD analysis performed on the sample surface shown in Figure 3(c) evidenced for the SPS-treated product a composition similar to that of initial SHS powders, with TiB$_2$ as a major phase and small amounts of orthogonal and cubic TiB as by-products. The latter outcome is also confirmed by EDS analysis. Regarding grains size, Figure 3(a)-3(b) indicate that they generally range from few microns up to 15 µm, at most.

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**Figure 3.** (a) Back-scattered SEM micrograph of the polished surface, (b) secondary electron image of the fracture surface, and (c) X-ray diffraction pattern of TiB$_2$ product obtained by SPS (I$_m$= 950 A, t$_D$= 20 min, P=60 MPa).
3.3. Topological characterization

The surface texture of a material has important effects on optical properties such as reflectance, absorbance and light scattering. Therefore, in order to investigate the intrinsic optical properties of the synthesized materials and evaluate the contributions arising from surface morphology, each sample was characterized from a topological point of view before performing optical measurements. The surface texture was characterized by evaluating the areal surface parameters on the SL surface (equivalent to the roughness surface) obtained by applying an L-filter on the SF surface. The average values of the 3D surface texture parameter measured on the studied samples are reported in Table 1, along with the corresponding standard deviation. For a better evaluation of TiB$_2$ properties, two other previously investigated fully dense borides (TaB$_2$ and ZrB$_2$) [11] were considered as a term of comparison.

The TaB$_2$ sample showed values of $S_a$ and $S_q$ higher with respect to those measured on the other borides. Since these parameters are related to the surface roughness ($S_a$) and the way in which light is scattered from a surface ($S_q$), this result indicates a slightly higher surface energy of TiB$_2$ compared to TiB$_2$ and ZrB$_2$ samples [68]. All the borides are characterized by close values of both $S_{sk}$ and $S_{ku}$ parameters. These parameters are related to the type of defects and to their distribution on the samples surface. In particular, negative values of $S_{sk}$ indicate the predominance of pores or valleys structure, while large and positive values (>3) of $S_{ku}$ indicate the presence of a certain amount of high peaks or deep valleys/pores. These parameters provide useful information about the optical characteristics of a surface, in fact, negative values of $S_{sk}$ and high values of $S_{ku}$ indicate a surface that can trap the incident photons and absorb them because of the multiple reflections from both sides of the pores/valleys.

The obtained results show that the studied borides have a quite similar surface texture, characterized by the prevalence of pronounced pores or valleys ($S_v$, maximum deep, in the range of 10-13 µm) and little amount of small peaks ($S_p$, maximum height, in the range of 1.4 – 3 µm).

| 3D parameters | 3D description                                 | TiB$_2$       | TaB$_2$       | ZrB$_2$       |
|---------------|-----------------------------------------------|---------------|---------------|---------------|
| $S_a$ (µm)    | Arithmetic mean height of the S-L Surface     | 0.237±0.057   | 0.440±0.042   | 0.211±0.028   |
| $S_q$ (µm)    | Root mean square height of the S-L Surface    | 0.50±0.20     | 0.884±0.069   | 0.44±0.11     |
| $S_{sk}$      | Skewness of the S-L Surface                   | -7.2±2.2      | -5.8±1.9      | -7.1±1.1      |
| $S_{ku}$      | Kurtosis of the S-L Surface                   | 94±40         | 51±29         | 83±15         |
| $S_p$ (µm)    | Maximum peak height in the S-L Surface        | 1.44±0.47     | 1.46±0.27     | 2.9±2.0       |
| $S_v$ (µm)    | Maximum pit height of the S-L Surface         | 10.6±3.7      | 12.9±3.0      | 9.6±2.6       |
| $S_z$ (µm)    | Maximum height of the S-L Surface             | 12.0±4.1      | 14.3±2.8      | 12.5±4.6     |

3.4. Optical properties

Figure 4 shows the acquired spectrum of TiB$_2$, together with those of TaB$_2$ and ZrB$_2$ for comparison [11]. The reflectance of TiB$_2$ nearly monotonically increases with wavelength, with
values growing from 33% to 60% as the wavelength was increased in the range 0.3-2 μm. At about 5.5 μm, reflectance is about 86% and asymptotically approaches 100% towards the infrared.

![Figure 4: Experimental spectral hemispherical reflectance of TiB$_2$ (continuous blue line) compared to that of ZrB$_2$ and TaB$_2$.](image)

When the comparison between the three borides is accounted for, we can notice that TiB$_2$ has a reflectance nearly superimposed to that of ZrB$_2$ and considerably lower than that of TaB$_2$ at wavelengths below 1.6 μm (see inset in Figure 4), a lower reflectance than other borides in the intermediate spectral region (1.6-6.0 μm) and a similar reflectance plateau at longer wavelengths. The spectral shapes and values of optical reflectance spectra are determined by different parameters: fundamental optical properties of the material (i.e. intrinsic properties connected to the chemical composition of the investigated surface) and morphological characteristics of the surface. From the morphological analysis of the surface reported in the previous paragraph, we can infer that the obtained spectral differences of the three borides directly arise from intrinsic characteristics of the different materials. In fact, the samples show very similar surface properties. In particular, they all are almost fully dense and have similar surface topologies. As for the roughness (Sa and Sq parameters), TiB$_2$ and ZrB$_2$ are very similar, while TaB$_2$ is characterized by a higher roughness. Fixed all other parameters, the effect of increasing roughness would be to decrease the optical reflectance. However, TaB$_2$ is the boride showing the highest reflectance for wavelengths shorter than 3 μm, while the small differences with respect to ZrB$_2$ at longer wavelengths lie within instrumental uncertainty and can be considered not significant. Thus we can conclude that the lowest reflectance of TiB$_2$ with respect to other borides, its smoother risefront towards infrared wavelengths and the slightly lower infrared reflectance plateau are intrinsic characteristics of this boride matrix. This fact affects sunlight absorption and thermal emittance properties of TiB$_2$, as discussed in the following.
From the acquired hemispherical reflectance spectrum $\rho^\wedge(\lambda)$, it is possible to calculate the integrated solar absorbance $\alpha$ using the equation:

$$\alpha = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} (1 - \rho^\wedge(\lambda)) \cdot S(\lambda) d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} S(\lambda) d\lambda}$$

(4)

where $S(\lambda)$ is the Sun emission spectrum [69] and the integration is carried out between $\lambda_{\min} = 0.3$ µm and $\lambda_{\max} = 3.0$ µm. The integrated thermal emittance $\varepsilon$ at the temperature $T$ can be evaluated as:

$$\varepsilon = \frac{\int_{\lambda_1}^{\lambda_2} (1 - \rho^\wedge(\lambda)) \cdot B(\lambda,T) d\lambda}{\int_{\lambda_1}^{\lambda_2} B(\lambda,T) d\lambda}$$

(5)

where $B(\lambda,T)$ is the blackbody spectral radiance at the temperature $T$ of interest and $\lambda_1 = 0.3$ µm and $\lambda_2 = 15.0$ µm. The importance of a high solar absorbance in spectrally selective materials has been pointed out in the literature [70]. As far as the thermal emittance $\varepsilon$ is concerned, TiB$_2$ is also the most emissive in comparison to the other diboride systems, due to the relatively lower reflectance value at mid-infrared wavelengths. Thus, the obtained spectral selectivity $\alpha/\varepsilon$ is 2.2 at 1000K and 1.7 at 1400K. These values are lower than those of dense monolithic ZrB$_2$ and TaB$_2$ [11] (3.9 and 4.0 at 1000K and 2.6 and 3.3 at 1400K, respectively), but still higher with respect to those of SiC ($\alpha/\varepsilon=1.0$ at 1400K [3]), which is the material currently used in solar furnaces [71], and only slightly lower than other previously investigated MoSi$_2$-added dense UHTCs, e.g. ZrB$_2$ ($\alpha/\varepsilon=2.0$ at 1400K [3]) and TaB$_2$ ($\alpha/\varepsilon=2.1$ at 1300K [7]).

4. Conclusion

The SHS and SPS techniques were combined in this work to produce bulk dense TiB$_2$ samples. In particular, the optimal SPS conditions identified for obtaining about 99.5% dense products were 1530 ±20°C, 20 min and 60 MPa. It should be noted that the latter conditions are relatively milder with respect to those reported in the literature, when considering the consolidation of commercially available TiB$_2$ powders either by conventional HP or SPS. In particular, only 80% dense materials were obtained when commercial TiB$_2$ powders were processed under the same SPS conditions. This fact also evidences the beneficial effect produced by the use of the SHS technique for powder synthesis. The obtained materials display a quite uniform microstructure with few micron-sized grains.
Furthermore, in view of the possible utilization of this system as solar absorber, the optical reflectance of bulk TiB$_2$ in the wavelength range 0.3-15 µm is evaluated for the first time to the best of our knowledge. The reflectance curve appears as step-like shaped, similarly to ZrB$_2$ and TaB$_2$. In comparison to other transition metal borides, TiB$_2$ is characterized by similar reflectance values in the wavelength range below, roughly, 2µm and above 6 µm and a lower reflectance in the intermediate region. The solar absorbance $\alpha$ is higher than that of other borides (e.g. ZrB$_2$ and TaB$_2$), while the spectral selectivity $\alpha/\varepsilon$ is higher than that of SiC and lower than ZrB$_2$ and TaB$_2$. However, if the comparison between TiB$_2$ and other borides is concerned, it should be mentioned also that TiB$_2$ has a lower density than ZrB$_2$ (4.5 g/cm$^3$ versus 6.11 g/cm$^3$) and considerably lower than TaB$_2$ (12.18 g/cm$^3$). The reduced weight is a considerable advantage for the proposed application of bulk solar absorbers for solar tower plants, where a large receiver must be firmly sustained at a considerable height. Finally, it should be mentioned that TiB$_2$ is appealing also from point-of-view of raw material procurement and cost, because titanium is much cheaper and easier to obtain than zirconium and tantalum.

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