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## Process and composition dependence of optical properties of zirconium, hafnium and tantalum borides for solar receiver applications

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### ABSTRACT

Ultra-high temperature boride ceramics have proved to show promising properties for novel solar receivers. The present work shows a further step towards their actual application, investigating how sintering technique and starting powders composition affect the properties of final materials. Thus we report on the comparative characterization of  $ZrB_2$ ,  $HfB_2$  and  $TaB_2$  produced by high pressure and pressureless techniques and with different amounts of  $MoSi_2$  sintering aid. We investigate microstructural, mechanical and optical properties, in the perspective to assess the material potential for novel solar absorbers operating at higher temperatures than those currently available. Moreover, a systematic study has been carried out on  $ZrB_2$ , producing with fixed high pressure sintering technique, a series of samples with  $MoSi_2$  compositions in the range 5–50 vol%. We show that the content of silicide and silicide-related secondary phases in the final pellets affects either the mechanical performance and the optical behavior. Thus, as far as the optical properties are concerned, the  $MoSi_2$  amount should be the lowest as possible to ensure a proper material consolidation whilst enhancing the absorbance/spectral selectivity.

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### 1. Introduction

Thanks to their ultra-refractory characteristics and their ability to withstand extreme and harsh environments, ultra-high temperature ceramics (UHTC) [1,2] based on boride, carbide and nitride materials are the best candidates for a variety of applications. Historically, their main application fields have been since a long time aerospace and military, as well as particularly demanding industrial contexts, e.g. thermonuclear reactors [3,4] and hypersonic applications [5–8]. Recently, we proved their intrinsic spectral selectivity and low thermal emittance and we proposed them as novel bulk solar absorbers for concentrating solar power (CSP), investigating different material parameters [9–20]. It should be noticed that CSP is considered one of the most promising renewable energy technologies [21], and, in addition, its efficiency increases with increasing operating temperature. Thus, the use of receiver materials able to sustain very high temperatures while maintaining good mechanical and thermal properties could

generate a real innovation in this field.

To date, the research on CSP receivers has been mainly focused on silicon carbide (SiC) [22,23] and alumina ( $Al_2O_3$ ) [24]. However, both these materials show serious drawbacks. SiC is a grey semiconductor with good solar absorbance and high oxidation resistance, but also high thermal emittance arising in large thermal losses at high temperature. On the other hand,  $Al_2O_3$  is characterized by high refractoriness, high thermal stability and oxidation resistance, but, being white, also by very poor sunlight absorption properties. Thus, grey low-emissive and intrinsically spectrally selective UHTCs have a great potential for solar applications, once their properties would be carefully characterized and weaknesses addressed.

UHTCs are usually densified with the addition of sintering aids [25] to overcome problems related to the difficult strong covalent bonds of these refractory ceramics. One of the most suitable additives is  $MoSi_2$ . It has been found that a 10–15 vol% content of this phase is enough to enable full densification by either hot pressing or conventional sintering [26,27].  $MoSi_2$  has also proved to be effective in improving the oxidation resistance and high temperature strength of UHTCs [25].

The literature reports a large interest about studying the effect

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of different type and amount of sintering additives on borides. However, the main investigated characteristics are thermal [28–30] and mechanical properties [29,31], oxidation behavior [32,33] and porosity [29], while, to the best of our knowledge, the impact on optical properties remains unexplored. Thus, being them a key parameter for solar applications, similarly to the analysis we recently carried out on carbides [34], in this work we systematically investigate optical properties of MoSi<sub>2</sub>-added zirconium, hafnium and tantalum diborides (ZrB<sub>2</sub>, HfB<sub>2</sub> and TaB<sub>2</sub>) as a function of the sintering aid amount or processing technique, correlating them to compositional and microstructural characteristics. For the three investigated borides, specimens with 10% and 20% MoSi<sub>2</sub> starting composition have been produced by hot pressing (HP) and pressureless (PS) sintering, respectively. In addition, fully dense ZrB<sub>2</sub>-based composites containing MoSi<sub>2</sub> from 5 to 50 vol% were prepared in order to decouple process- from composition-related parameters and to study the effect of the secondary phase on the microstructural evolution, roughness, mechanical and optical properties.

## 2. Experimental

Commercial powders were used for the preparation of the materials listed in Tables 1 and 2: hexagonal ZrB<sub>2</sub> (H. C. Starck, Germany, Grade B), mean particle size: 1.5 μm, impurities (wt%): C 0.25, O 2.0, N 0.25, Fe 0.1, Hf 0.2; hexagonal HfB<sub>2</sub> (Cerac Inc., Milwaukee, USA), mean particle size: 2.2 μm, impurities (wt%): Al 0.001, Fe 0.002, Zr < 0.5; hexagonal TaB<sub>2</sub> (Materion Adv. Chemicals, Milwaukee, USA), mean particle size: 0.9 μm, impurities (wt%): Al 0.04, Cd < 0.0007, Cr < 0.0005, Fe 0.07, Nb 0.02, Pb < 0.0004; tetragonal MoSi<sub>2</sub> (Aldrich, Milwaukee, USA), mean particle size: 2.8 μm, impurities (wt%): O 1.0. Samples to be sintered by hot pressing (HP) contained 10 vol% of MoSi<sub>2</sub>, whilst those densified by pressureless sintering (PS) contained 20 vol% MoSi<sub>2</sub>. Moreover a series of composites containing MoSi<sub>2</sub> from 5 to 50 vol% were prepared by hot pressing, as previously mentioned.

Matrix and additive were weighed in the proper amount and mixed through mechanical mixing for 24 h in absolute ethanol using SiC milling media. Subsequently the slurries were dried in a rotary evaporator and sieved through 250 μm screen. 30–45 mm-diameter pellets were green shaped by uniaxial pressing with 20 MPa.

The pellets to be sintered by hot pressing were directly placed in the furnace and hot pressed in low vacuum (~100 Pa) using an induction-heated graphite die with an uniaxial pressure of 30 MPa during the heating and a dwell at the maximum temperature set on the basis of the shrinkage curve, as reported in Tables 1 and 2. On the other hand, the pellets to be sintered without applied pressure, were preliminarily consolidated by cold isostatic pressing at 25 MPa and then sintered in a graphite furnace (Astro

industries Inc., Santa Barbara, USA) with a heating rate of 600 °C/h under flowing argon atmosphere (~0.1 MPa) in the temperature range 1750–1950 °C, as indicated in Table 1. All the composites cooled down naturally.

On the sintered materials, the bulk densities were measured by Archimedes' method and confirmed by SEM inspection. The relative density was thus estimated as the ratio between the measured value and the theoretical value determined through the rule of mixtures on the basis of starting nominal compositions.

The microstructure of the sintered ceramics was analysed on polished surfaces by scanning electron microscopy (FE-SEM, Carl Zeiss Sigma NTS GmbH, Oberkochen, DE) and energy dispersive x-ray spectroscopy (EDS, INCA Energy 300, Oxford instruments, UK). Quantitative calculations of the microstructural parameters, like residual porosity, mean grain size and secondary phase content, were carried out via image analysis with a commercial software package (Image-Pro Plus<sup>®</sup> version 7, Media Cybernetics, Silver Springs, MD, USA).

The topological characterization of the surfaces was performed with a non-contact 3D profilometer (Taylor-Hobson CCI MP) on two areas of 0.08 × 1 cm<sup>2</sup> at the center of each sample and the topography data were analysed using a commercial software (Talymap 6.2). The evaluation of 2D texture parameters, like mean surface roughness (Ra) and distance between the highest asperity and the lowest valley (Rt), was performed on 4 different profiles (2 for each area) extracted from the 3D data and the gaussian filter (λc) for the separation of the roughness and waviness components was set according to the ISO 4288:2000. The 2D parameters were calculated as average of estimated values on all sampling lengths over each profile.

The room temperature flexural strength was measured according to the existing standard for advanced ceramics, method ENV 843-1, on chamfered bars with dimensions, 25 × 2.5 × 2.0 mm<sup>3</sup> (length by width by thickness, respectively), using a fully-articulated silicon carbide four-point fixture with a lower span of 20 mm and an upper span of 10 mm using a screw-driven load frame (Instron mod. 6025). The high temperature strength, up to 1770 K, was measured according to the ENV 820-1 standard. For the high-temperature tests, a soaking time of 18 min was set to reach thermal equilibrium. For each material, five samples were tested.

The hemispherical reflectance spectra were acquired using two instruments: a double-beam spectrophotometer (Lambda900 by Perkin Elmer) equipped with a Spectralon<sup>®</sup>-coated integration sphere for the 0.25–2.5 μm wavelength region and a Fourier Transform spectrophotometer (FT-IR “Excalibur” by Bio-Rad) equipped with a gold-coated integrating sphere and a liquid nitrogen-cooled detector for the range 2.5–16.5 μm.

**Table 1**

Composition, sintering parameters (T: maximum temperature, t: dwell at T, P: applied pressure), final and relative densities (ρ), mean grain size (m.g.s.), smallest (Min g.s.) and largest (Max g.s.) grain size and secondary phases of the borides sintered with MoSi<sub>2</sub>. Porosity is estimated by image analysis.

Label	Matrix	MoSi <sub>2</sub> vol%	Sintering	T,t,P °C,min,MPa	Final ρ g/cm <sup>3</sup>	Rel. ρ %	Pores %	m.g.s. μm	Min g.s. μm	Max g.s. μm	Secondary phases by SEM-EDS vol%
Z10HP	ZrB <sub>2</sub>	10	HP	1850,10,20	6.1	98.3	3.7	2.4 ± 0.6	1.4	3.9	8.5 MoSi <sub>2</sub> , 1.4 SiO <sub>2</sub> , 0.7 SiC
Z20PS		20	PS	1950,60,-	6.1	99.0	0.8	2.6 ± 0.7	1.3	4.1	18 MoSi <sub>2</sub> , 2 MoB, 0.5 SiO <sub>2</sub>
H10HP	HfB <sub>2</sub>	10	HP	1900,8,30	10.1	96.4	0	0.8 ± 0.3	0.3	2.3	5 MoSi <sub>2</sub> , 3 HfO <sub>2</sub> , 2 SiO <sub>2</sub>
H20PS		20	PS	1950,60,-	10.0	98.0	1.4	1.4 ± 0.8	0.4	4.9	15 MoSi <sub>2</sub> , 2 Mo <sub>5</sub> Si <sub>3</sub> , 0.5 HfO <sub>2</sub>
T10HP	TaB <sub>2</sub>	10	HP	1690,10,30–40	10.2	95.4	1.3	3.8 ± 1.1	1.7	6.7	3 MoSi <sub>2</sub> , 9 SiO <sub>2</sub> /SiC
T20PS		20	PS	2100,180,-	9.2	(90.4)97.0	3.0	38.4 ± 13.6	13.6	84.2	10 MoSi <sub>2</sub> , 8 Si, 4 SiC

PS: pressureless sintering

HP: hot pressing

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