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Optical properties of ZrB_2 porous architectures

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ABSTRACT

Porous ceramic materials are currently used as volumetric sunlight absorbers in concentrating solar power systems. As the efficiency of thermodynamic cycles rapidly increases with the operating temperature, the favorable characteristics of so-called ultra-high temperature ceramics (UHTCs) can be successfully exploited in novel solar absorbers. The present work reports, for the first time to the best of our knowledge, on optical properties and microstructural analysis of novel ice-templating porous ZrB_2 UHTCs, to evaluate their potential as volumetric solar receivers. We demonstrate that the different complex structures that can be obtained with the freeze casting technique show promising optical properties. The idea of conjugating an highly tailorable morphology, useful for optimizing gas fluxes and heat exchanges between absorber and gas, to the spectral selectivity which is a characteristics of ZrB_2 can be a promising route for increasing the efficiency of thermal solar systems.

1. Introduction

A general rule for concentrating solar power systems is that the efficiency rapidly increases with increasing working temperature. Thus, for solar thermal exploitation, a large effort is put for raising the system operating temperatures by developing novel solutions [1–4]. For the plant approach with central solar tower, a critical parameter for temperature increasing is the choice of the receiver material, which is devoted to absorb the sunlight collected by the mirrored surface and to efficiently transfer the energy to the thermal exchange medium, keeping at minimum radiative losses due to thermal emission. Porous ceramics are presently used as volumetric absorbers of solar radiation for application in concentrating solar power systems. Air at relatively low temperature is drawn through the porous absorber toward the back, gradually being heated by convection from the solid absorber. The gas temperature at the front face of the absorber should then be relatively low, while the temperature at the back can be much higher. To date, existing volumetric absorbers produce high temperature at the front face, but they do not yet provide the level of performance needed for efficient collection and conversion of the solar radiation. The needed superior performance of high-temperature volumetric absorbers can be achieved by optimization of the morphology and optical properties of the porous absorber. This includes the creation of gradients of absorber structure and composition to allow fine control of optical absorption rate and convective heat transfer. Besides metals and metallic alloys [5], few ceramic materials have been studied up to now for this application, basically belonging either to the family of silicon carbide (SiC, a gray semiconductor with good sunlight absorption and high oxidation resistance) and SiC-based materials [3,6] or being white ceramics like alumina [4] or cordierite [6], which are characterized by very high thermal stability, oxidation resistance and high refractoriness, but with non-optimal sunlight absorption properties due to their white color.

Zirconium, hafnium and tantalum boride, nitride, and carbide-based materials and composites are called ultra-high temperature ceramics, UHTCs, because they combine outstanding robustness and refractoriness (melting temperatures above 3000 °C) [7] and are widely recognized as the unique materials for harsh service environments, especially for aerospace, rocket propulsion and energy applications. Very recently, different UHTCs have been proposed for solar thermal absorbers [8–12] thanks to their spectral selectivity properties and low thermal emittance. ZrB_2 has already proved to be a suitable material for this application from several points of view [13–15]. The ultra-high melting point of ZrB_2, together with the unique combination of good thermal conductivity and chemical stability appear intriguing for employing it in high temperature novel solar furnaces, where the front surface of the absorber can even reach temperatures as high as 1700 K [16]. Moreover, both room-temperature reflectance spectra and high-temperature emittance favorably compare ZrB_2 against other ceramics used as volumetric absorbers such as SiC.

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In this work we characterize, for the first time to the best of our knowledge, ZrB_2 porous architectures obtained by freeze-casting of aqueous suspensions [17,18]. With this technique, porous structure with main unidirectionally oriented pores can be produced [19]. Changing the slurry characteristics (for example powder composition, solid load, type and amount of dispersant) or the temperature gradients during freezing, the macro-structures can be tailored. The ice network results in macro-pores mainly aligned in the same direction or arranged into randomly distributed dendritic forms.

Several samples are investigated including both monophasic ZrB_2 and composites containing SiC particles, and their structural and optical properties are assessed and compared.

2. Materials and methods

2.1. Materials

The starting powders were commercial products: ZrB_2 powder (H.C. Starck grade B, Karlsrhue, Germany), β-SiC powders (H.C. Starck BF12, Karlsrhue, Germany), α-Si_3N_4 powder (Baysinid, Bayer, Leverkusen, Germany).

Different aqueous suspensions were prepared using pure ZrB_2 (labeled as M="monophasic") or the composite (vol%): 76 ZrB_2–20 SiC–4 Si_3N_4, (labeled as C="composite"), where SiC is added as a reinforcing phase whilst Si_3N_4 is just a sintering additive to enhance densification [20]. Two commercial ammonium polyacrylates, namely Duramax D3005 and Dolapix PC33, with different molecular weights and pH range of activity were used as dispersants [21]. Duramax D3005 is already known to promote a better stabilization of the ZrB_2–SiC slurry compared to Dolapix PC33 [21]. In order to modify the porous structure (lamellar or dendritic) according to the effect of the slurry formulation or the cold transmission [17], the powder suspensions were produced by varying the dispersants type and amount and/or the solid loading (35–48 vol%), while the slurries were cast into plastic or metallic cylindrical molds with different diameter/height ratios (1–4), as reported in Table 1 Further details concerning the influence of the processing parameters on the developed micro-macrostructures were previously reported [17,18].

The slurries were freeze cast and dried (Edwards Mod.MFD01, Crawley, UK) using a cooling temperature of −40 °C and chamber vacuum value of 10 Pa. Samples were pressureless sintered at 2100 °C for 1 h in flowing argon.

The morphological and microstructural features of the as-produced materials were observed by SEM (E-SEM FEI Quanta 200, FEI Company). Pore size distribution and open porosity in the range 0.0058–100 μm were analyzed by mercury intrusion porosimetry, MIP (Thermo Finnigan Pascal 140 and Thermo Finnigan Pascal 240). The bulk density of the samples was determined by weight-to-volume ratio and the percent values of the total porosity was estimated as [1-(bulk density/theoretical density)] × 100. The theoretical density values used for M and C samples were 6.1 and 5.4 g/cm^3, respectively.

For comparison, a pure dense ZrB_2 sample was also included in the investigation.

Table 1
Powder suspensions and molds details.

Sample label	Dispersant		Solid loading (vol%)	Mold	
	Type	(wt%)		Type	Diameter/height
M1	Duramax	2.9	35	Metal	4
M2	Dolapix	4	45	Metal	1
M3	Dolapix	4	45	Plastic	1
C1	Duramax	5.8	38	Plastic	4
C2	Dolapix	6	48	Plastic	1
C3	Dolapix	6	48	Plastic	4
C4	Dolapix	4	48	Plastic	1
C5	Dolapix	6	48	Plastic	2

2.2. Optical characterization

Optical reflectance spectra at room temperature in the 0.25–2.5 μm wavelength region were acquired using a double-beam spectrophotometer (Lambda900 by Perkin Elmer) equipped with a 150 mm diameter integration sphere for the measurement of the hemispherical reflectance. The spectra in the wavelength region 2.5–15.5 μm have been acquired using a Fourier Transform spectrophotometer (FT-IR "Excalibur" by Bio-Rad) equipped with a gold-coated integrating sphere and a liquid nitrogen-cooled detector. In all cases the reflectance spectra are acquired for quasi-normal incidence angle.

3. Results

3.1. Structural characterization

The structural and textural characteristics of monophasic and composite samples under investigation are listed in Table 2 Typical macro and microstructural features are shown in Figs. 1–3, where images of the top surface at different magnification are reported for each sample listed in Table 2.

Monophasic samples generally had a much higher degree of total porosity (49–57%) compared to composite samples (39–48%) (Table 2). This was mainly due to the absence of sintering aid, and/or different water content of the slurry. In addition pore volume, morphology and dimension were heavily affected by the starting composition, casting conditions and densification, as detailed in previous papers [17,18]. M samples showed main unidirectional pore channels separated by ZrB_2 ceramic plates, both oriented in the freezing direction (Fig.1).

The wide channel-like pores visible in the SEM images (Fig.1) contribute in lowering the density of the whole M samples and consequently in increasing their total porosity, while they can be out of the detection range of MIP. For this reason, for each sample the open porosity value is generally lower than the corresponding total porosity (Table 2), since it does not account for all the macro- and ultramacro-pores larger than 100 μm, which are particularly evident in the SEM images of monophasic samples (Fig.1). Lamellae as well as channel-like pores are grouped and oriented in different directions which reflect the freezing directions. The ceramic walls are constituted by a highly porous microstructure due to lack of the sintering aid in M samples (Fig. 1d). Both the average width of pores and the wall thickness increased in the order M1 < M2 < M3. Because of the reduced wall thickness in M1, the lamella edges are constituted by one or two ZrB_2 monolayers.

For M samples, the MIP size distribution of pores was bimodal with peaks of frequency at around 1–2 μm and 20–30 μm (M2) or even at 100 μm (M3) of pore size, thus close to the detection limit of the instrument (Table 2). In addition, small pores (< 5 μm, i.e. located in correspondence of the first peak of frequency) represent the main contribute to the total accessible pore volume, accounting for the 50% and 65% respectively for M2 and M3.

In the case of composite samples (Figs. 2–3) the pore size distribution is bimodal with peaks of frequency at about 0.8 μm and 10–50 μm of pore size (Table 2). Further, in C samples the relative contribution of small and big pores is opposite to that found for M