Ultra-High Temperature Ceramics for solar receivers: spectral and high-temperature emittance characterization

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We report on the preparation, room temperature spectral reflectance and high-temperature thermal emittance characterization of different boride and carbide Ultra-High Temperature Ceramics (UHTCs). The investigated samples are compared with a reference material for solar absorber applications, i.e. silicon carbide. We show that spectral and thermal emittance properties of UHTCs are promising for novel solar receivers. [DOI: http://dx.doi.org/10.2971/jeos.2012.12052]

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1 INTRODUCTION

Solar thermal technology is considered a promising energy supply for the future of the mankind because it is safe, sustainable and cost-effective. However, the key for a more efficient operation of thermodynamic cycles is reaching the highest temperature as possible. For this reason, in all the different temperature ranges that are peculiar of each system architecture, there is a considerable effort for the temperature increasing [1]–[3]. Tower solar plants are particularly promising and are attracting important investments both from private and public companies, because they allow to exploit mature technologies of conventional fossil fuel plants, besides having an intrinsically higher efficiency than solar photovoltaics. At present, the maximum operating temperatures of a solar power plant are usually less than 900 K because of the rapid degradation of its components. The receiver is the most critical element. It must 1) efficiently absorb the sunlight collected by the whole mirror field, 2) keep low losses and 3) efficiently transfer the thermal energy to the exchange media. Therefore the main challenge for increasing the operating temperature of thermal plants is the development of novel receiver materials able to resist to damage at very high temperatures while keeping good spectral selectivity, good thermal conductivity and favorable radiative properties at the operating temperatures. Carbides and borides of zirconium, hafnium and tantalum are referred to as Ultra-High-Temperature-Ceramics (UHTCs), thanks to their characteristic melting temperatures exceeding 3200 K. Moreover, these materials have the physical properties of ceramics and the electronic properties of metals, i.e., high hardness and strength with high thermal and electrical conductivities, together with the highest melting points of any known material. UHTCs are considered the best-emerging materials for applications in aerospace and advanced energy systems. Very recently our group has proposed them for solar receiver applications [4]–[7]. After having examined the potential for this specific application of an extended class of carbides and borides separately, this work compares for the first time the optical properties of the reference UHTCs composites in both classes of materials, enlightening also their mechanical behavior. Thus, we report on the preparation, room temperature spectral reflectance and high-temperature thermal emittance comparative characterization of hafnium and zirconium carbides and borides (HfC, ZrC, HfB_2 and ZrB_2, respectively), in the perspective to evaluate the material potential as novel solar absorbers in solar tower plants. For a more significant property assessment, the investigated UHTC materials are compared with silicon carbide (SiC), a material currently under use in solar towers [8].

2 MATERIALS PREPARATION

Commercial powders were used to prepare ceramic materials based on ZrC, HfC, ZrB_2 and HfB_2. The sintering parameters, microstructural characteristics and mechanical properties are summarized in Table1. The powders were sintered at 1800°C/h to 1930°C in graphite furnaces. Further details on materials preparation are available in [9]–[13]. Some of the materials (borides and SiC) were densified with low amounts of sintering aids in order to improve the final density. UHT-carbides were instead sintered by hot pressing at 1930°C

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Label	Mean grain size (μm)	HV (GPa)	E (GPa)	σ_{RT} (MPa)	σ_{1500} (MPa)
HfC [9, 11]	∼7	19±1	450±20	470±10	-
HfB_2 [12]	∼2	22.0±0.5	530±5	700±60	600±50
ZrC [9, 10]	∼5	18±1	460±20	410±40	-
ZrB_2 [13]	∼3	16.0±0.4	490±4	530±50	500±60
SiC [14]	∼0.5	22.0±0.8	384±4	750±50	160±10 (1300°C)

TABLE 1 Density, mean grain size and properties of UHTCs : HV: microHardness, E: Young's modulus, σ_{RT}: flexural strength at room temperature, σ_{1500}: flexural strength at 1500°C in air.

FIG. 1 Prepared samples. From left to right: ZrC, ZrB2, SiC pellets. The diameter of all specimens is 40 mm.

with no sintering aids. After densification, bulk densities were measured by the Archimedes method and the microstructural characteristics were evaluated on fracture surfaces using a scanning electron microscopy (SEM, Cambridge S360, Cambridge, UK). For the mechanical characterization, hardness, Youngs modulus and strength were measured according to the procedures described in [9]–[13].

For the optical characterization measurements, pellets of 40 mm diameter and 2 mm thickness were prepared (Figure 1).

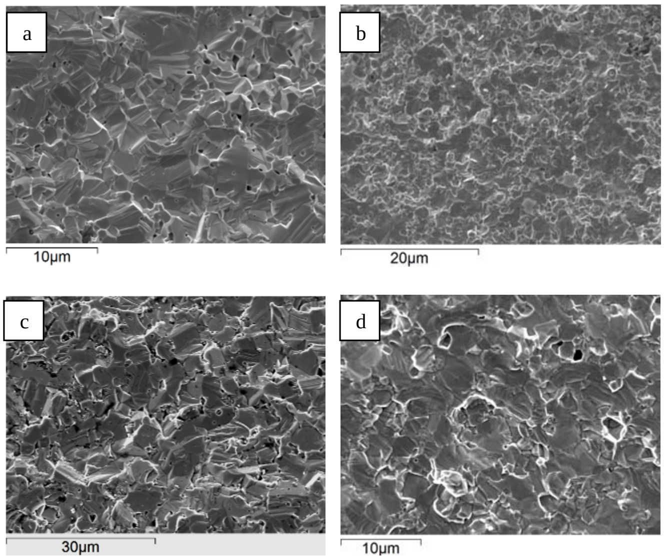

FIG. 2 Fracture surfaces of sintered UHTCs: a) pure HfC, b) HfB_2- based composite, c) pure ZrC, d) ZrB_2-based composite.

and strength comparable to HfB_2, but the lowest HT strength and stiffness amongst the considered materials.

3 MICROSTRUCTURE AND MECHANICAL PROPERTIES OF BORIDES AND CARBIDES

Typical microstructures of sintered samples after the hot pressing cycles are provided in Figure 2. The final densities of ZrB_2- and HfB_2-based composites were approaching the theoretical density. The microstructures were spatially uniform and consisted of rounded relatively equiaxed grains with mean grain dimensions of 2 and 3 μm for HrB_2 and ZrB_2, respectively. In the ZrC and HfC monoliths <5 vol % of fine closed porosity with pore dimensions in the range 0.3-1 μm was observed and a more faceted morphology, with mean grain size around 5-7 μm. The SiC based material had a uniform microstructure with rounded <1 μm grains and a porosity content of 5%.

Typical values of mechanical properties for the UHTC class of materials and SiC are reported in Table 1. UHTCs possess high hardness (18-22 GPa) and stiffness (450-530 GPa). Even more, boride-based composites displayed a superior stability at high temperature, retaining their 4-pt flexural strength up to 1500°C in air (500 and 600 MPa for ZrB_2 and HfB_2, respectively). Despite the lower mean grain size, SiC has hardness

4 OPTICAL CHARACTERIZATION

For optimum efficiency the solar absorber should have the maximum possible absorbance at solar spectrum wavelengths while exhibiting a minimum infrared emittance. This may be obtained using intrinsic selective absorbers. A solar selective surface efficiently captures solar energy in the high intensity visible and the near infrared spectral regions, while maintaining poor radiating properties at the thermal infrared wavelengths.

To evaluate the spectral selectivity of samples at room temperature we acquired the room-temperature specular reflectance spectra, using a double-beam UV-VIS-NIR spectrophotometer (Perkin Elmer Lambda900) for the 0.2 to 2.4 μm wavelength range and a Fourier transform infrared spectrometer (Bio-Rad Excalibur) for in the 2.4-25.0 μm region. High-temperature characterization has been carried out using the MEDIASE setup [15]–[17] of the MegaWatt Solar Furnace in the French Pyrenees. Specimens were put at the focus of the 1-MW solar furnace, allowing them to reach temperatures higher than 1000K in few seconds. The solar flux incident on the samples is adjusted with the choice of the number of working heliostats and/or the aperture of the door in front of the chamber. Fig-

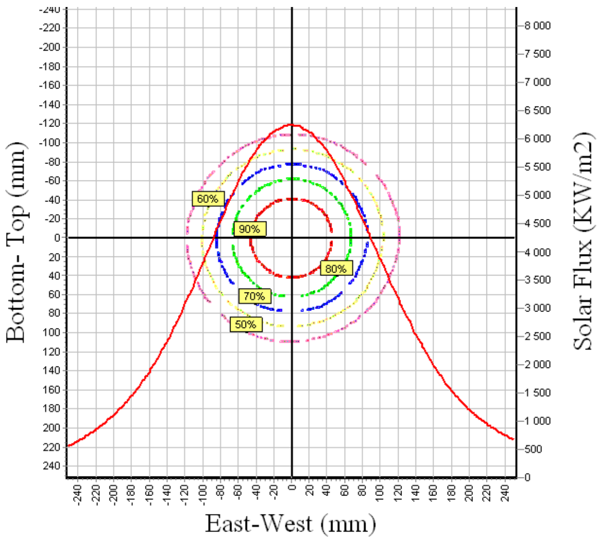

FIG. 3 Solar irradiance distribution of the MegaWatt solar furnace on the focal plane.

ure 3 shows the solar irradiance distribution of the Megawatt solar furnace on the focal plane, taken with the same number of heliostats as in the experiments on UHTCs. We can appreciate that the solar flux is almost constant for a disk of 40 mm diameter, like our samples. A slight modification of the solar flux distribution with respect to Figure 3 could take place at small door apertures. However, according to our measurements, it does not significantly affect the homogeneity of the temperature distribution on the samples.

Reflectance spectra showed similar results for all the investigated UHTC samples, with S-shaped curves characterized by a low reflectance in the UV-VIS, an almost monotonic reflectance increase in the near infrared and finally a reflectance plateau in the mid infrared, which are the signature of metal-like optical properties [18]. Figure 4 compares, for both the hafnium and zirconium case, the respective carbide and boride materials. The insets show the A.M. 1.5 solar spectrum superimposed to the measured curves. We can see that all the UHTC curves qualitatively display the same metal-like behavior, with some differences that are mainly concentrated in the UV-VIS-NIR part of the spectrum and are more significant in the hafnium-based materials. The markedly different optical characteristics of SiC are apparent from Figure 4. In fact, the SiC spectrum has a well defined reststrahlen band at around 12 μm, emerging from a low reflectance background (around 20% reflectance value below 7.5 μm and an average value of 30% between 15 and 25 μm).

The spectral absorptance $\alpha(\lambda)$ in opaque materials in given by:

$$\alpha(\lambda) = 1 - \rho(\lambda) \quad (1)$$

where $\rho(\lambda)$ is the spectral reflectance. On the other hand, for the Kirchoffs law, at a given temperature the spectral absorptance is equal to the spectral emittance. Therefore, from the measured reflectance spectra we can give a first estimation of the material potential for solar absorber applications:

1) if the sunlight absorption is concerned, SiC is generally more performing than UHTCs, even if HfC has comparably good absorption properties. In the wavelength region below

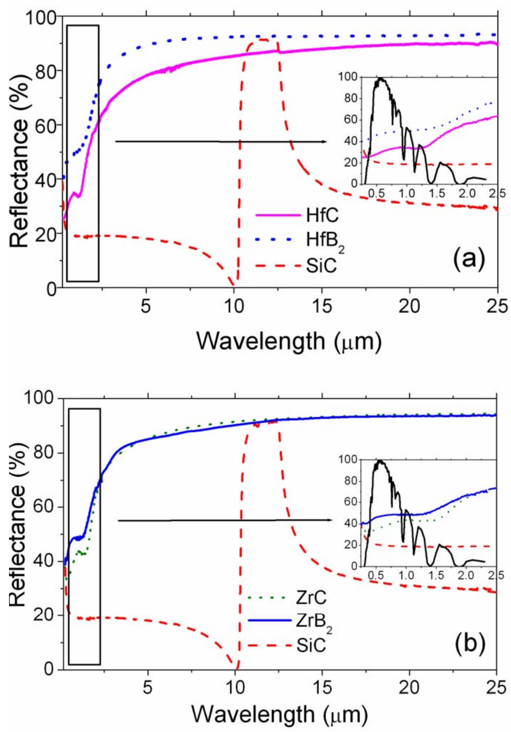

FIG. 4 Comparison of the room temperature reflectance spectra of (a) hafnium carbide and boride and (b) zirconium carbide and boride. The reflectance spectrum of the reference SiC is also depicted (dashed red line). Sunlight spectrum with AM 1.5 is shown in the insets (black continuous line).

1 μm, where the sun emission is maximum, UHTCs show reflectance values from 20% to 40%, to be compared to the 20% of SiC. The most absorbing among the investigated UHTCs is HfC, as said, the lowest is HfB_2. Both ZrC and ZrB_2 lie in an intermediate position, with, also in this case, a slight higher sunlight absorption of the carbide sample than the boride one.

2) UHTCs are greatly winning over SiC if we consider the thermal emittance properties. Their considerable higher reflectance in the whole wavelength region of the thermal infrared very favorably compares them to SiC as for the thermal re-radiation losses expected from the solar receiver. This result is confirmed by the direct high temperature emittance measurements described below. It should be noticed that SiC is a hard semiconducting material currently used in volumetric receivers [8], as well as in several industrial applications.

Thermal emittance is obtained by measuring the radiance emitted by the sunlight-heated samples in the 0.6-40 μm wavelength range, using the MEDIASE setup developed at PROMES-CNRS laboratory. MEDIASE consists of a high-vacuum chamber with ultimate pressure limit of 10^{-6} mbar, equipped with a hemispherical silica glass window of 35 cm diameter. The sample is put on a water-cooled holder, at the focus of the MegaWatt solar furnace, and its temperature is measured using a pyro-reflectometric method [19]–[21]. The directional radiance is measured by means of a radiometer on the back face of the sample at different angles thanks to a movable, computer-controlled three-mirror system. The spectral response of the system is calibrated against a reference blackbody. The directional emittance is then calculated as the ratio between the measured sample radiance and the blackbody ra-

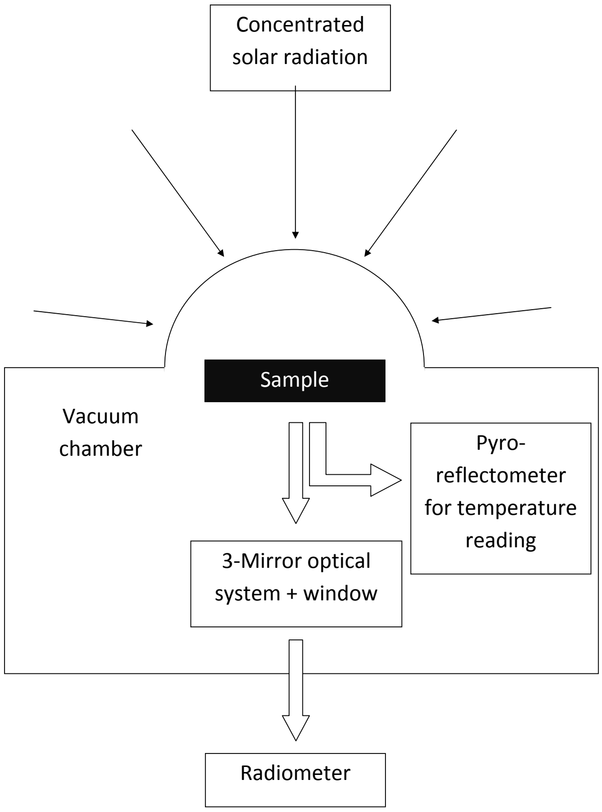

FIG. 5 Block scheme of the MEDIASE experimental setup.

diance at the same temperature. Finally, the total emittance is obtained by integration of the angular values. Figure 5 shows the scheme of the experimental setup for high-temperature emittance measurements.

Figure 6 compares the measured total hemispherical emittance of UHTCs to that of SiC, measured in the same conditions. SiC emittance changes from 0.6 at 1100 K to 0.8 at around 1400 K, while, for UHTCs, the emittance lies in the range 0.3-0.6 for HfC, around 0.4 for HfB_2 (at temperatures between 1300 and 1450 K), 0.3-0.7 for ZrC and around 0.4 for ZrB_2. Borides show a lower emittance increase as a function of the temperature with respect to carbides. The two families of UHTCs have similar emittances up to about 1200 K, while at higher temperature the emittance of borides is lower. From Figure 5 we can therefore appreciate the superior performances of UHTCs with respect to SiC for solar receiver applications thanks to their significantly lower emittance in all the investigated 1100-1450 K temperature range.

5 CONCLUSIONS

The main challenge in present solar energy exploitation is the efficiency increase that, for thermodynamic solar plants, translates in a higher temperature operation. Thus the ideal solar receiver material should withstand high temperatures while having a good spectral selectivity i.e. both a high solar absorption and a low emittance at the furnace operating temperatures. The present work reports on the spectral reflectance and high-temperature emittance characterization of several carbide and boride Ultra High Temperature Ceramics (UHTCs). UHTCs are well known as materials devoted to work in extremely high temperature environments, like thermal shields for aerospace vehicles and nozzles for rocket motors. For a more significant assessment of UHTC performances as potential novel solar receivers, we compared them with Silicon Carbide, obtaining very promising results.

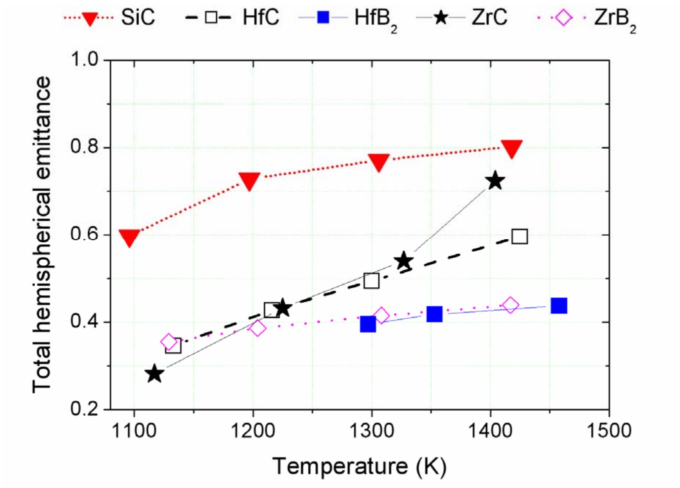

FIG. 6 Total hemispherical emittance of the investigated samples as a function of the temperature.

6 ACKNOWLEDGEMENTS

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