Tantalum diboride-based ceramics for bulk solar absorbers

Diletta Sciti\textsuperscript{a}, Laura Silvestroni\textsuperscript{a}, Jean-Louis Sans\textsuperscript{c}, Luca Mercatelli\textsuperscript{b}, Marco Meucci\textsuperscript{b} and Elisa Sani\textsuperscript{*b}

\textsuperscript{a} CNR-ISTEC, Institute of Science and Technology for Ceramics, Via Granarolo 64, I-48018 Faenza (Italy)
\textsuperscript{b} CNR-INO National Institute of Optics, Largo E. Fermi, 6, I-50125 Firenze, Italy
\textsuperscript{c} PROMES-CNRS Processes, Materials and Solar Energy Laboratory, 7 rue du Four Solaire, 66120 Font Romeu, France

* Corresponding author, email: elisa.sani@ino.it

ABSTRACT

Ultra-high temperature ceramics (UHTCs) are the ideal material for extreme conditions thanks to very high melting points, high refractoriness and good thermo-mechanical properties at high temperatures. This paper reports, for the first time to the best of our knowledge, on the microstructural and optical characterization of several tantalum diboride (TaB\textsubscript{2}) samples with density values from 67\% to full density. Pristine samples have been investigated at room temperature by means of SEM, XRD and spectral hemispherical reflectance measurements. Thermal emittance in the temperature range 1050-1800 K has been measured. Structural, compositional and optical properties after high temperature exposure have been characterized as well and property changes have been explained. The obtained results favorably compare TaB\textsubscript{2} over conventional solar absorbers for novel solar plants operating at higher temperatures.

Keywords: borides; optical properties; emittance; solar absorbers; solar plants; concentrating solar power.
1. Introduction

Among all the renewable energy sources, solar thermal technology [1] and in particular the solar tower plant approach [2] is considered the most promising for the future for different reasons: it has an intrinsically higher efficiency than solar photovoltaic and allows exploiting mature technologies of conventional fossil fuel plants. For these reasons the tower power plant technology is attracting important investments both from private and public companies. However, the key for a more efficient operation of thermodynamic cycles is reaching the highest temperature as possible. The receiver is the most critical element [3-6]. It must satisfy several requirements [7-9]: 1) a high solar absorbance to be able to efficiently absorb the sunlight collected by the mirror field, 2) a low thermal emittance, so that thermal re-radiation losses by the heated absorber are kept low and 3) good thermal properties, for efficiently transferring the thermal energy to the exchange medium. Thus 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 3200K. 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 ultra-refractory carbides such as HfC, TaC, ZrC and borides like HfB₂ and ZrB₂ for solar receiver applications [10-14], because of their favourable optical and radiative properties. TaB₂ is instead rather unexplored due to either difficult procurement of the starting raw materials or to its difficult densification. The relatively recent discovery and implementation of sintering aids [15] has significantly eased the processing conditions required to produce dense, fine-grain-size TaB₂ with a desirable sets of properties and made it possible to start a thorough thermo-mechanical and optical characterization.

In this work, TaB₂-based materials doped with 10vol% of MoSi₂ were sintered at increasing temperatures to obtain different levels of density or porosity. Porosity affects the surface roughness, which in turn, affects the optical properties both at room and high temperature. Emittance tests were carried out in the 1050-1800K range, and the surfaces were analyzed after exposure at high temperature to reveal possible microstructural changes. Reflectance spectra at room temperature
were acquired before and after the high temperature treatment. Then, the spectral features were correlated to surface changes and to the measured high temperature emittance.

2. Experimental procedure

Commercial powders were used to prepare the ceramic composites: hexagonal TaB$_2$ (Materion, Milwaukee, WI), purity 99.5%, -325 mesh, mean grain size 0.91 μm, impurities Al: 0.04, Fe: 0.07, Nb: 0.02; tetragonal MoSi$_2$ (<2 μm, Sigma-Aldrich, Steinheim, Germany), particle size range 0.3–5 μm and oxygen content 1 wt%; C (Degussa EB 158). A mixture with 10 vol% of MoSi$_2$ and 3 vol% of carbon black were prepared. Carbon was included in the mixture to reduce residual silica in the final microstructure and promote the formation of silicon carbide during sintering. The powder mixture was ball milled for 24 h in absolute ethanol using silicon carbide milling media. Subsequently the powders were dried in a rotary evaporator and sieved through a 60-mesh screen. Hot-pressing was conducted in low vacuum (~100 Pa) using an induction-heated graphite die with a constant uniaxial pressure of 30 MPa, a heating rate of 20°C/min and free cooling. Different temperatures in the 1720-1900°C range were adopted to obtain different levels of density. At first, a fully dense material was produced, then on the basis of the shrinkage curves, the following sintering temperatures were selected in order to get samples with relative densities in the range 67-93%. After sintering, the densities were measured by weight to volume ratio or by Archimede method.

The crystalline phases were identified by X-ray diffraction (Siemens D500, Germany). The bulk microstructure was analysed using scanning electron microscopy (FE-SEM, Carl Zeiss Sigma NTS Gmbh Öberkochen, Germany) and energy dispersive spectroscopy (EDS, INCA Energy 300, Oxford Instruments, UK) on fractured and polished cross-sections. Mean grain size was determined through image analysis on SEM micrographs of polished surfaces using commercial software program (Image Pro-plus 4.5.1, Media Cybernetics, Silver Springs, MD, USA). At least 100 grains per specimen were measured for the determination of the mean grain size. Mercury porosimetry was employed to measure the pores amount, size and distribution in the bulk. The sintered materials were cut by electro discharge machining as disks with 40 mm diameter and 3 mm height, for optical characterization. The dense materials were further finished by electrodischarge machining (EDM) followed by conventional diamond machining. Onto the discs, the mean surface roughness (Ra) was
measured according to the European standard CEN 624-4 using a commercial contact stylus instrument (Taylor Hobson mod. Talysurf Plus) fitted with a 2 µm-radius conical diamond tip over a track length of 8 mm and with a cut-off length of 0.8 mm. Scanning electron microscopy was used to analyze surfaces before optical tests at room and high temperature, to analyse the surface morphology and identify possible contaminations deriving from electrodischarge machining.

As for optical properties, the hemispherical reflectance spectra were acquired with two instruments: a double-beam spectrophotometer (Lambda900 by Perkin Elmer) equipped with a Spectralon©-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 2.5-14.3 µm.

The high temperature emittance was measured with the experimental chamber MEDIASE, heating the sample by concentrating solar power at the focus of the 1 MW solar furnace (Figure 1). MEDIASE is composed by a high-vacuum chamber, equipped with a hemispherical silica glass window of 35 cm diameter. A radiometer sensitive to 0.6-40 µm wavelength range was used to collect the light emitted by the heated sample, measuring the directional radiance on the back face of the sample at different angles thanks to a movable, computer-controlled three-mirror system. The emittance at a given angle θ and a given temperature T was calculated as the ratio between the measured directional spectral radiance at the considered temperature and the blackbody directional spectral radiance at the same temperature. Hemispherical emittance values were obtained by integration of the angular values over a half space, assuming hemispherical symmetry of the emission lobe. The spectral response of the whole optical system was calibrated against a reference blackbody. The surface temperature was read near the center of the sample to minimize border effects, using a pyro-reflectometer specifically developed at PROMES-CNRS [16-18]. The relative standard uncertainties of the temperature measurement are typically from 0.5 to 1%, while the relative standard uncertainty of the emittance measurement is 2.5%.
3. Results

3.1 Characterization of bulk materials

<table>
<thead>
<tr>
<th>Label</th>
<th>Sintering cycle</th>
<th>Bulk density</th>
<th>Relative density</th>
<th>Mean grain size</th>
<th>% pore percentage</th>
<th>Average pore dimension</th>
<th>Roughness (Ra)</th>
<th>$\alpha/\epsilon$ ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C/min</td>
<td>g/cm³</td>
<td>%</td>
<td>µm</td>
<td>%</td>
<td>µm</td>
<td>µm</td>
<td></td>
</tr>
<tr>
<td>TaB67</td>
<td>1600/1</td>
<td>7.31±0.02</td>
<td>67</td>
<td>0.8±0.4</td>
<td>29.6</td>
<td>0.24</td>
<td>0.25</td>
<td>1.3</td>
</tr>
<tr>
<td>TaB78</td>
<td>1750/1</td>
<td>8.48±0.02</td>
<td>78</td>
<td>1.1±0.4</td>
<td>18.8</td>
<td>0.17</td>
<td>0.16</td>
<td>1.7</td>
</tr>
<tr>
<td>TaB82</td>
<td>1780/1</td>
<td>8.95±0.02</td>
<td>82</td>
<td>1.2±0.5</td>
<td>17.9</td>
<td>0.13</td>
<td>0.2</td>
<td>1.8</td>
</tr>
<tr>
<td>TaB93</td>
<td>1850/1</td>
<td>10.11±0.02</td>
<td>93</td>
<td>1.5±0.5</td>
<td>12.2</td>
<td>0.09</td>
<td>0.15</td>
<td>2.1</td>
</tr>
<tr>
<td>TaB100</td>
<td>1900/1</td>
<td>10.86±0.02</td>
<td>100</td>
<td>3.5±1.0</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table I: Investigated materials: sintering cycles, densities, pore dimensions, roughness and calculated $\alpha/\epsilon$ ratios after high-temperature experiments.

Sintering cycles, density values and other microstructural parameters are reported in Table 1. The densification started at 1440°C and was completed at 1900°C. A progressive decrease of the final sintering temperature led to a consequent decrease of the relative density, as expected. Fig. 2 shows polished sections of the fully dense material (TaB100). According to XRD (not shown), besides TaB$_2$, traces of MoSi$_2$ and SiC were detected. On the contrary, by SEM-EDS low density Si-based phases were also detected, such as SiO$_2$, SiOC and SiC. In Fig. 2b, for instance, SiC particles embedded in amorphous silica are visible. A possible reaction explaining the observed phases are:
Reaction (1) is essentially driven by the presence of carbon in the powder mixture and by the inevitable oxygen contamination on the powder particle surfaces and predicts the formation of stoichiometric SiC, amorphous silica and release of Mo. Mo can enter TaB$_2$ lattice and form solid solutions, as previously observed [15]. The difficult identification of SiC in x-ray diffraction spectra can be due to either the low amount (below the instrument detectability limit) or the low crystallinity degree. Low density phases were also clearly present along grain boundaries, as shown in Fig. 2c. Another possible outcome of reaction 1 is formation of a mixed SiOC phase, with undefined stoichiometry, as ascertained by SEM-EDS analyses.

Figure 2: Polished surface of dense TaB$_2$-based ceramic sintered at 1900°C showing a) overall microstructure, b) SiO$_2$/SiC agglomerate, c) secondary phases and wetted grain boundaries.
**Figure 3:** Fracture surfaces of partially porous TaB2-based ceramics sintered at a) 1600°C, b) 1750°C, c) 1780°C, d) 1850°C.

Fig. 3 shows examples of the fracture surfaces of the partially porous materials. Fracture surfaces reveal that when the material has 67% relative density, open interconnected pores are still present and the sintering additive is still agglomerated, but as long as the temperature increases, MoSi$_2$ fills the voids and is progressively converted into SiC. With density increase, open porosity becomes closed porosity. At the same time, the maximum and average pore dimensions decrease, as reported in Table 1.
Figure 4: Surface morphology of the discs before (left column) and after (right column) emittance tests. a, b) TaB67, c, d) TaB78, e, f) TaB82, g, h) TaB93, i, l) TaB100. Circle and arrow in a) indicate presence of voids and MoSi2 agglomerates, respectively.
As-machined surfaces are shown in Fig. 4, left column. According to SEM analyses, porosity decreases with increasing the sintering temperature as expected, being open in TaB67. In all the other cases, closed pores were the predominant features. Debris and fractured grains were observed for intermediate density levels, e.g. in TaB78 and 82, due to final diamond machining. When the density increased above 90%, this feature disappeared due to the higher compactness of the bulk material. Correspondingly, the surface roughness decreased with increasing density, see Table 1. The fully dense sample (TaB100) shows coarsened grains, especially in comparison with lower density compositions, but the surface is still quite rough. In all the samples, surface contamination from oxygen was detected by EDS. On one hand this could be due to presence of some residual oxygen-containing phases in the bulk. However, oxygen contamination could also be due to final machining, either electro discharge machining (EDM) or conventional diamond tool machining. EDM is a thermal process where material is removed by a succession of electrical discharges occurring between the tool electrode and the workpiece. The mechanisms of material removal are melting, evaporation and thermal spalling. Moreover, EDM can cause significant contamination from electrode elements including Cu, Fe and other metals. On the other hand, for mechanical machining, material removal implies abrasion mechanisms, with consequent local increase of the contact temperature. Both kinds of machining can thus cause surface oxygen enrichment. In the authors’ intentions, diamond tool machining carried out after EDM was meant to remove such a contaminated layer. However, EDS analyses showed that contamination of metallic elements is still present onto the surfaces, even after extensive cleaning in ultrasonic bath and heating at 100°C in conventional furnace. Some examples of surface contamination are reported in Fig. 5 as dark areas. Other dark contrasting phases visible in SEM images were SiC or SiOC based phases, as for the bulk, see EDS spectra in Fig. 5c,d. Looking at the debris morphology, it is possible to argue that dark agglomerates, such as those shown in Fig. 5b are due diamond machining on soft silica based phases depicted in Fig. 2b. Finally, XRD spectra were also collected on the materials surface but they only evidenced the presence of the main crystalline phases, TaB₂ and light traces of MoSi₂ and SiC. Extra phases due to machining are thus amorphous, or too shallow or just too low in volumetric fraction to be detected; though relevant for emittance tests.
Figure 5: Surface contamination before emittance tests in: a) TaB67, arrows indicate contaminants b) TaB85, circles refer to sites where EDS spectra are collected, c) EDS spectrum showing SiO-rich based phases containing Cu, Zn due to EDM machining, d) oxygen contamination on the Ta-based phase.

Figure 6: Surface morphology of TaB78: a) before and b)-d) after emittance tests. Note diffusion phenomena which led to change of particle morphology from sharp (a) to rounded grains (b) and formation of Si-rich phase at the MoSi$_2$ sites in c)-d).
After emittance tests, the surfaces were again analysed (Fig. 4, right column) and, although visual inspection did not evidence significant changes in colour, SEM-EDS showed that removal of surface contaminants and surface diffusion phenomena took place. Particles with sharp edges observed on the as machined surfaces became curved and partially sintered, displaying surface vaporization/condensation phenomena and formation of liquid phase (Fig. 6). These mechanisms led to closure of small pores between the loose debris. According to EDS analyses, pure MoSi$_2$ was hardly detected on the surface of the sample. Instead, dark contrasting Si-rich phases containing O, Mo, and C were found, an example is reported in Fig.6. Another interesting phenomenon observed on the surface, was the condensation of deposits deriving from vapour phase, as show in Fig 7. Their morphology suggests they are amorphous structures deriving from vapour phase condensation. As for the X-ray diffraction spectra, it must be remarked that reflections are collected not only by the surface but on also from the materials bulk. For these spectra we indeed observed the presence of crystalline reflections from MoSi$_2$ as for the sintered materials and the main reflection from cubic silicon carbide, (Fig. 8) that was barely visible before emittance tests.

**Figure 7:** Formation of whiskers on TaB67 after emittance tests deriving from vapor phase condensation.

**Figure 8:** Example of X ray diffraction spectra of TaB90 collected on a) as sintered and b) after emittance tests showing traces of SiC and MoSi$_2$. 

11
3.3 Optical characterization before and after emittance tests

**Figure 9:** Hemispherical reflectance spectra of the different TaB2 samples a) before and b) after the high-temperature treatment. Spectra of SiC and MoSi2 are shown for comparison (specular reflectance).

Fig. 9 shows the hemispherical reflectance spectra of borides measured at room temperature before and after the high temperature tests in the solar furnace. In the same Figure we also show the hemispherical reflectance spectrum of bulk SiC and the specular reflectance spectrum of bulk MoSi2, for comparison. All the hemispherical reflectance spectra show absorption peaks (i.e. transmittance minima) around 4.2 μm and in the range 5.8-6.8 μm, which are instrumental artefacts due to molecular absorption by gas constituting the ambient air. The specular reflectance spectrum of MoSi2 does not show this artefact because of the considerably shorter path length experienced by the light in the specular reflectance setup, as compared to the multiple-reflection light path length within the integrating sphere. All the borides seem to show some SiC impurities, as demonstrated by the shoulder on the spectra around 13 μm wavelength, corresponding to the typical Reststrahlen peak of SiC and resulting from reaction of constituent MoSi2 and C, as explained before. Moreover, the samples with 67%, 78% and 100% densities also show some residuals of MoSi2, around 3 μm, whilst for the TaB100 sample, also a feature near 7.2 μm can be noticed. The samples with densities in the range 80-100% show reflectance values which increase with the density, as expected. However, the reflectance curve of TaB100 is characterized by multiple features, absent in the other samples.

If we compare the post-test optical measurements (Fig. 9b) to the pre-test ones (Fig. 9a), it is possible to appreciate some general trends: the common reflectance values increase and the slope increase of curves especially in the 0.5-2.5 μm range. Also in this case, the reflectance...
monotonically increases with the sample density. All the samples appear to show small traces of SiC. Moreover, small traces of MoSi$_2$ cannot be ruled out, due to the shoulder in the curves around 3 $\mu$m wavelength. In any case, the amount of MoSi$_2$ (if any) is consistently lower than in the pre-test spectra.

Figure 10 compares the spectrum of the fully dense TaB$_2$ to the reflectance curves of several carbide and boride UHTC ceramics. All UHTCs show a high reflectance value at mid-infrared wavelengths and a lower reflectance towards the near-infrared-visible ranges. The change from the low to the high reflectance regime takes place in different spectral regions, which are a characteristic of the material. Tantalum-based samples (TaB$_2$ and TaC) show quite similar spectra each other and are characterized by a curve rise front located at shorter wavelengths with respect to the other UHTC.

![Hemispherical reflectance spectra of different UHTC materials. All the spectra are acquired for dense samples.](Figure 10)

3.4 Emittance

Fig. 11 shows the measured emittance at high temperature. For each sample, experimental points are connected in a chronological order, i.e. some samples have undergone one or more heating/cooling cycles (TaB67, TaB78 and TaB82). With the exception of the sample with 67% density, which has the highest emittance with values around 0.7, the other borides have values between 0.3 and 0.5. All the samples show a weak dependence of emittance on temperature.
A common trend for all the samples exposed to temperature cycling is that emittance always decreases when the measurement is repeated. This effect is particularly relevant in TaB78, as discussed later.

![Measured hemispherical emittance on the various TaB₂-based ceramics.](image)

**Figure 11:** Measured hemispherical emittance on the various TaB₂-based ceramics.

4. **Discussion**

4.1 **Thermal effects on the optical properties of TaB₂**

From room-temperature spectra (Fig. 9) it is apparent that TaB₂ has a step-like optical behavior as previously found for other refractory metal boride and carbides [10-14]. The metal-like optical behavior of the investigated boride can be clearly recognized by step-like reflectance curves with low reflectance in the UV-VIS and high reflectance values in the medium infrared. However, the analytical curve of TaB₂ reflectance shows dependence on many factors including the porosity, the surface finish and presence of secondary phases, due to either addition of sintering agents or reactions occurring during sintering or the high temperature exposure. Emittance is also affected by the presence of porosity and shows a dynamic response to changes in temperature. Furthermore, after exposure, reflectance spectra are significantly changed (Fig. 9b). These aspects are discussed below.

Before analyzing possible microstructural variation induced by the high temperature exposure, it is necessary to understand how secondary phases and porosity affect room temperature optical spectra of the as sintered materials. As for secondary phases, MoSi₂ additions are not always
traceable by optical measurements. In the present case, for instance, only TaB100 shows a clear shoulder around 2.7 µm belonging to MoSi$_2$. Smaller shoulders in the same position are also evident on TaB67 and 78, whilst no clear evidence of this phase is observed in the optical spectra of TaB82 and 93. Previous studies have confirmed that clear presence of MoSi$_2$ in the optical spectra occur only when the volumetric amount is higher than 15-20 vol% [11,12]. In case of lower additions, MoSi$_2$ shoulder can be detected or not, depending on the surficial distribution of silicide particles. For instance, presence of large MoSi$_2$ agglomerates as those depicted in Fig. 2a and 3a could explain the marked shoulder in the TaB100 and TaB67 spectra of Fig. 9a. Even when not detected by optical measurements, presence of MoSi$_2$ in all the sintered materials is out of doubt, as confirmed by X-ray diffraction (Fig. 8). Diffraction peaks are collected from the materials bulk and thus surficial effects become less important. On the other hand, optical measurements are only sensitive to surface effects.

As for porosity, experimental data indicate that it strongly affects the reflectance of TaB$_2$ samples. Looking at the optical spectra collected before the emittance tests (Fig. 9a), reflectance of TaB67 is significantly lower than that of TaB82, TaB93 and TaB100, though similar to TaB78, due to the pore ability to partially trap radiation. It is worthy to note that in the wavelength range 0-3 µm, the TaB67 reflectance is higher than TaB78, becoming lower in the 3-12 µm range. This can be due to several reasons. TaB67 has a quite inhomogeneous surface morphology characterized by large sintered aggregates up to 10 µm wide, spaced out with voids of about the same dimensions (Fig. 4a). The aggregates are quite dense and appear to be often filled by spurious residuals of the final machining. (Fig 4a). Available pore/voids in the range 3-12 µm favor radiation capturing of shorter wavelengths. On the other hand the surface morphology of TaB78 is more homogenous, which explains the regular aspect of the spectrum.

After emittance tests relevant changes are observed in the optical spectra collected at room temperature (Fig. 9b). It can be noticed that reflectance increased compared to pristine materials. The spectra maintain S-shaped curves, i.e. their intrinsic optical selectivity. As for porosity, the same trend is observed as for as sintered samples. The higher the porosity, the lower the reflectance. The reflectance of TaB67 is markedly lower than for the other samples, especially in the 3-12 µm range, again due to the presence of large voids with the same dimensions. As for secondary phases, presence of MoSi$_2$ is more difficult to track, whilst almost all the spectra reveal the presence of a small peak corresponding to silicon carbide at around 12 µm. As already mentioned, MoSi$_2$ was detected by X-ray diffraction even after emittance tests, so it is at least present in the material’s bulk. On the other hand, SiC appeared both on XRD spectra and on optical spectra and EDS analyses confirmed that on the surface, MoSi$_2$ phases were replaced by Si-rich phases, containing
traces of Mo, O, C. The most plausible explanation is further conversion of MoSi$_2$ to form SiO$_2$ or SiOC phases with reactions similar to those occurring during sintering (1). Other phenomena occurring during high temperature exposure in high vacuum are volatilization of silica:

\[
\text{SiO}_2 = \text{SiO}(g) + \text{CO}(g)
\]  

(2)

Or crystallization of SiC from SiOC phases according to:

\[
\text{SiOC} + \text{C} \rightarrow \text{SiC} + \text{CO}(g)
\]  

(3)

\[
\text{SiOC} \rightarrow 0.5\text{SiC} + 0.5\text{CO}(g) + 0.5\text{SiO}(g)
\]  

(4)

Reactions (3) and (4) are favored by the high temperature exposure in high vacuum and explain the presence of SiC reflections in the XRD spectra. These reactions may occur both on the surface and in the bulk.

As for emittance, this property is dependent on the starting porosity, as well. Some features are worthy to note: emittance is markedly higher for TaB67 but rather similar for samples with higher porosity, such as TaB78, 82, 93,100. This is due to the fact that in TaB67, most of porosity is still open and this gives rise to a very rough surface.

A common trend for all the samples exposed to temperature cycling is that emittance always decreases when the measurement is repeated. This effect is particularly relevant in TaB78. The most reasonable explanation resides in the surface diffusion phenomena observed on the tested discs. As previously mentioned, in most cases, a surficial effect of closing small pores amongst the debris was observed. This thermal effect led to partial surface compaction which resulted in a more continuous surface (i.e. less porous) compared to the pristine one. This also explains the higher room temperature reflectance observed on the same samples after high temperature tests.

Surficial changes induced by exposure to high temperature are of extreme interest because they suggest that partially sintered materials are not stable enough for the application requirements. Moreover, even in completely dense materials, surface modifications can lead to optical properties changes, due to change of the surface roughness. This means that both density and surface finish must be carefully controlled.

4.2 Materials performance vs porosity
For a qualitative estimation of material performances in solar absorber applications, from the acquired spectra we calculated the $\alpha/\varepsilon$ ratio between solar absorbance $\alpha$ and thermal emittance $\varepsilon$ at 1300 K, according to the following equation:

$$\frac{\alpha}{\varepsilon} = \left( \int_{0.3\mu m}^{2.3\mu m} (1 - \rho^\wedge(\lambda)) \cdot S(\lambda) d\lambda \right) \left( \int_{0.3\mu m}^{2.3\mu m} S(\lambda) d\lambda \right)^{-1}$$

$$\left( \int_{0.3\mu m}^{14.3\mu m} (1 - \rho^\wedge(\lambda)) \cdot B(\lambda, 1300K) d\lambda \right) \left( \int_{0.3\mu m}^{14.3\mu m} B(\lambda, 1300K) d\lambda \right)^{-1}$$

(5)

where $\rho^\wedge(\lambda)$ is the experimental spectral hemispherical reflectance, $S(\lambda)$ is the sunlight spectral irradiance for air mass $m=1.5$ [19] and $B(\lambda, 1300K)$ is the blackbody spectral irradiance at 1300 K. For “rough” samples, such as TaB78 and TaB100, we considered the reflectance spectra measured after the high-temperature treatment, as they are most representative of a solar absorber in operating conditions (especially because of removed machining residuals). It should be emphasized that Eq. (5) is only a qualitative estimation of the correct $\alpha/\varepsilon$ ratio, that requires that the spectral hemispherical reflectance $\rho^\wedge(\lambda)$ is measured at the same temperature of the blackbody.

The $\alpha/\varepsilon$ ratios for the samples used for high-temperature experiments are listed in Table I, calculated for the post-test spectra and for blackbody at 1300 K. We can appreciate that the samples become more performing as the density increases up to 90%, while there is no practical difference between 90% and 100% density samples. In fact, porous samples show a higher solar absorbance than dense specimens, but this happens at the expense of the emittance, which is also higher, entailing thus a lower $\alpha/\varepsilon$ ratio.

4.3 Tantalum boride vs other UHTCs and Silicon carbide
As a final comment, it is useful to compare the investigated TaB$_2$ with previously investigated UHTCs and silicon carbide [10-14]. This latter is the reference material for high-temperature solar absorbers. Figure 12 shows the comparison between emittance values (referred to the color temperatures in our apparatus [18]) obtained for TaB$_2$ 100% and those measured previously. The experimental apparatus for high-temperature investigations has been updated since published reports and an improved temperature measurement is possible for the present work. This setup allows the use of so-called “cross temperature”, i.e. the temperature of the surface is established using the two-color pyroreflectometry and a convergence algorithm [16-18]. However, the present apparatus also gives the value of color temperature to allow a comparison of the present data to previous results. A discussion of the color and cross temperatures is beyond the scope of the present work and can be found in the literature [16-18]. Here it is only useful to mention that for our samples, color temperature is usually slightly higher than cross temperature, at thus the emittance calculated on the color temperature basis is slightly lower than the emittance calculated taking the cross temperature as reference. Thus, to allow the comparison between the investigated TaB$_2$ samples and the previous data on different UHTCs and SiC, the color temperature has be considered. From Fig. 12 we can appreciate the similarity between the emittance values of TaB$_2$ and TaC, as confirmed by the similar spectral features already evidenced. Among borides, TaB$_2$ has the lowest emittance. On the other hand, the emittance of ZrC and HfC is generally higher than borides, and the emittance of SiC is by far the highest.

**Figure 12:** Comparison between the hemispherical emittance obtained for different UHTCs (dense samples). The emittance shown here is referred to the color temperature [18].
As for the different TaB$_2$ samples investigated in the present work, for TaB67, which is the most emissive sample we produced, we obtained emittance values, in terms of color temperature, of about 0.6, i.e. in the same temperature range investigated for SiC. To note that SiC emittance was 0.6 only at 1100 K and quickly rose to about 0.8 at increasing temperatures. On the other side, for TaB100 the emittance was around 0.3. SiC is a better solar absorber than borides, thanks to its lower reflectance, about 30% hemispherical reflectance values across the whole sunlight spectral range. However, the calculated $\alpha/\varepsilon$ ratio for SiC is about 1, which is lower than for TaB67 ($\alpha/\varepsilon$=1.3), and about a half than for the 85%-100% dense borides, ($\alpha/\varepsilon$=1.7-2.1). From these considerations, we can conclude that TaB$_2$-based materials are promising for application as solar absorbers and have the potential to overcome SiC performances.

5. Conclusions

In this work we report on the production and characterization of TaB$_2$ ceramic samples with different density levels (67%, 78%, 82%, 93% and 100%). The samples have been structurally and optically characterized. Microstructural features are investigated by means of SEM-EDS and XRD techniques. Optical properties have been studied looking both at the room temperature optical reflectance in the wavelength range 0.3-14.3 $\mu$m and to thermal emittance for temperatures in the range 1050-1800 K. Compositional, structural and optical property change after high temperature exposure are assessed. Relationships amongst porosity level, surface roughness, distribution of secondary phases and optical properties have been outlined and we demonstrated that TaB$_2$ is promising for solar absorber applications, thanks to its intrinsic spectral selectivity and low thermal emittance at high temperature.

Acknowledgements

Authors are grateful to Mr. Mauro Pucci and Mr. Massimo D’Uva (INO-CNR) and to C. Melandri and D. Dalle Fabbriche (ISTEC-CNR) for technical assistance.

References


Table Captions
Table I: Investigated materials: sintering cycles, densities, pore dimensions, roughness and calculated $\alpha/\varepsilon$ ratios after high-temperature experiments.

Figure Captions

Fig. 1: Scheme of the MEDIASE setup. 1: hemispherical window; 2: water cooled thermal shield and sample holder; 3: specimen; 4: three-mirror goniometer; 5: optical fiber and measurement head; 6: bichromatic pyro-reflectometer 7: water cooled chamber; 8: radiometer

Fig.2: Polished surface of dense TaB$_2$-based ceramic sintered at 1900°C showing a) overall microstructure, b) SiO$_2$/SiC agglomerate, c) secondary phases and wetted grain boundaries.

Fig.3: Fracture surfaces of partially porous TaB2-based ceramics sintered at a) 1600°C, b) 1750°C, c) 1780°C, d) 1850°C.

Fig.4: Surface morphology of the discs before (left column) and after (right column) emittance tests. a, b) TaB67, c, d) TaB78, e, f) TaB82, g, h) TaB93, i, l) TaB100. Circle and arrow in a) indicate presence of voids and MoSi2 agglomerates, respectively.

Fig. 5: Surface contamination before emittance tests in: a) TaB67, arrows indicate contaminants b) TaB85, circles refer to sites where EDS spectra are collected, c) EDS spectrum showing SiO-rich based phases containing Cu, Zn due to EDM machining. d) oxygen contamination on the Ta-based phase.

Fig. 6: Surface morphology of TaB78: a) before and b)-d) after emittance tests. Note diffusion phenomena which led to change of particle morphology from sharp (a) to rounded grains (b) and formation of Si-rich phase at the MoSi$_2$ sites in c)-d).

Fig. 7: Formation of whiskers on TaB67 after emittance tests deriving from vapor phase condensation.

Fig.8: Example of X ray diffraction spectra of TaB90 collected on a) as sintered and b) after emittance tests showing traces of SiC and MoSi$_2$. 22
Fig. 9: Hemispherical reflectance spectra of the different TaB2 samples a) before and b) after the high-temperature treatment. Spectra of SiC and MoSi2 are shown for comparison (specular reflectance).

Fig. 10: Hemispherical reflectance spectra of different UHTC materials. All the spectra are acquired for dense samples.

Fig. 11: Measured hemispherical emittance on the various TaB2-based ceramics.

Fig. 12: Comparison between the hemispherical emittance obtained for different UHTCs (dense samples). The emittance shown here is referred to the color temperature [18].