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Compositional dependence of optical properties of zirconium, hafnium and tantalum carbides for solar absorber applications

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Abstract

Besides ultra-refractoriness and favorable mechanical and chemical characteristics, carbides of early transition metals show intrinsic spectral selectivity, making them appealing for high-temperature solar absorber applications. However these kinds of ceramics can be produced using many processing methods resulting in different compositions, density and surface finishing. Thus the present work reports on the systematic study of microstructural, mechanical and optical properties of dense zirconium, hafnium and tantalum carbides as a function of the sintering method (high pressure or pressureless), implying use of 10 or 20 vol% of $MoSi_2$ as sintering aid. The spectral hemispherical reflectance of Zr-, Hf- and Ta-carbides has been measured in the 0.25–16.5 μm wavelength range and correlated to the surface microstructure and roughness. Room and high temperature fracture strength has been measured as well.

Keywords: Carbides; Ultra-high temperature ceramics; Optical properties; Solar absorbers; Solar plants; Concentrating solar power

1. Introduction

Concentrating solar power is one of the most promising renewable energy technologies. Sun radiation is collected and concentrated upon a receiver (e.g. a pipe, a surface, ..). A heat-carrying fluid transports the heat to a power station. The heat is used to produce steam that drives an electricity turbo-generation unit (Romero and Steinfeld, 2012). The obtainable efficiency thus increases with increasing operating temperature.

The solar receiver is a key element and a large effort is devoted to the development of novel receiver architectures able to raise the plant operating temperature (Kalogirou, 2004; Yan and Chen, 2010; Naito et al., 1996; Capeillère et al., 2014). As for the receiver material, up to now the research has been addressed mainly to refractory ceramics, like silicon carbide (SiC) Fend et al., 2004; Hischier et al., 2012; Mey et al., 2014, alumina (Karni et al., 1998) and, more recently, ultra-high temperature carbides and borides (Sani et al., 2011a,b, 2012a,b, 2013, 2014; Sciti et al., 2013, 2014, 2015) and black zirconia (Sani et al., 2015). Blackbody-like absorbers (e.g. SiC) show high radiation losses, thus corrective actions have been recently proposed including, for instance, the addition of external reflectors (Weinstein et al., 2014), which, however, considerably increase the system complexity. Moreover, the importance of spectral selectivity in high temperature solar absorbers

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has been studied in the literature (Burlafinger et al., 2015), and the simplest approach in this case is identifying materials with intrinsic selectivity properties.

Recent studies on ultra-high temperature ceramics (UHTCs) have shown that carbides and borides of zirconium, hafnium and tantalum possess, besides other favorable characteristics like high thermal conductivity high hardness and strength and the highest melting points of any known material, also good spectral selectivity and low emittance at high temperatures (Sani et al., 2011a,b, 2012a,b, 2013, 2014; Sciti et al., 2013, 2014, 2015). The main weakness of these carbides is their poor resistance to oxidation, so they are primarily proposed for operation in vacuum, like in the device described in Bellucci et al. (2015), or under inert atmosphere. However, it should be emphasized that the introduction of secondary phases able to produce silica-based glass (like SiC, $MoSi_2$, $TaSi_2$ and all transition-metal silicides) greatly improves their oxidation resistance (Sciti et al., 2009; Silvestroni and Sciti, 2010).

UHTCs can be produced through a variety of processing methods, compositions and with full density or tailored porosities. Previous works on optical properties of UHT-carbides was focused on the screening of different compositions, in terms of type and amount of secondary phases, sintering aids, levels of porosity, etc. One study (Sani et al., 2012a) demonstrated the intrinsic selectivity of refractory carbides as a general characteristic. However, drawing precise relationships between surface, microstructure and optical spectra was not feasible due to the non-systematic change of microstructural features. Other works put in evidence the lower emissivity of these carbides with respect to silicon carbide, which is again related to their spectral selectivity. For instance, the total hemispherical emissivity of ZrC, HfC, TaC at 1200 K lies in the 0.3–0.4 range, against 0.8 of SiC at the same temperature (Sani et al., 2011a,b). These values can notably increase with increase of the surface roughness/porosity. For instance, for HfC-based materials, a porosity increase from 5 to 30 vol% led to significant gain of emissivity from 0.4 to 0.55 (Sani et al., 2013).

A precise knowledge of factors affecting optical properties of these ceramic is of great importance for material optimization in view of solar absorber applications. Therefore, the aim of this work is a systematic study of optical properties amongst dense ZrC, HfC and TaC, containing 10 and 20 vol% of $MoSi_2$ as sintering aid and controlled surface roughness.

2. Experimental

Commercial powders were used for the preparation of materials: cubic ZrC (Grade B, H.C. Starck, Germany), mean grain size 3.8 μm, impurities (wt%) C:1.5, O:0.6, N:0.8, Fe:0.05, Hf:2.0; cubic HfC (Cerac Inc., USA), mean grain size 1.04 μm, impurities (wt%) Zr:<0.6, O:0.35, Cd:0.002; cubic TaC (Cerac Inc., USA), mean grain size 1.21 μm, impurities (wt%) Ti:0.04, Nb:0.03, Na:0.03, Fe:0.02, Ca:0.01; tetragonal $MoSi_2$ (Aldrich, USA) mean grain size 2.8 μm, impurities (wt%) O:1.

Matrix and additive were weighed in the proper amount, ultrasonically treated and mixed through mechanical mixing for 24 h in absolute ethanol using ZrO_2 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 Table 1. 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) at 1950 °C, as indicated in Table 1. For all composites, free cooling followed.

On sintered materials, the bulk densities were measured by Archimedes' method and confirmed by SEM inspection.

The microstructure of sintered ceramics was analyzed on fractured and 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 commercial software package (Image-Pro Plus® version 7, Media Cybernetics, Silver Springs, MD, USA).

A standard procedure for surface finishing was adopted to exclude any influence of polishing time, pressure and grade on the optical spectrum recorded. The optical surface of all specimens was polished using diamond paste from 30 μm down to 0.25 μm grain size.

The topological characterization of the surfaces was then carried out with a non-contact 3D profilometer (Taylor-Hobson CCI MP) on two areas of $0.08 \times 1\ cm^2$ at the center of each sample and the topography data were analyzed using commercial software (Talymap 6.2). The evaluation of 2D texture parameters (average roughness, Ra, and maximum distance between peak and 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.

Mechanical properties of carbides were measured in previous works (Sciti et al., 2009; Silvestroni and Sciti, 2010) and the procedure is here described for the sake of clarity. It has to be mentioned that, for the hot pressed samples, values of strength were determined on compositions with slightly higher content of $MoSi_2$, e.g. 15 vol% (Sciti et al.,