Solar Energy Materials & Solar Cells 132 (2015) 460–466

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Femtosecond laser treatments to tailor the optical properties of hafnium carbide for solar applications

D. Sciti [a,*], L. Silvestroni [a], D.M. Trucchi [b], E. Cappelli [b], S. Orlando [c], E. Sani [d]

[a] CNR-ISTEC, Institute of Science and Technology for Ceramics, Via Granarolo 64, I-48018 Faenza, Italy
[b] CNR-ISM, Institute of Structure of Matter—Montelibretti Section, Via Salaria km 29.300, I-00015 Monterotondo Scalo, Italy
[c] CNR-ISM, Institute of Structure of Matter—Tito Scalo Section, Zona Industriale, 85050 Tito Scalo (PZ), Italy
[d] CNR-INO, National Institute of Optics, Largo E. Fermi, 6, I-50125 Firenze, Italy

ARTICLE INFO

Article history:
Received 18 June 2014
Received in revised form
3 September 2014
Accepted 26 September 2014

Keywords:
Hafnium carbide
Molybdenum disilicide
Ceramic
Solar absorber
Femtosecond laser
Patterning

ABSTRACT

HfC-based materials are promising composites for application as solar absorbers. Being a ceramic with some metallic character, HfC shows intrinsic spectral selectivity, but quite a high reflectance at the wavelengths of the Sun spectrum. In this work, a femtosecond laser treatment has been specifically tailored to increase the solar absorbance of a composite 70 vol% HfC–30 vol%$MoSi_2$. We investigated the morphological surface changes induced by the femtosecond laser on both phases, proposing a mechanism for surface modifications on the basis of microstructural analysis. Despite the presence of two ceramic phases with different physical properties, the laser was able to modify both phases simultaneously upon specific parameters. The effect of the surface texturing on the optical spectrum was analyzed. By use of specific laser interaction and patterning parameters, the formation of a regular surface pattern allowed the absorbance-over-emittance ratio to be increased from about 1.8 to 2.1.

1. Introduction

Hafnium carbide is one of the highest melting point compounds (~3900 °C) and belongs to the class of the so-called Ultra-High-Temperature-Ceramics (UHTCs). It is worth mentioning its high hardness, high electrical conductivity and chemical stability.[1–3] HfC is a potential candidate material for aerospace applications, because of the high melting point and low self diffusion coefficient [1–7]. Recently it has been found that HfC also has the characteristic of being an intrinsic solar selective material and thus potentially very interesting for solar energy applications [8–11] as absorbers operating at temperatures typically of 1200 K or higher.

The main challenge in present solar energy exploitation is the efficiency increase that, for thermodynamic solar plants, translates in a higher temperature operation, i.e. >800 K [11,13]. Thus, the ideal solar receiver material should withstand high temperatures with good oxidation properties, while having both a high solar absorption and a low emittance at the furnace operating temperatures. In previous works we have demonstrated that HfC-based materials favorably compare to other ceramics presently used for this application, such as alumina and silicon carbide thanks to both the better spectral selectivity and the considerably lower thermal emittance, with subsequent superior energy storage capability [9]. If the solar absorbance is concerned, the reflectance spectrum at room temperature of HfC consists of a step-like, almost S-shaped curve with a low reflectance in ultraviolet (UV) wavelength region and reflectance increasing with the wavelength for the spectral region above 3 μm [9]. A composite containing 10 vol% $MoSi_2$ as sintering aid showed a reflectance varying from 40% to almost 80% for wavelengths shorter than about 2 μm [8]. This *S*-shaped curve behavior is peculiar of this class of materials and indicates their ability to be optically selective. The ideal absorber however has a null reflectance up to around 2 μm and a 100% reflectance for wavelengths longer than 3 μm. Therefore an increase in the visible-near infrared spectrum absorbance (i.e. a reflectance decrease) is desired in order to improve the ability of the material to selectively absorb the solar radiation. A typical stratagem is the creation of a surface periodic pattern with periods lower than 2 μm, able to capture the optical radiation [12,13]. However, for superhard UHTC materials, patterning through conventional ceramic processing techniques is a difficult task. Laser machining is a flexible and non-contact technique particularly suited for producing surface textures [14–22]. The possibility to control the technological parameters of radiation allows the achievement of unique and tailored surface structures. Generally,

---

* Correspondence to: Via Granarolo 64, 48018 Faenza (RA), Italy. Tel.: +39 0546 699748.
E-mail address: diletta.sciti@istec.cnr.it (D. Sciti).

http://dx.doi.org/10.1016/j.solmat.2014.09.037

the surface modifications induced by laser on ceramics depend either on laser processing parameters, such as wavelength, fluence, number and duration of pulses, spot size, beam homogeneity, beam angle of incidence, ambient pressure; or material-specific factors, such as microstructure, composition, optical absorption coefficient and thermal conductivity [14–22]. Short and ultra-short pulse lasers have been investigated in the literature for machining structures in a variety of solid materials [23,24]. A general result is that the heat diffusion into the surrounding material is reduced when the pulse duration is decreased [25]. Therefore, ultra-short pulses are particularly appealing as surface structures are obtained with minimized heat-affected zones.

In this work a femtosecond laser is used to produce a regular pattern on HfC-based materials. The addition of $MoSi_2$ is useful for the densification of samples. It has been found that a 10–15 vol% content of this phase is enough for full densification by either hot pressing or conventional sintering [5]. For the specific purpose of this work, the content of $MoSi_2$ was intentionally raised for a better understanding of the laser-material interactions in the two involved phases. We report, for the first time to the best of our knowledge, on the optimization of the laser machining of a superhard and ultra—high temperature ceramic, to obtain a regular surface texture particularly useful for increasing the solar absorbance. The morphological aspects characterizing the material are analysed, as well as optical properties in the spectral range 0.3–16 μm.

2. Experimental

2.1. Materials

The Hafnium Carbide based composite was densified by pressureless sintering at 1900 °C, with a 30 vol% content of $MoSi_2$ as sintering agent. Details on the material processing are reported in [3]. The sintered material is nearly pore-free and characterized by crystalline HfC (bright contrast areas in Fig. 1a) and $MoSi_2$ (dark contrast areas). An intermediate grey phase of mixed reaction product $(Hf,Mo)_5Si_3$ is also present in minor amounts [3]. From the sintered pellets, discs of approximately 4 cm diameter were prepared by conventional diamond machining. Mechanical polishing was then performed up to a final roughness of 0.04 ± 0.005 μm.

2.2. Laser treatments

Laser treatments were carried out using a femtosecond Ti:sapphire laser, operating at 800 nm wavelength, 100 fs pulse duration. Preliminary tests were carried out with a laser repetition rate of 1000 Hz, in ambient air analyzing the effect on the materials of different laser fluences and scanning speeds:

$$\text{Case A}: 17\ \text{J/cm}^2 \text{and } 0.6\ \text{cm/s};$$

$$\text{Case B}: 15\ \text{J/cm}^2 \text{and } 0.8\ \text{cm/s};$$

$$\text{Case C}: 6\ \text{J/cm}^2 \text{and } 1\ \text{cm/s}.$$

The spot size is 100–150 μm. Areas of approximately 1.0 cm^2 were treated by laser radiation at normal incidence, moving the sample with an XY stage and generating a scanning pattern of parallel lines. Spacing between the lasered lines was 75 μm. The patterned surface microstructures were then analysed 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, High Wycombe, U.K.). After the described preliminary tests, a 3 cm diameter disc was laser textured (case D) using optimized conditions and further analyzed by SEM-EDS and optical measurements. The experimental parameters in this case were: laser repetition rate 10 Hz, laser fluence 15 mJ/cm^2, scanning speed 0.8 cm/s. Moreover, this treatment was carried out in low vacuum (~100 mbar) to limit the effects of oxidation.

2.3. Optical measurements

The hemispherical reflectance spectra for quasi-normal incidence angle was measured onto the patterned disc at room temperature in the wavelength region from 0.3 to 16 μm using two instruments: (1) a double-beam spectrophotometer (Lambda900 by Perkin Elmer) equipped with a Spectralon®-coated integration sphere for the range 0.3–2.5 μm and (2) 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 μm. For the sake of comparison, an unpatterned sample was also investigated.

3. Results

3.1. Microstructural features

Fig. 1a illustrates the typical bulk morphology of these samples, e.g. a dense microstructure where the two constituent phases (HfC and $MoSi_2$) can be clearly distinguished, by their image contrast. HfC is the brighter phase, $MoSi_2$ is the darker one. The original surface morphology after polishing and before laser treatment is shown in Fig. 1b.

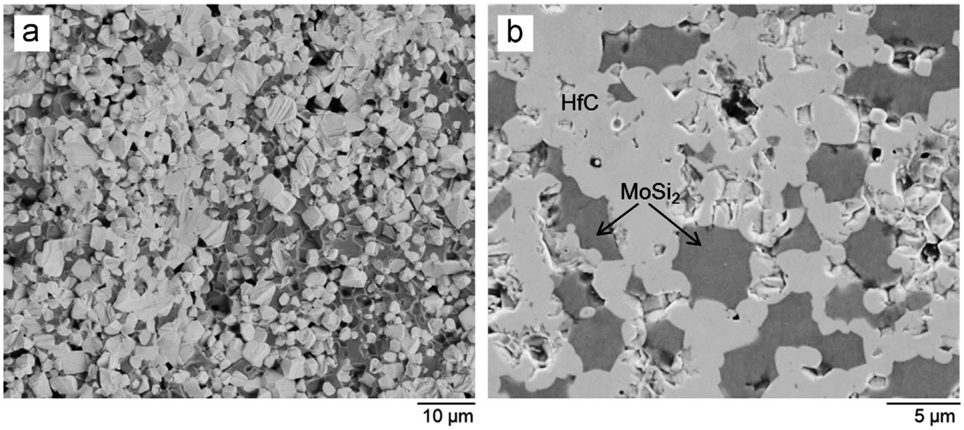

Fig. 1. Microstructural features of the HfC-based material, (a) fracture surface, (b) polished surface before laser patterning.