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

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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\textsubscript{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.

Keywords: Hafnium carbide, Molybdenum disilicide, ceramic, solar absorber, femtosecond laser, patterning
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% MoSi2 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,
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 MoSi₂ 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 MoSi₂ 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 MoSi₂ 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 MoSi₂ (dark contrast areas). An intermediate grey phase of mixed reaction product (Hf,Mo)₅Si₃ 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:

Case A: 17 J/cm² and 0.6 cm/s;
Case B: 15 J/cm² and 0.8 cm/s;
Case C: 6 J/cm² and 1 cm/s.

The spot size is 100-150 µm. Areas of approximately 1.0 cm² 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/cm², 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

Figure 1a illustrates the typical bulk morphology of these samples, e.g. a dense microstructure where the two constituent phases (HfC and MoSi2) can be clearly distinguished, by their image contrast. HfC is the brighter phase, MoSi2 is the darker one. The original surface morphology after polishing and before laser treatment is shown in Figure 1b.

![Figure 1: Microstructural features of the HfC-based material, a) fracture surface, b) polished surface before laser patterning](image)

The surfaces were prepared by mechanical polishing as described above and reveal some irregularities/voids due to it. Figure 2a shows instead an example of the laser-treated areas. The laser path creates a series of grooves shown in Figure 2b.

![Figure 2: Laser-treated areas, a) laser path, b) grooves created by laser treatment](image)
Figure 2: a) Preliminary tests on the ceramic disc, b) magnification of a laser areas showing grooves.

Figure 3: Surface morphology of the lasered samples in different conditions and related EDS spectra collected onto the HfC and MoSi₂ phases. Cases A, B, C. Inset in case A shows voids left by HfC grain removal (see arrows).

The microstructure inside the grooves is affected by the laser parameters. Figure 3 compares the surface morphologies obtained in the three tested combinations.

Case A: fluence 17 J/cm², speed 0.6 cm/s. Low magnification images show that laser treatment created grooves, as shown in Fig. 2b. Higher magnification images of the microstructure inside the grooves (Fig. 3a) show a very disordered microstructure with evident melting phenomena, especially localized on MoSi₂, which suggests that locally reached temperatures may overcome 2000°C, i.e. the melting point of MoSi₂ (2020°C [26]). EDS analyses reported presence of oxygen and large melted areas containing Si, Mo, O and Hf (see EDS spectra in Fig. 3). Other areas show material removal (especially located on HfC grains, see inset in Fig. 3a).
Case B represents an intermediate situation, with fluence of 15 J/cm² and speed of 0.8 cm/s, respectively. The appearance of a periodic structure inside the grooves is observed (Fig. 3b) and this structure forms irrespective of the underlying phase HfC or MoSi₂, but is interrupted in correspondence of pre-existent surface holes. Oxygen contamination is recognized both in MoSi₂ original areas, and in HfC ones (see EDS spectra).

Case C: fluence 6 J/cm², 1 cm/s speed. By decreasing the fluence, a very mild surface modification was obtained, Fig. 3c. A light series of grooves is formed, but, increasing the magnification, the underlying microstructure is still visible, with recognizable constituent phases, HfC, MoSi₂ and pre-existent holes. A careful SEM analysis reveals however presence of some wavy structures inside the grooves, especially located on MoSi₂ phases, whilst the HfC phase is unmodified. Oxygen contamination can be observed, but it is milder compared to the previous cases.

Choosing laser conditions similar to those of case B, a 3 cm diameter disc was fully patterned (case D), see the photo in Fig. 4.

Figure 4: Picture of the lasered disc. The missing portions of the disc were cut for microstructural analysis

Details on the surface microstructure are shown in Fig. 5 a-f, where higher magnification images evidence some features of the modification induced by the laser treatment. Surface morphology is similar to case B, though the surface modification is less deep. Working in low vacuum instead of air reduced the extent of surface oxidation as explained later, resulting in more ordered microstructure.
Figure 5: Surface morphology of Case D patterning: a) overview, b)-d) details of the microstructure showing melting and liquid phases onto MoSi$_2$ and liquid phase onto HfC, e) EDS spectra collected onto MoSi$_2$ (left) and HfC (right), f) modified layer thickness.

It is also apparent that MoSi$_2$ modification was deeper compared to HfC (Fig.5 c,d). MoSi$_2$ grain morphology disappeared and a molten/recast structure with shallow oxidised layers appeared
onto the original MoSi$_2$ regions. Despite the treatments were conducted in low vacuum, EDS analysis confirmed the presence of oxygen and lower Hf/C ratio compared to the original material (Fig. 5e). Oxidised layers had wavy structures, and a precipitation of small particles was observed (Fig. 5d). HfC grains were still recognizable, but exhibited grooves along grain boundaries which are typical of thermal etching processes. According to EDS analyses, C and O enrichment were observed for both phases (see EDS spectra in Fig. 5e). Again, a shallow oxidised layer covered the HfC grains with a wavy structure and small reprecipitated particles. On the cross section, it is evident that the extent of laser interaction with the ceramic is very shallow, as the modified layer is less than 50 nm deep (Fig. 5f). Finally, the spatial period of the waving structure is around 800 nm, i.e. it corresponds to the central wavelength of the laser.

### 3.2 Optical spectra

The comparison of hemispherical reflectance spectra for the Case D treated sample and the untreated surface is shown in Fig. 6. The reflectance of the grooved sample is lower than that of the original surface in the spectral range for wavelengths lower than about 1.5 µm, while increases towards longer wavelengths, becoming higher than that of the untreated material. This behavior allows expecting the laser treated surface to show an increased solar absorbance $\alpha$ with a reduced thermal emittance $\varepsilon$, and thus a more favorable $\alpha/\varepsilon$ ratio in comparison to the original HfC sample.

Figure 6: Hemispherical reflectance spectra in the wavelength region 0.3-16 µm. The inset shows the detail of the 0.3-2.3 µm range with superimposed the sunlight spectrum (dashed blue line).
4. Discussion

4.1 Microstructure modification induced by the femtosecond laser

Since the early 1970’s, researchers have reported on the appearance of spontaneous periodic surface ripples following laser irradiation [27-30]. The ripples, also named Laser Induced Periodic Surface Structures (LIPSS), are small undulations on the surface with spatial periods closely related to the central wavelength of the laser. They occur at a wavelength close to the central wavelength of the laser light and it is generally believed that their long axis is perpendicular to the laser polarization, even if in some cases ripples are also observed independently of the polarization direction. Their formation is not a well understood phenomenon yet. According to some reports, liquid phases are present during ripple formation, which is in agreement with the microstructural features of the present work. Other phenomena reported to occur during this kind of treatment are oxygen enrichment (if treatment in carried out in air) and or amorphisation. There is also discrepancy on the specific laser processing that give rise to ripples, including the number of laser pulses, as well as the energy involved (below and above the material ablation threshold). Although discussion on physical phenomena, such as relationships between the polarization direction of the laser and ripple formation, is beyond of the scope of this work, we can instead make some considerations on the chemical modification of the surface. There is a limited number of papers that analyse the effects of femtosecond laser processing on non-oxide ceramics, and these cases only concern monophasic ceramics, such as AlN [28]. Few papers can be found instead for composites materials, such as the present one, where two well distinguished ceramic phases are the constituents of the microstructure. For instance, submicropatterning was reported for a Al₂O₃-TiC composite upon femtosecond laser patterning at low fluence [24], only for TiC regions, but no studies were conducted to obtain simultaneous patterning of both phases. Even if a larger number of experiments is needed for drawing more definite conclusions, the work we carried out allows us to identify several general characteristics:

1) Ripples are generated only for specific ranges of laser fluences.

2) Due to the fact that MoSi₂ and HfC have different physical properties, the laser-ceramic interaction is different in the two phases.
3) The ripple morphology suggests the presence of a liquid phase. The nature of this liquid phase is not known, but in optimized conditions, such as those of Case D, ripples are homogeneously created on either HfC or MoSi$_2$ phase, despite the different melting point of the starting phases (~3900°C [31] and 2020°C [26]).

4) Local oxygen and carbon contamination is observed throughout the sample surface.

5) Grooving formation is observed onto HfC grain boundaries.

6) Re-precipitation of nano-grains is observed onto both phases.

7) The distance between undulations corresponds to the laser wavelength, i.e. is around 800 nm.

The laser-material interaction, although taking place in a very short time, gives rise to thermal mechanisms having different intensities for the two phases we have. At first, it should be recalled that the melting temperature of MoSi$_2$ is much lower than that of HfC (2020°C and 3900°C, respectively). Moreover, at 800 nm the absorptance of MoSi$_2$ is higher than that of pristine HfC (80% vs. about 70% by direct measurement). Finally, it should be observed that both phases are prone to oxidation when exposed to air or oxygen at high temperature, but the produced oxides have different thermal characteristics. MoSi$_2$ oxidises according to [32]:

$$\text{MoSi}_2 + 3.5\text{O}_2(g) = \text{MoO}_3(s) + 2\text{SiO}_2(s)$$  \hspace{1cm} (1)

Silica forms a protective scale which is stable up to 1700°C, i.e. its melting point [32]. According to thermo-analytical studies, HfC starts to oxidise at 400°C [33]:

$$\text{HfC} + 2\text{O}_2(g) = \text{HfO}_2 + \text{CO}_2(g)$$  \hspace{1cm} (2)

HfO$_2$ is a very stable oxide, with melting temperature around 2800°C [34]. Throughout the sample, the formation of a liquid phase is largely suggested by the morphology, however its composition is difficult to identify and must be compatible with both HfC and MoSi$_2$ underlying phases. EDS analyses suggest that this liquid phase has a different composition depending on the fact that it is originated on HfC or MoSi$_2$, and it is more easily formed on the silicide than on the carbide, in agreement with the lower melting temperature and higher absorbance of MoSi$_2$. On the basis of the
observed morphologies we can roughly estimate the surface temperature reached during laser scanning, with particular reference to case D. In MoSi$_2$, local melting suggests temperatures of the order of 2000°C. At this temperature in air or low vacuum, oxidation of MoSi$_2$ also occurs but a solid silica surface layer will only form during cooling down, when the temperature is below 1700°C. The final appearance is thus a shallow silica layer observed on the molten/recast MoSi$_2$. Around 2000°C, though, HfC is very far from its melting point and thus the explanation for liquid phase and ripple formation must found elsewhere. During the temperature increase, HfC oxidises according to reaction (2), but HfO$_2$ itself cannot be the sole reason for liquid formation as it melts at 2800°C. Such a high temperature, however, is not suggested by the surface morphology. Indeed if such a high temperature would be reached, we should observe vaporization and creation of holes at MoSi$_2$ sites. Thus we can conclude that the temperature must be lower. Another possibility to have liquid phase on HfC at lower temperature is the formation of metallic Hf, if the laser directly dissociates HfC, according to:

$$\text{HfC} \rightarrow \text{Hf} + \text{C} \quad (3)$$

which would also explain the evident carbon enrichment on the surface. Hf has a melting point of 2233 °C and thus could be the origin of liquid phases. Alternatively, the Hf-O phase diagram indicates the existence of a Hf-HfO$_2$ eutectic at 2200°C when the oxygen content is around 37 at% [34]. Thus, simultaneous presence of oxidation and dissociation effects could originate liquid phases.

Another option is formation of intermediate liquid phases, for example Hf-Si-O phases. However, EDS analyses did not reveal any Si onto HfC/HfO$_2$ phases. We thus could make the hypothesis that liquid phase onto HfC grains is originated either by metallic Hf melting or by Hf-HfO$_2$ eutectics. The presence of oxygen, however, suggests the latter hypothesis is more probable. The phenomena occurring suggest that oxidation can play an important role in the final morphology for HfC. Indeed, working in low vacuum (case D) instead of air (case C) reduced the extent of surface oxidation resulting in more ordered microstructure. From these considerations, we can summarize the occurred events as follows:

- For case A, the energy involved in the laser/material (fluence 17 mJ/cm$^2$) interactions lead to very high surface temperature, exceeding 2200°C. MoSi$_2$ morphology suggests profuse
melting, whilst thermal stresses cause HfC pullout. The surface is not stable and the creation of a regular pattern is not possible.

- For case C, the laser/ceramic interaction is too mild. HfC is almost unaffected but some ripples start to appear on MoSi$_2$ sites, suggesting temperatures lower than 2000°C. In fact, the temperature range compatible with formation of liquid phases onto either the MoSi$_2$ and HfC phases and consequent creation of ripples is 2000-2200°C.

- Case B suggests that with fluences lower than 15 mJ/cm$^2$, liquid phases of different nature are originated onto HfC and MoSi$_2$ phases and are the optimized conditions for obtaining simultaneous patterning of both phases.

- Finally, working in low vacuum instead of air (case D) reduces the oxidation phenomena and may result in a shallower surface modification.

### 4.2 Influence of the surface patterning on the optical properties

In this paragraph, we calculated the absorbance to emittance ($\alpha/\varepsilon$) ratio at a reference temperature of 1200 K, well above the maximum service temperature of surfaces currently employed as absorbers (~ 800 K [13]). From the experimental room-temperature hemispherical reflectance $\rho^\cap(\lambda)$ we calculated a) the total solar absorbance $\alpha$ according to the equation:

$$\alpha = \frac{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} (1 - \rho^\cap(\lambda)) \cdot S(\lambda) d\lambda}{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} S(\lambda) d\lambda}$$ \hspace{1cm} (4)

where $S(\lambda)$ is the Sun emission spectrum [35] and the integration is carried out between $\lambda_{\text{min}}=0.3$ μm and $\lambda_{\text{max}}=2.3$ μm; and b) an estimated hemispherical emittance $\varepsilon$ at 1200 K in the wavelength range ($\lambda_1=0.3$ μm, $\lambda_2=16$ μm) according to:

$$\varepsilon = \frac{\int_{\lambda_1}^{\lambda_2} (1 - \rho^\cap(\lambda)) \cdot B(\lambda,1200K) d\lambda}{\int_{\lambda_1}^{\lambda_2} B(\lambda,1200K) d\lambda}$$ \hspace{1cm} (5)
where B(λ,1200K) is the blackbody spectral radiance at 1200K. It should be noticed that the obtained ε value is only an approximate indication of the actual value at the considered temperature. In fact, for a rigorous approach, the reflectance ρ used in equation (5) should be measured at the same temperature of blackbody. Analogously, as the sample temperature increases in consequence of sunlight absorption, for a rigorous calculation of α, the reflectance spectrum ρ considered in equation (4) should be measured at the sample operating temperature. Anyway, in our case, if we take into account the α/ε ratio, we do not expect large deviations from the calculated values because the investigated samples are all made of the same material and the considered 1200K temperature is too low to foresee surface changes. The obtained values of α/ε are 2.1 for case 3 sample and 1.8 for the untreated surface, thus demonstrating the advantageous effect of femtosecond laser texturing to improve the performances of solar absorbers. An even larger α/ε increasing can be obtained with further optimized laser-material interaction and patterning parameters.

5. Conclusions
Oxidation and melting phenomena take place during femtosecond laser treatments of a composite HfC-MoSi2. Only specific laser parameters lead to simultaneous patterning of both phases, HfC and MoSi2. Patterning is governed by formation of liquid phases onto the surface. MoSi2 patterning occurs through direct melting of the phase, while HfC patterning occurs through formation of liquid phases in the Hf-HfO2 system, implying a direct role of oxidation in the process.
The room-temperature optical investigation shows that patterning modifies the spectral reflectance curve. In particular, the optical absorbance at wavelengths shorter than about 1.5 µm is increased with respect to the pristine material, while the effect is reversed at longer wavelengths. This allows estimating a higher α/ε ratio and thus superior performances of the textured material for solar absorber applications.

Acknowledgements
The authors would like to thank the European Community for the financial support of the European Project E²PHEST²US “Enhanced Energy Production of Heat and Electricity by a combined Solar Thermionic-Thermoelectric Unit System”— GA 241270 in the framework of the Seventh Framework Program, topic “Energy”.

References
Figure Captions

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Figure 2: a) Laser path on the ceramic disc, b) magnification of a lasered areas showing grooves.

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Figure 5: Surface morphology of Case D patterning: a) overview, b)- d) details of the microstructure showing melting and liquid phases onto MoSi₂ and HfC, e) EDS spectra collected onto MoSi₂ (left) and HfC (right), f) cross section of the treated sample showing the modified thickness.

Figure 6: Hemispherical reflectance spectra in the wavelength region 0.3-16 µm. The inset shows the detail of the 0.3-2.3 µm range with superimposed the sunlight spectrum (dashed blue line).