Improving solar radiation absorbance of high refractory sintered ceramics by fs Ti:sapphire laser surface treatment

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A B S T R A C T

Samples of high refractory pressure-less sintered carbide ceramics (HfC based), polished by mechanical grinding to a surface roughness $R_a \sim 40$ nm, have been surface treated, in vacuum, by fs Ti:sapphire laser, operating at 800 nm wavelength, 1000 Hz repetition rate and 100 fs pulse duration, at fluence varying in the range ($\sim 6$–25)J/cm$^2$, to optimize their solar radiation absorbance, in such a way that they could operate as absorber material in an innovative conversion module of solar radiation into electrical energy. To this aim, an area of approximately 9.6 cm$^2$ was treated by the fs laser beam. The beam strikes perpendicularly to the sample, placed on a stage set in motion in the x, y, z-directions, thus generating a scanning pattern of parallel lines. The experimental conditions of laser treatment (energy fluence, speed of transition, overlapping and lateral step distance) were varied in order to optimize the radiation absorption properties of the patterned surface. In laser treated samples the absorption value is increased by about 15%, compared to the original untreated surface, up to a value of final absorbance of about 95%, all over the range of solar radiation spectrum (from UV to IR). The morphological and chemical effects of the treatment have been evaluated by SEM–EDS analysis. At very high fluence, we obtained the characteristic ablation craters and local material decomposition, while at lower fluence (in any case above the threshold) typical periodic nano-structures have been obtained, exploitable for their modified optical properties.

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1. Introduction

High-performance ceramics have been considered excellent structural materials for many engineering and high-temperature applications, because of their high hardness, high-temperature strength and good corrosion resistance. Hafnium based ceramics show unique properties, including extremely high melting temperature and hardness, high thermal and electrical conductivity as well as chemical stability. These properties make HF-based ceramics good candidates for high-temperature structural applications, including engines, plasma arc electrodes, furnace elements, and also as high temperature solar radiation receiver.

As a matter of fact, an ideal radiation absorber should have: a solar radiation absorbance as high as possible to increase the concentrated radiative-thermal energy conversion efficiency, a melting point far higher than operation temperatures, mechanical resistance at high temperatures and high critical thermal shock resistance, to face possible operation temperature gradients.

The Hf-based sintered carbide HCM-5 (HfC+5% MoSi$_2$) could be considered a good radiation absorbing material; however, its absorbance value, although good, does not reach optimal values of $\alpha$, namely, greater than 90%. Advanced technical ceramics, indeed, are usually produced from powders and densified to solid products by high-temperature pressing and sintering techniques. These procedures produce grains of different sizes, many grain-boundaries and micro-structural defects like pores, glassy phases and flaws, which partially affect the final properties of materials. That is why it is necessary to develop a treatment that makes as uniform as possible the outer layer, and subsequently another “specific patterning” treatment to make the surface able to trap, at best, the solar radiation. A viable solution could be specific laser processing by ultra-short pulses, thus avoiding mechanical tool wear and minimizing thermal and mechanical stress [1].

Since nature routinely produces nanostructured surfaces able to perform specific tasks, such as the self-cleaning lotus leaf, or the high anti-reflection function observed in the moth eye [2,3], scientists and engineers have made every effort to have been able to...
mimic some of these natural structures in the laboratory and in real-world applications [4–10]. Periodic arrays of silicon nanotips, for example, have been created, on Si wafer, with sub-wavelength structures that can suppress the reflection of light from the ultraviolet, through the visible part of the spectrum, to the terahertz region. The antireflection properties of the silicon result from changes in the refractive index caused by variations in the height of the silicon nanotips, and can be explained by models simulating the low reflection from moth eyes. These improved anti-reflection properties of the Si surfaces have been applied in renewable energy and electro-optical devices, like photovoltaic modules [8–13].

The idea was to extend the application of this process of fs-laser nano-structuring, which involves the generation of ripples with a periodicity far below the wavelength of the incident light, also to rough and defective surfaces, typical of ceramic composites sintered at high temperature, following the pioneering work of Dumitru et al. [14] and Rudolf et al. [15]. The choice of an ultra-short pulsed laser is motivated, in addition, by the different interaction with solid materials of short compared to ultra-short laser pulses. It has been shown that heat diffusion into the surrounding material is sensibly reduced, and heat affected zones minimized. Due to the rapid energy deposition, the material is heated to very high temperatures, leading to direct evaporation. The amount of molten material is negligible, the process shows excellent repeatability and the generated structures are characterized by minimal damage and burl-freeness [1.15]. The process efficiency is higher and the process quality is enhanced, since there is no interaction between the expanding plasma and the incident laser pulse (plasma shielding effect), as light absorption and ablation are sufficiently separated in time [16].

Our work was specifically aimed at exploring the possibility of treating the surface of a complex ceramic material as Hf-based sintered carbides, to obtain a nanostructured surface with anti-reflecting properties.

2. Experimental

2.1. Sintered HfC composite preparation and characterization

Technical grade sintered polycrystalline hafnium carbide/molibdenum silicide [HCM5] composite, (HfC + 5\% MoSi2) has been prepared by pressure-less sintering, at 1950 °C, holding time 90 min, in Argon flux. The sintered samples were properly polished and analyzed with scanning electron microscopy (Cambridge S360, Cambridge, U.K.), and energy dispersive X-ray spectroscopy (EDS; INCA Energy 300, Oxford Instruments, High Wycombe, U.K.).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental parameters of Ti:sapphire fs laser surface treatments.</th>
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<tbody>
<tr>
<td>Sample</td>
<td>Ti:sapphire (800 nm, 100 fs, Repetition rate: 1000 Hz)</td>
</tr>
<tr>
<td>Sintered ceramic composite</td>
<td>Roughness $R_d$ ($\mu$m)</td>
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<tr>
<td>HCM 5 (HfC + 5% MoSi2)</td>
<td>0.04 ± 0.005</td>
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<td>0.31 ± 0.04</td>
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<td>0.23 ± 0.02</td>
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<td>0.09 ± 0.008</td>
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<td>0.07 ± 0.005</td>
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$R_d$ arithmetic average of absolute values $R_d = \frac{1}{n} \sum_{i=1}^{n} |y_i|$.  
$R_t$ maximum height of the profile $R_t = R_{peak} - R_{valley}$.  

![Fig. 1. SEM/EDS images of sample HCM5. (a) Fractured surface of as grown sample. (b) Polished surface. (c) High magnification image showing the various phases (HfC and MoSi2) and a reaction phase (Hf, Mo),Si3. (d) The relative EDS spectrum.](image-url)
2.2. fs Ti:sapphire surface laser treatment

An ultrashort Ti:sapphire pulsed laser source (Spectra Physics Spitfire Pro XP, 800 nm, 100 fs) operating at a constant wavelength of 800 nm, repetition rates 1000 Hz, and fluence in the range 6–25 J/cm² was used. The laser beam was focused by a plano-convex lens, focal distance 300 mm, perpendicular to the ceramic sample, to an area of ~100 μm diameter. A micrometric x, y, z fully automated translation stage, moving at variable speed, was employed to obtain, with the laser beam, a regular pattern of parallel lines, over square or circular areas ranging from ~1 cm² to ~38 cm². All treatments were carried out in vacuum (~10⁻⁷ mbar). Some pre-screening treatments were carried out on small areas of the same substrate, at different speed and fluence, in order to perform a preliminary selection of the optimum conditions of treatment. Experimental conditions for this preliminary work are summarized in Table 1.

2.3. SEM characterization, absorbance in the UV–vis–IR region and roughness evaluation

Laser treated samples were subsequently analyzed by SEM/EDS to examine the morphological characteristics and to give an assessment of changes in local chemical composition, compared to the untreated original sample. A rough estimation of the different surface roughness, obtained with various treatments, was performed with a commercial contact stylus instrument (Taylor Hobson mod. Talysurf Plus) profilometer. The absorbance of treated samples,
compared to untreated surface, was evaluated by an UV-VIS-NIR spectrometer (Perkin Elmer Lambda 950), equipped with an integrating sphere.

3. Results and discussion

The pre-screening treatments of surface micromachining were carried out on small square areas of sintered ceramic substrate, at four different conditions of fluence and residence time (Table 1), analyzing both the effects of laser irradiation on structure and chemistry, and the potential, desirable changes of optical absorption/reflection of light.

The effects of laser treatments, at different conditions of fluence and processing speed, are visible in the image of the sample, taken with an ordinary camera (Fig. 2). Analyzing the absorbance spectra (Fig. 3) it appears evident how the treatments have been able to produce significant changes of absorbance, for three kinds of treatment, raising the value well over 90%, in the region UV–vis–NIR, while, in the fourth case, the variation is negligible.

Examining in detail the areas processed, significant changes, both in morphology and in roughness values, were observed, depending both on the laser fluence, and on the speed with which the laser beam passes over the sample. These changes are evident in the overall SEM pictures of the various treatments (Fig. 4). Going into details of the treated surfaces and comparing them with the original specimen, polished with a diamond paste to a roughness $R_a \sim 0.04 \mu m$, we can observe a mild effect, with ripple generation for treatment 3, associated to a slight oxidation process, from SEM/EDS analysis (Fig. 5a), compared to the original polished surface (Fig. 5b); while a more pronounced oxidation and a jagged, disordered surface has been generated with treatment 1 (Fig. 5c).

From a comparative analysis of the four treatments, it is clear that not only fluence but also the speed, at which the laser impinges
on the surface, affects the final characteristics of the treated areas of the composite material. In particular, key differences can be highlighted between two treatments, at virtually the same fluence, but using transit speed halved or doubled, as in tracks 1 and 3 (Table 1).

In track 1, with slower speed of transition, 4 cm/s, we observe a strong effect of laser treatment with partial ablation/re-deposition, and a final morphology more rough and disordered, while, in zone with treatment 3 a more controlled effect with a regular pattern has been generated. This pattern is also characterized by regular and almost parallel waves with constant period of about 750 nm, perpendicular to the macroscopic grooves dug by the passage of the laser, very similar to the "ripples", observed on metal surfaces, single crystal semiconductor and ceramics [18–23], treated by ultra-short lasers.

**Fig. 6.** Scheme of the surface laser treatment: parallel micro-grooves dug on the surface by laser scanning along x-axis. Bi-dimensional groove array generated by the combined motion in the x, y-direction.

**Fig. 7.** SEM images of the treated surface (Φ = 25 J/cm²) at increasing magnification: (a) a regular array of parallel grooves generated by laser rastering at ~12 cm/s velocity and 75 μm lateral step (d). (b) Elongated nanostructures (~200 nm) generated, inside the grooves, perpendicular to the laser path (and to the laser polarization). (c) Ripple generation (~100 nm) inside a laser hole.
Laser processing performed at lower fluence (9 and 12 J/cm²), in general, produces milder effects, less exploitable for the absorption of the radiation in the UV-vis range; in the case of track 4, characterized also by higher speed of processing (and low residence time), the effect is practically negligible, also in term of absorbance variation. The roughness values, $R_a$ and $R_t$, measured with a commercial profilometer, corroborate the evidence from the study of surface morphology by SEM.

The roughness measurements are able to determine both the average value of the surface roughness, given by the parameter $R_a$, and the intensity and depth of the individual treatments, by the measure of the peak-to-valley distance, given by the value of $R_t$, which helps for an evaluation of the local damage, or the ability to operate a deep modification of the surface.

In our case, using the same fluence, but treatment time or residence time of double values (compare samples 1 and 3), the value of $R_t$ is less than twice, while the average roughness $R_a$ is multiplied by a factor greater than three, that means a general and widespread damage over the entire involved area.

This preliminary data have convinced us to select, for the sample to be installed in the conversion module, a higher value of fluence, but associated with a high speed of the process, in order to obtain a pattern of well-defined grooves with high values of $R_t$, associated to low average roughness $R_a$, which implies a more controlled treatment of the surface.

Starting from these guidance results, very promising for a good increase in sunlight absorption, we treated the surface of the absorber sample, a disk of sintered HCM5, 3 cm diameter, in high vacuum, to avoid any potential surface oxidation, at fluence of $\sim 25$ J/cm² and speed transition of about 12 cm/s. The lateral step was optimized at $\sim 75$ μm, to obtain a partial overlapping and a continuous and homogeneous pattern over the entire surface (see the general scheme of the laser processing in Fig. 6a and b). SEM details, at increasing enlargements, show the laser dug micro-grooves (Fig. 7a), associated to a general surface nano-structuring, with formation of “coarse” ripples, perpendicular both to the laser polarization and to direction of the treatment, characterized by edge distances of $\sim 1/4$ and $1/8$ of the laser wavelength (Fig. 7b and c). This coarse, not very precise and defined structure of the ripples is caused by the high inhomogeneity, porosity and presence of defects of the original surface of HIC sintered ceramics; however, to these nanostructures it is associated a remarkable property of light absorption, due to multiple internal reflection and entrapment of the solar radiation. The significant increase in absorbance can be seen in Fig. 8a, showing the optical properties of treated surface, versus untreated. This property is even more evident if we consider an elaboration of such characteristic, as a function of solar radiation.

To weigh the efficiency of each absorbing material, with respect to the spectral content of the solar radiation, we can use the absorbed solar power per wavelength unit, defined as the product between the absorbance and the incident solar spectral irradiance $W_{solar}$. This parameter is shown in Fig. 8b, as a function of radiation wavelength, for the surface of the laser treated, compared to untreated sample.

This acquired property to absorb sun radiation of HCM5 ceramic composite, as a result of the fs laser treatment, has been technologically exploited, using the “engineered” specimen as the active absorber material in a thermionic–thermoelectric conversion module of sunlight into electricity. The overall processes, laser treatments and the HCM-based ceramic modulus have also been patented [24].

4. Conclusion

A fs laser treatment has been used to modify the surface of a sintered complex ceramic material, hafnium carbide based (HCM5), trying to generate a definite periodic pattern able to improve significantly the original light absorbance property of the high refractory material.

The laser treatment, performed under defined experimental conditions, has been able to generate a micro-patterned array also on the surface of a high refractive complex sintered ceramic.
significantly modifying the surface reflectivity, and the light absorbance, measured in the UV–vis–NIR region.

A detailed examination of surface roughness, associated to a morphological SEM/EDS analysis, reveals that a minor reflection of natural light is associated with treatments, carried out at fluence of the order of 15–25 J/cm², taking constant the repetition rate at 1000 Hz, and moderate scanning speed (order of 15–20 cm/s) of the substrate translational stage, moving in front of the laser beam. The process of parallel micro-groove formation is associated to generation of nano-ripples, inside the grooves and perpendicular to the laser path and its polarization, as well known for ultra-short laser interaction with different materials.

The improved antireflection properties are mainly caused by the formation of nano-ripples, with dimensions and edge-distances approximately exact fractions of the laser wavelength (1/4 and 1/8 $\lambda_{fs}$).

The highly textured surface attained allows increased solar absorbance, by multiple reflection process, among the needle-like or dendritic nano-structures.

This property has been technologically exploited to increase significantly the solar light trapping of absorber specimens made of refractory ceramic, housed in a solar platform.

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References