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Abstract. Crystalline silicon carbide (SiC) is a very attractive material in the fields of microelectronics, MEMS and biomedicine mainly due to its chemical inertness and mechanical strength. It is used for SiC MEM sensors, micro motors and resonators [1]. In the biomedical field, SiC is emerging as a promising material for additional coating of biomaterials due to its other useful properties (hardness, lightness, impermeability and good compatibility). For instance, in combination with bioglass, it is used for bone regeneration and as coating of some metal alloys, as it forms a bone-like layer on the surface upon contact with body fluids [2].
We studied the results of microporous modifications on the SiC surface irradiated by ultrashort laser pulses in view of further biomedical applications. The nanostructures were formed on the surface of a silicon carbide sample by using a regeneratively amplified Ti:sapphire femtosecond laser emitting at 800 nm. The SiC samples were irradiated as the laser light parameters (power, energy and number of applied pulses) were varied and the surface morphological changes were investigated. Modification of the topography of the silicon carbide substrates could substantially improve the bioactivity properties of this material, which, after proper laser parameters optimization, could make its biomedical application even more successful.

1. Introduction

Ultra-high temperature ceramic materials (UHTCs), including borides, nitrides and carbides have been widely used for high temperature electrodes, thermal protection systems, etc. Silicon carbide (SiC) is considered to be an important structural ceramic material because of its properties, such as high oxidation resistance, good mechanical parameters, high temperature and high wear resistance, good thermal shock resistance due to the high thermal conductivity, etc. [3]. Silicone-carbide fabrication in general follows two approaches: (1) deposition of preceramic polymers as a precursor for SiC on the surface of microporous ceramic supports followed by pyrolysis in inert atmosphere and (2) deposition of SiC slurry prepared from SiC particles dispersed in an alcoholic medium with polymer binder, followed by sintering at high temperature, which is known as ceramic processing [4] and was used in

this study. SiC/SiC composites are mainly processed through three different methods – chemical vapor infiltration (CVI) whereby the silicon carbide is used in gas phase to first grow SiC whiskers on nanowires; polymer impregnation and pyrolysis (PIP), and melt-infiltration (MI). However, these methods have some disadvantages – the free Si from the MI method, for example, can lower the composite's resistance to oxidation and creep [5]. SiC is also used in MEMS (Micro-Electro-Mechanical-System) for devices such as high-pressure and high-temperature sensors. Another newly emerging application is in tissue engineering, where it is used for carbon fibers coatings (CF), as it improves the wettability and the corrosion resistance of this material [7]. However, the effective patterning of SiC has been a serious problem due to the combination of its properties: high hardness, fragility and high chemical inertness. The most common etching methods include: (1) molten salt corrosion, (2) electrochemical corrosion or photo-electrochemical corrosion, (3) reactive ion etching (RIE) and inductively coupled plasma etching (ICP) and (4) mechanical machining, all of which present multiple difficulties in silicon-carbide processing. Femtosecond laser (fs-laser) modification is a practicable and relatively new method for SiC deep etching that has the advantages of minimal thermal damage, high resolution and lack of etching masks [6]. In this study, fs-laser irradiation was used to form surface patterns on SiC pellets prepared by cold pressing and sintering. The samples were irradiated as the laser parameters (power, energy and number of applied pulses) were varied and the morphological surface changes were investigated by measuring the surface roughness and the water contact angle (WCA) before and after fs modification.

The silicon-carbide has a very large field of application, such as automotive industry and aerospace for coatings and thermal isolations, petrochemical and environmental industry for filters, electronics for coating, MEMS and high pressure sensors, optics, etc. [6]. Topography modification of the silicon carbide substrates could essentially improve this material's bioactivity properties, which, after proper laser parameters optimization, could make its biomedical applications even more successful.

2. Materials and methods

2.1. Sample preparation

The source SiC material (HQ-F Starceram from HC Stark) is a ready-to-press powder containing organic additives with granulate size < 75 μm and a d50 of around 27 μm. The pellets were die-pressed at 20 MPa for shaping and further CIPed (cold isostatically pressed) at 1950 bar for another 2 min. At the next step, the samples were debinded gradually in N_2 atmosphere at an increment of 30 °C per hour to 500 °C and from 500 °C to 850 °C at 60 °C per hour. The SiC tablets were kept at 850 °C for 90 min and were left to cool down naturally to room temperature. The sintering conditions were as follows: from room temperature to 1700 °C under vacuum at 5 °C per min; from 1700 °C to 2150 °C at 5 °C per min under Ar atmosphere; dwell time at 2150 °C of 2 hours. The cooling process started at 2150 °C to 1700 °C at 5 °C per min under Ar and from 1700 °C to room temperature at 5 °C per min under vacuum. The density of the pellets obtained was 98% of the theoretical density (according to the Archimedes method).

2.2. Laser treatment

The processing of the SiC samples was carried by using a Ti:sapphire laser (Quantronix- Integra-C) system with a 130-fs pulse duration at a central wavelength of $\lambda = 800$ nm, fixed energy at $E = 0.415$ J/cm^2 and a variable number of laser pulses $N = 2 \div 30$ (figure 1 (a)).The experiments were performed in air with the laser beam focused to a focal spot with diameter $d = 50$ μm using a lens with a 10-cm focal length. The sample was positioned perpendicularly to the focused beam on a high-precision XYZ translation stage. The experimental setup was controlled by LabView software. The samples were processed by raster surface scanning of the focused laser beam over the material surface at precisely-defined separation intervals d_x (between the parallel lines) and d_y (between the spots in a single line) in order to avoid a spatial overlap between the separate laser spots.

2.3. 2D roughness analysis

To evaluate the surface topography of the SiC pellets before and after the fs laser treatment, a TESA Rugosurf 10-10G profilometer (ISO4287/JISB0601) was used equipped with a diamond needle for 2D roughness measurement – λ_{cutoff} of 0.80 mm and n_{cutoff} of 5. The roughness parameter R_a was obtained, defined as the mean of the deviations of the surface height from the median line, according to the DIN 4776 standard. Every R_a value represents an average of five roughness measurements of every of the fs-processed and of the control SiC sample surface areas.

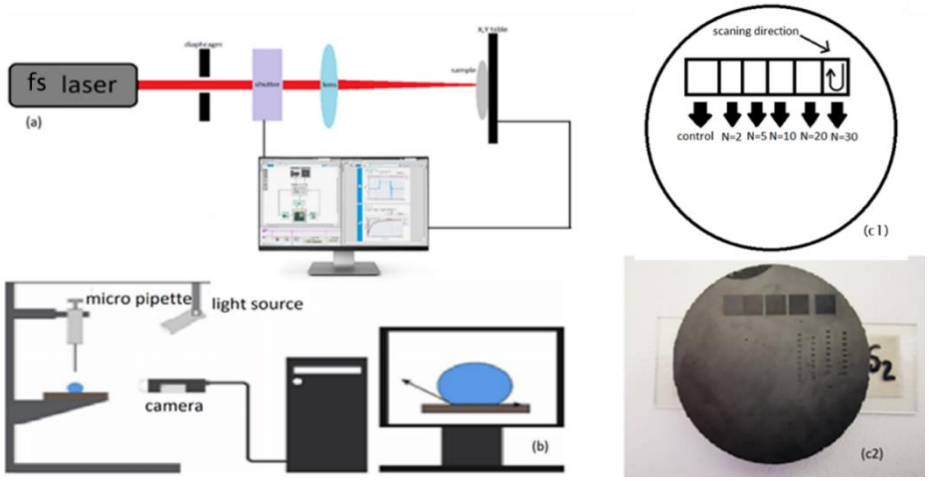


Figure 1. Schematic representation of the experimental setups: (a) setup for fs laser microprocessing of SiC pellets, (b) setup for measuring the water contact angle, (c 1, 2) scheme and optical image of the irradiation geometry on the pellet surface**.**

2.4. Water contact angle (WCA) evaluation

After the ultrafast laser treatment, the SiC samples were positioned on a XYZ horizontal stage. The water contact angle evaluation was performed on a homemade installation in air with a 0.5 µl distilled water droplet on the control and on the laser-modified surface areas of the samples for time periods of 0.5 – 9 s, then the water droplet was removed. The measurements were performed following a reliable evaluation procedure (a contact-angle goniometry method) – the droplet was deposited by a micropipette positioned above the sample surface and a high-resolution camera captured the image (Huawei P40 pro camera on super macro mode with additional macro lens). The image was then analyzed by ImageJ analysis software equipped with a contact-angle measurement plug-in. The set up for WCA evaluation is presented in figure 1 (b).

3. Results and discussion

Figure 2 shows representative optical images of SiC pellets (SiC1-80 and SiC2-320, where 80 and 320 are the pressures in kN used for die pressing) patterned with $n = 2 – 30$ fs pulses and a fixed laser energy $E = 0.415$ J/cm^2; figure 3 shows the corresponding 2D roughness analysis, namely, the roughness parameter (R_a) dependence on the number of fs pulses applied on the two types of SiC pellets investigated. The two figures show how the topography profile changes when the number of pulses applied is varied (2, 9, 10, 20, 30 with a fixed $E = 0.415$ J/cm^2), compared to the fs-untreated control surface.

As can be seen in figure 3, the surface roughness varies with the number of fs pulses applied – the maximum value of R_a for the SiC1 sample is for 30 pulses, while for the SiC2 pellet, R_a max is observed for $N = 10$. An interesting result is that in the SiC1 areas irradiated with 2, 5, 10 fs pulses, the surface becomes smoother than the untreated control zone. This effect could be explained by the fact that applying fewer laser pulses initiates a gentle removal of the material remaining after the initial polishing

of the surface. As the results presented in both figures 2 and 3 clearly show, the fs-laser surface modification method could be used for controlling precisely the SiC surface topography by gently varying the laser parameters – the number of pulses applied. Various structuring of the SiC surface could thus be achieved and, as a result, the modified biocompatible ceramic could find further biomedical applications [2] – as in regenerative medicine and bone tissue engineering – e.g., for cells scaffolds or for biocompatible coatings.

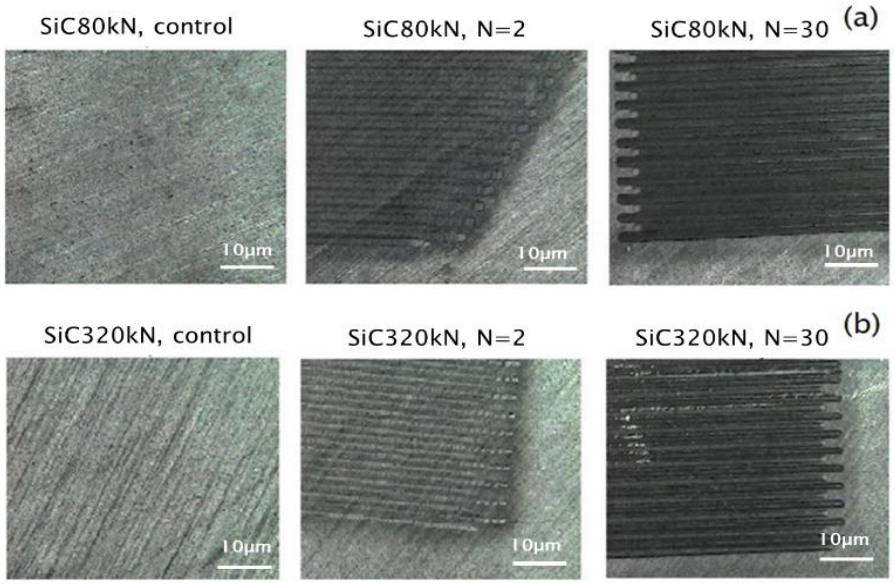


Figure 2. Optical images (×1000 magnification) of SiC samples (SiC1-80 (a) and SiC2-320 (b) control surfaces, compared to areas of the corresponding pellets patterned by N = 2 and 30 fs pulses with $E = 0.415$ J/cm^2.

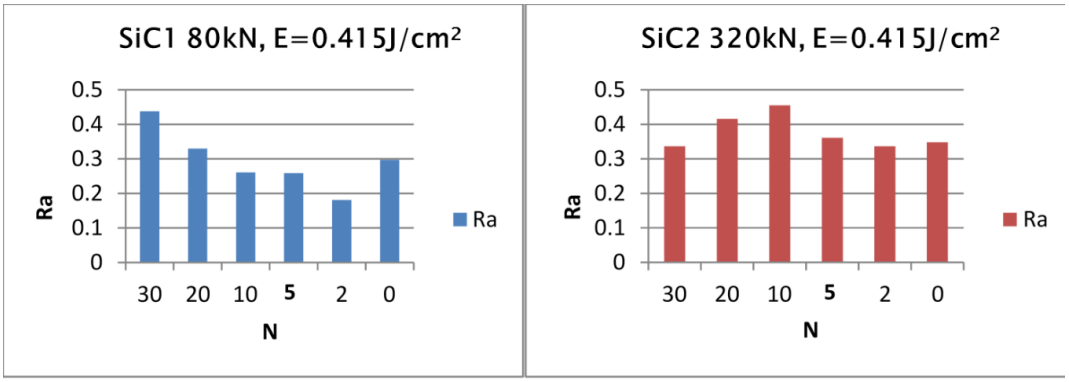
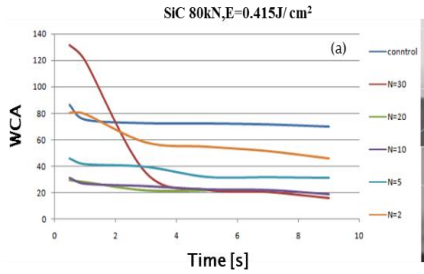


Figure 3. 2D roughness analysis: roughness parameter (Ra) dependence on the number of fs pulses (N) applied to the two SiC samples investigated.

The wettability properties of the SiC samples after irradiation with a varying number of laser pulses revealed drastic changes in the hydrophilicity of the treated surface. As can be seen in figure 4, the highest values of WCA for sample SiC1-80 are achieved for $N = 30$. Moreover, the highest detected value of the WCA for $N = 30$ (131.4°) abruptly decreases after 3 s (120°) to become 16.1° after 9 s – the sample surface changes from highly hydrophobic to super hydrophilic. Figure 5 presents analogous changes with time in the wettability properties of the SiC2-320 sample after laser modification. The highest value of the WCA for this sample is registered in the surface area irradiated with $N = 20$ (72°);

a sharp decrease is then observed after 3.5 s only (46.9°); the surface becomes super hydrophilic at the end of the measurement. This effect could be explained by the fact that the water contact angle is affected not only by the surface chemistry, but also by the surface roughness. Bearing in mind the diverse effects induced by laser modification, the wettability properties could be explained by three conditions: a Wenzel state (homogeneous wetting), a Cassie-Baxter state (heterogeneous wetting) or in an intermediary state.

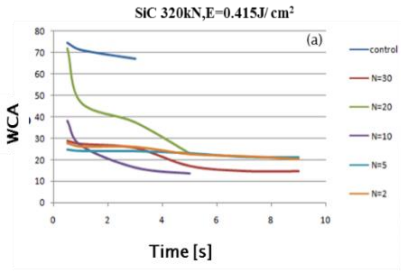


(d)

Time[s]	clear SiC	SiC80kN N=30	SiC80kN N=20	SiC80kN N=10	SiC80kN N=5	SiC80kN N=2
0.5	86.6	131.4	29.4	30.9	45.7	80.4
1	75.2	120	28	26.6	41.4	79.6
3	72.4	35.2	21.6	24.8	39.4	58
5	72.2	22.3	21.5	22.4	31.7	54.7
7	71.4	20.7		21.9	31.5	51.4
9	69.7	16.1		18.8	31	45.8

Figure 4. WCA measurement of fs-modified SiC1-80 sample (a, d) compared to the control surface, and optical image of the water droplet on the surface of SiC1-80 fs-modified by N = 2 (b) and N = 30 (c) after 9 s.

However, as can be seen in the figures, increasing the number of laser pulses applied increases the hydrophilicity of the processed parts of the samples, and more so with time (0.5 – 9 s). Thus, one could achieve a simultaneous control over the surface roughness and hydrophilicity of the sample in view of enhancing further the functionality of this biocompatible material.



(d)

Time [s]	clear SiC	SiC320kN N=30	SiC320kN N=20	SiC320kN N=10	SiC320kN N=9	SiC320kN N=2
0.5	74.6	28.7	72	38.1	24.7	27.8
1	71.3	27.3	46.9	26.7	24.1	26.2
3	67.2	25.4	37.6	16.5	24	26
5		17.2	23.1	13.8	23.1	22.6
7		14.9			21.5	21.6
9		14.8			21.3	20.2

Figure 5. WCA measurement of fs-modified SiC2-320 sample (a, d) compared to the control surface, and optical image of the water droplet on the surface of SiC2-320 fs-modified with N = 2 (b) and N = 30 (c) after 9 s.

4. Conclusions

The data obtained clearly demonstrates that the fs-laser processing enables various structuring of the SiC topography allowing fine tuning of its wettability properties and achieving diverse modification. Thus, the SiC material could find further biomedical or other applications that demand precise and fine structuring.

Acknowledgments

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