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Laser surface texturing of ceramics and ceramic composite materials – A review

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Abstract:

The surface texturing of ceramics is generally performed through acid-based etching and machining; however, laser texturing may be considered as a more precise, reproducible and eco-friendly process. Furthermore, laser ablation may be used to produce complex patterns on ceramic surfaces, thus offering new surface engineering opportunities. The studies so far conducted on this topic have mainly been application-driven, and since a wide variety of lasers have been used for surface texturing, it is difficult to have a comprehensive understanding of this technique applied to ceramics and ceramic composite materials. Laser texturing requires a great deal of knowledge of the material and the laser source parameters to optimise the process in order to obtain the expected results. It is therefore important to expand the research on the laser texturing of ceramics and CMCs in order to build a relevant amount of literature that can be used to identify the most appropriate parameters for each application. This review provides an overview of most of the technological aspects considered relevant for the laser surface texturing of ceramics and CMCs, and includes the fundamentals of laser-material interactions and a summary of the used equipment and parameters. Furthermore, most of the techniques related to the modifications of surface material induced by a laser are critically reviewed, and the new horizons that are opening up, in the context of the modification of surfaces to improve the performances of materials for several applications, are discussed.

Keywords: (A) Finishing; (B) Composites; (B) Surfaces; (E) Biomedical applications.

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1. Introduction

The specific discipline known as surface engineering concerns the optimisation of the surface of a material in order to enhance the performance of the material for a specific application. For example, the optimisation of adherend surfaces, in order to guarantee a sound joint, is an important and critical step in the joining technology. The surface engineering field is quite broad and includes different methods.. Three branches can in particular be identified: surface modification without compositional changes, surface modification with compositional changes and, finally, coating solutions[1].

Among the techniques that can be used to modify surfaces, laser-based ones are particularly versatile and can guarantee a high level of control of the process. Lasers are widely used to process materials in order to modify not only the surface but also the bulk. For instance, they are currently used in the additive manufacturing industry in Selective Laser Sintering (SLS) and in Selective Laser Melting (SLM) processes, in particular to produce metallic parts, but, carbon fibre reinforced silicon carbide matrix (C/SiC) composites have also recently been obtained through the infiltration of molten silicon in a selective laser sintered preform [2]. Laser heating can also be used to clad material through the melting/sintering of powders on the surface of a substrate [3]. It is worth noting that laser technologies are increasingly used for a broad range of applications that involve ceramic materials (i.e the potential use of lasers for additive manufacturing or joining processes) but these topics will be not discussed in the present review.

Furthermore, lasers are exploited in welding, where they allow the size of the heat affected zone (HAZ) to be limited and the molten pool to be localised precisely. Laser

welding is performed to join metals [4] and also polymers[5], and encouraging results have recently been observed for ceramic material joining, when a femtosecond pulsed laser is used [6]. The laser technology has been exploited to join ceramic materials through the application of a joining material, such as brazing alloys or glass-ceramics. Some studies have been conducted, for instance, to search for reliable joining techniques that can be used to join silicon carbide fibre reinforced silicon carbide (SiC/SiC) composites for nuclear applications using laser to heat the glass-ceramic solder [7,8].

Bulk machining is another laser application that is used in particular when the material to be processed is hard and the samples are thin. Laser techniques are of great interest, for example, for the production of micro-holes through SiC/SiC composites with high precision [9,10].

The above mentioned applications can attest the growing popularity that the laser-based technologies have recently experienced in the ceramic materials field and they are useful to highlight the importance of exploring the most recent trends in their use for surface engineering.

To this end, the aim of this review is to provide an overview of the state of the art in the surface texturing of ceramics and ceramic matrix composites (CMCs) using laser beam techniques. To the best of the authors' knowledge, very few studies are available on the topic, and most of these studies are application-driven, thus making it difficult to identify any recurring findings. Most of these studies have been published over the last five years, thereby attesting a growing interest in these techniques. They are presented here to provide an updated collection of laser surface texturing applications on ceramics and ceramic matrix composites in different fields. As will be shown, more research is needed

to characterise the behaviour of the various ceramic materials when their surface is processed by means of laser radiation to build a strong theoretical background about this technology and to identify opportunities, limitations and standards for laser surface texturing on ceramic and CMCs.

The first section provides useful information on the laser-material interactions involved in laser ablation. The subsequent sections present the different applications of laser texturing to different groups of ceramic materials: bioinert ceramics, silicon carbide and silicon nitride, ceramic coatings and CMCs. The choice of these categories of ceramic materials can be considered effective to present the available literature on the topic, thus providing a wide overview on the laser texturing with a focus on different applications. To conclude, the last section offers a summary about the presented information.

2. Laser-material interactions

Maiman [11] was the first person to operate a LASER (Light Amplification by Stimulated Emission of Radiation) device in 1960 and, nowadays, this technology is largely used in several industrial and medical applications. This section provides a summary of the general laser-material interactions to allow a better understanding of the laser texturing process.

When a laser light hits a target material, it is partially reflected, partially transmitted and partially absorbed. The electromagnetic wave that hits the material has an electric field and a magnetic field that interact with the electrons of the atoms of the material [12]. This energy exchange results in the excitation of the electrons in the substrate, which is

accompanied by an increase in thermal energy. The temperature distribution on the laser target area depends on the heat balance equation (1), which is calculated considering the heat flux as one-dimensional [13]:

$$\rho C \frac{\delta T}{\delta t} = \alpha I + k \frac{\delta^2 T}{\delta x^2} \quad (1)$$

where ρ is the density, C is the heat capacity, α is the coefficient of absorption and k is the thermal conductivity of the material. The laser-induced excitation on the material surface may result in heating, which in turn may induce melting and vapourisation. When vapour forms, the excitation provided by the electromagnetic field leads to ionisation and the formation of plasma.

Laser devices can use a continuous wave or short pulsed wave. The former category conveys uniform energy onto the material surface, while the latter involves intermitting pulsing, which allows a higher peak power to be achieved. The pulse duration is short enough (lower than milliseconds) to transfer new energy to the target area before that conveyed by the previous pulse has dissipated [14]. When an ultrafast pulsed laser (femtosecond and picosecond) is applied to process materials, the time scale is shorter than the energy exchange with the material lattice, thereby allowing multiphoton absorption. These devices are more expensive, but provide a higher micro-texturing application precision and the confinement of the thermal load [15].

Laser surface texturing exploits laser-material interaction mechanisms to produce ablation, whereby the material is selectively removed from the surface. Both pulsed and high intensity continuous wave lasers are used to ablate materials. Three main mechanisms are associated with the ablation process: photo-chemical (bond-breaking),

photo-thermal (temperature increase) and photo-physical (ejection of material from the surface due to a laser-induced shockwave) [16].

Photochemical ablation depends on the laser wavelength: if the photons possess a comparable energy with that of the material bonds, bond-breaking can occur. Alternatively, when a pulsed laser is used in an ultra-fast regime, the bond can be broken due to multiphoton absorption[16]. As mentioned before, an ultra-short pulsed laser enables multiphoton absorption, because the pulse duration is shorter than the energy dissipation from the electrons to the lattice. The absorbed photons excite the electrons in the material, whether they are free or bonded. When a dielectric material is treated, the band gap is often too high to permit the excitation of the electrons from the valence band to the conduction band, but this energy barrier can be overcome when more than one photon is absorbed. When a sufficient number of material surface electrons are promoted to the conduction band, the optical properties change and the material takes on a metal-like behaviour which lasts as long as the excitation state lasts [17].

A phenomenon called *Coulomb explosion* can take place for a low radiation fluence and before the activation of the thermal ablation processes. This non-thermal ablation involves the formation of an electric field, as a result of the ejection of high-energy electrons from the lattice and uncompensated positive ions on the surface. When the electric field is high enough the ions are ejected from the surface. Thermal ablation occurs several picoseconds later when the electrons dissipate energy to the lattice. Three main processes can be identified: vaporisation (when the material temperature exceeds the boiling threshold), spallation (high laser-induced stresses that generate a shockwave, which leads to the molten material being ejected) and phase explosion (the temperature

increases so fast that the material cannot gradually evaporate and an entire superficial region therefore explodes in a mixture of vapour and droplets)[17].

Ultra-short pulses (fs scale) can have a negligible thermal effect, because the energy is concentrated in the target area and the ablation takes place before thermal dissipation.

Fig. 1 compares the effects of a long pulsed laser beam and those of an ultrafast pulsed laser. The shorter the pulse is, the smaller the affected area, and the femtosecond pulse can therefore be the best option for high-precision surface structuring.

In short, when a laser device is chosen to obtain ablation on a target material, the following parameters should be considered: intensity, spatial and temporal coherence, the angle of incidence, polarisation, the laser wavelength, which depends on the laser source, the energy per pulse, which depends on the supplied power and the repetition rate, the number of cycles, the repetition rate, i.e. frequency of the laser pulses, the scanning speed, the repetition number, i.e. number of overlapped scanning layers necessary to create the final pattern, pulse overlapping, which depends on the scanning speed and the repetition rate, and the focal distance.

Matching the laser parameters with the material properties is crucial to obtain the desired structure on the material surface and to reduce the formation of detrimental defects.

3. Laser surface modification of ceramic and Ceramic Matrix Composite (CMCs) materials

In the last decade, surface texturing, through laser ablation, has been studied by focusing on the surface processing of ceramic materials. The performance of a laser used to structure ceramic surfaces has been compared with other traditional processes (micromachining, micromolding, etc) [19], and investigations have been conducted on the effects of the pattern morphologies on surface wettability [20–22]. Another work that has testified the interest towards the investigation on the patterns obtainable through laser texturing has been conducted by Li et al. [23], who compared the effectiveness of obtaining micro-pits on an alumina surface comparing two different laser processing strategies, ring cutting and single pulse intervals, and a nanosecond pulsed laser. They have reported that the single-pulse intervals strategy provided higher efficiency and smaller compressive stresses compared to the ring cutting strategy, that was indicated as more beneficial to produce micro-pits with larger diameters.

Among the possible textures that can be observed on laser-treated surfaces, the patterns classified as Laser-Induced Periodic Surface Structures (LIPSS) have been investigated in order to establish the mechanisms behind their formation, and it has been found that these patterns can be obtained on any type of material using ultrashort pulsed lasers [24]. The growing interest in LIPSS as a research topic is clearly shown in Fig. 2. These patterns consist of nanometric ripples on the surfaces, which show a periodic spacing with less of a distance than the laser wavelength used for the surface processing. The ripples can be divided into two categories, depending on their period, which is usually indicated as Λ . When the period is near that of the laser wavelength λ , the structure is called a low-spatial frequency LIPSS (LSFL), while period values much lower than λ identify high-spatial frequency LIPSS (HSFL) [25]. The laser-material interaction mechanisms behind the formation of these structures are very complex, and they are not yet fully understood

from a theoretical point of view. Surface plasmon-laser interactions are considered key aspects in the formation and growth of ripples on all solid materials, dielectrics included [26]. The interference generated by the incident laser beam and surface waves that results in a periodic distribution of the laser intensity and energy-minimizing self-organisation mechanisms can be identified as viable causes for the LIPSS formation [25].

Although an exhaustive explanation is not available, from a theoretical point of view, an empirical approach can provide useful information on how to obtain these structures. Indeed, it has been reported that the main experimental parameters that are involved in the formation of periodic ripples are the laser wavelength, the beam incidence angle, the beam polarisation, the number of laser pulses for each point and the refractive index of the medium through which the treatment is conducted (i.e. air) [25].

LIPSS have successfully been obtained on a thin film of polycrystalline β -SiC with a periodicity of about 200 nm, without modification of the crystal phase, using a femtosecond-pulsed laser beam with the aim of investigating the possibility of modifying the coating without affecting the substrate [27]. Homogeneous LIPSS have been produced in the metallic phase of an alumina-zirconia-niobium composite, by means of a femtosecond laser, applying a lower laser fluence than the ablation threshold of the ceramic material [28]. This resulted in a better water wettability of the composite because of the nanotexturing of the metallic phase and the particle redeposition, which also increased the roughness of the ceramic matrix. Furthermore, LIPSS were produced on a zinc oxide (ZnO) substrate with a femtosecond laser; the modification of the surface morphology (periodic ripples formation) and the introduction of Zn interstitial defects

enhanced the sensitivity of gas detection devices to NO₂ [29]. Ehrhardt et al.[30] produced LIPSS on fused silica, using a nanosecond pulsed laser (Fig. 3.a), through the design of an appropriate layered system (interlayer, absorbing layer and confinement layer) to achieve confined ablation on the surface of the fused silica substrate. (Fig. 3.b). In this way, they extended the range of lasers available for the creation of submicrometric ripples on dielectric materials.

3.1. Bioinert ceramics

Laser roughening of zirconia has been studied over the last decade, in particular for medical applications. Zirconia, together with alumina and zirconia-alumina composites, are bioinert materials that are suitable for orthopaedics and dental applications. Their bio-inertness results in a poor efficiency of the osteointegration process, but, through surface roughening, adhesion to the bone can be increased [31]. Laser techniques can promote roughness modifications and surface texturing with high precision, both of which can improve bone adhesion.

Zhou et al. [32] used laser ablation with a femtosecond laser to increase the roughness of a yttria-stabilised zirconia (YSZ) surface and improve bone integration. They reported an increase in the roughness value for the laser pulse energy, the absence of intergranular cracks and no appreciable variations of the surface composition after the laser treatment, except for a small increase in the amount of monoclinic-ZrO₂. In another work, Carvalho et al.[33] studied two different micro-textures obtained using a femtosecond laser on alumina toughened zirconia, and observed no chemical or phase changes on the surface

and an improved cell metabolic activity compared to that of the untreated material. Furthermore, they reported that the growth of the cells was guided by the laser-induced topography of the surface. Carvalho et al. [34] had already observed this tendency of cells to grow according to the designed micro-texture in a previous work, in which periodic microgrooves were produced on the surface of alumina toughened zirconia samples using a femtosecond laser. In that case, nanostructured LIPSS were produced, through laser interference, with an orientation perpendicular to the microgrooves on the surface. They reported that cells tended to grow in function of the microstructured grooves rather than in function of the perpendicular direction of the LIPSS nanotexture (Fig.4). Chen et al. [35] reported that the application of a picosecond pulsed laser to fabricate a fish scale superficial texture on an alumina substrate was found to be beneficial, as far as cell proliferation is concerned.

Veneer ceramics are used in dental applications to restore the appearance of teeth, and they should be able to adhere perfectly to the dental prosthesis or to the damaged tooth. Tuncel et al.[36], with the aim of enhancing the bond strength with veneer ceramic by increasing the roughness, explored the effect of a nanosecond pulsed fibre-based laser on yttria-stabilised zirconia. They compared the laser-modified surfaces with sandblasted ones, and found that the average roughness of the former group was three times greater than the latter. However, the remarkable roughness increase induced by the laser treatment did not provide a higher bond strength, and no statistically significant differences were observed between the two groups.. Moreover, sandblasting increased the monoclinic zirconia content, whereas the local heating provided by the laser treatment resulted in a decrease in the monoclinic phase, compared with the reference samples (untreated).

Arami et al. also studied the laser pre-treatment of zirconia with two different microsecond pulsed lasers (Nd: YAG and Er:YAG) to enhance the shear bond strength of the composite resin repair coatings on zirconia [37]. Composite resin used for repairs is a polymeric matrix coating material that is applied to protect the underlying tooth or prosthesis and to restore the aesthetic appearance [37]. The Nd:YAG laser provided more roughness, but also less shear strength, which was even lower than that of the untreated samples, probably due to thermal damage. The roughness provided by the Er:YAG laser was lower than that of Nb:YAG and it was comparable with that achieved by sandblasting. However, the Er:YAG laser provided a lower shear bond strength than the sandblasting process.

Again focusing on dental zirconia, a femtosecond pulsed Ti:Sapphire laser was studied to pre-treat zirconia before bonding with a metal or ceramic bracket in order to enhance the bond strength [38]. It was observed that this resulted in an enhanced bond strength, probably due to the high-precision surface texturing provided by the femtosecond pulsed laser because of the absence of a thermal effect. A comparison of the surface morphology of the untreated YSZ and the femtosecond pulsed laser textured YSZ is shown in Fig.5.

Abdullah et al [39,40] also utilised a laser for the veneering step as an alternative to a pre-treatment, to evaluate the enhancement in bond strength between zirconia and veneering ceramic when it is proposed for the veneering step by. They found that the use of a laser could produce promising results, with respect to traditional sintering, by enhancing the bond strength without inducing phase transformation in yttria-stabilised zirconia.

Baino et al.[41] exploited a nanosecond Nd:YVO₄ laser source to texture alumina-zirconia acetabular cups for hip joint prosthesis, using a method they had previously

developed for flat surfaces. They observed that the surface roughness depended on the laser process parameters, and they were able to achieve a hierarchical texture that they hypothesised could promote osteointegration because the roughness values can be tailored to the same range as the osteoblastic cell size (15-30 μm). Moura et al.[42] found that the use of a laser treatment was promising for the promotion of a better bone adhesion to the surface of yttria-stabilised zirconia (YSZ), compared to the same samples sandblasted and etched. It is evident that when comparing the laser surface treatment with the traditional sandblasting and etching process, the great advantages of lasers are the possibility of tailoring the surface texture, the time savings and the eco-friendly nature of the laser approach.

An interesting phenomenon that was observed when a zirconia surface was exposed to laser is the darkening effect [41,42]. This darkening phenomenon was observed in both of the aforementioned experiments after a laser treatment and a thermal treatment were carried out in an oxidising atmosphere to restore the pristine white appearance of zirconia. Fig. 6 shows the appearance of the laser textured full-scale acetabular cup made of zirconia [41] prior to and after the thermal treatment.

According to Pereira et al.[43], the presence of sub-oxides on the surface of laser treated samples of yttria-stabilised zirconia might be responsible for the darkening effect instead of the pristine oxide due to oxygen loss. This explanation is coherent with the results of Guo et al. [44] who investigated the darkening of YSZ when used in oxygen sensor applications in a reducing environment. They reported that the phenomenon was due to an oxygen deficiency, which they considered was responsible for the formation of the colour centres. Therefore, a thermal treatment might restore the original appearance through oxidation, which reverses the oxygen deficiency on the laser treated surface.

Faria et al.[45] proposed an alternative approach based on the laser texturing of the yttria-stabilised zirconia when it is in the green state prior to sintering. Two different structures were produced, one formed by cavities and the other consisting of pillars, with good control of the chosen morphology. Both of these laser-induced morphologies provided higher wettability with deionized water and a higher bone transfer compared to traditional sandblasted and etched samples. However, the presence of pillars and cavities on the treated surfaces resulted in a lower level of mechanical properties, but most of the laser treated samples exhibited higher flexural strength values than the minimum value required for the application. Liu et al. [46] successfully fabricated microgrooves on green zirconia by optimising the process parameters, and they observed that the combination of high frequency, low scan speed and high laser power resulted in the formation of a sintered layer in the working area accompanied by a large heat affected zone.

Laser engraving is used extensively in prosthesis applications to make parts identifiable. However, it is very important that the treatment does not compromise the performance of the prosthesis. Gremillard et al.[47] studied the effects of engraving, performed by means of an Nd:YAG laser, on alumina toughened zirconia and zirconia toughened alumina samples. After performing a hydrothermal ageing to simulate the body environment, they did not find any relevant differences in the properties between the laser treated areas and the untreated ones. They evidenced that the defects originating from the engraving process were not critical for the mechanical behaviour.

Summarising, the studies presented in this section suggest that laser texturing is a promising strategy to improve the performance of bioinert ceramics. The possibility to texture the surface of these materials could enhance the tissue integration and it can disclose new opportunities unavailable with traditional processes like sandblasting.

Furthermore, no detrimental damage or changes of phase composition have been reported after laser treatment. However, it should be noticed that not always the laser textured material performed better than the sandblasted one as reported in [37]. This highlights the importance of selecting appropriate laser parameters and textures.

3.2. Silicon carbide and silicon nitride

Silicon carbide has a wide range of applications. For instance, it is used in electronics to exploit its semiconductor properties, in thermal applications as a heating element and as a heat sink because of its thermal conductivity and thermal resistance, in aerospace applications because of its thermomechanical stability and in grinding applications for its high level of hardness. Furthermore, silicon carbide provides irradiation stability and this makes it interesting for nuclear applications [48]. Silicon carbide also offers high chemical resistance, which makes etching difficult. This, together with the high level of hardness, make it difficult to modify a surface using traditional processes, like wet etching and mechanical machining [49]. Similar issues are related to the surface texturing of silicon nitride, another high-performing ceramic. To solve this challenge, many works have focused on the surface modification of silicon carbide (SiC) and silicon nitride (Si_3N_4) by means of laser beam techniques.

Suess et al.[50] studied the laser-induced modification of SiC in air to enhance joint strength through the formation of a nanostructured silica layer on the surface. The used laser system was a nanosecond pulsed Nd:YVO₄ laser. They found agglomerates of spherical silica nanoparticles on the laser-treated surfaces, which resulted in an increase in the surface area, which in turn promoted the infiltration of the adhesive materials used

in the joining process and higher wettability. However, no improvement of the shear strength was achieved, as a result of the formation of a detrimental nanometric graphite layer at the SiO_2/SiC interface, which led to adhesive failure. The different microstructures formed by the laser on the surface of the SiC are shown in Fig. 7. In Fig.7.a , going downward from the top, it is possible to detect: the nanostructured columnar silica, the dense silica layer, the single phase region that contains the detrimental nanometric graphite layer over a nano-SiC one, then a biphasic layer made of onion-rings like graphite and nano-SiC and finally the underlying unaffected SiC. Fig. 7.b. provides a scheme that highlights and makes explicit the different structures visible in Fig. 7.a.

Salvo et al.[51] conducted a similar work on a polycrystalline Si_3N_4 , using the same laser system, to pre-treat a ceramic surface for adhesive joining with a laser treatment in air. The laser-treated surface presented a nanocolumnar morphology characterised by an open porosity, which allowed the formation of an interlocked structure at the adhesive/ceramic interface, thus providing joints with a higher apparent shear strength. Furthermore, the treatment did not appear to have any detrimental effects on the properties of the substrate.

A laser treatment has also been proposed as an assisting technology for the traditional grinding process. Li et al. studied the effect of a continuous wave laser beam used to pretreat, by localised heating, the surface of reactive-sintered SiC before the grinding step. The surface was exposed locally to laser radiation for 60 s at different powers, ranging from 20 W to 70 W, before undergoing grinding. They observed that the higher the power was, the higher the local softening due to the thermal effect of the laser. The laser assisted grinding of SiC proposed by Li et al. has been reported to be successful in achieving lower grinding forces and lower levels of roughness on the ground surface [52].

Another approach to laser-assisted grinding is based on the surface texturing of the workpiece and/or the tool rather than on surface laser-induced heating. Kadivar et al.[53] proposed a laser-assisted micro-grinding process for Si_3N_4 , and investigated the effect of laser treatments conducted on both the tool (using a femtosecond pulsed laser) and the Si_3N_4 workpiece (using a Yb:YAG picosecond pulsed laser) prior to grinding and finding that the process efficiency increased. Azarhoushang et al [54] also demonstrated the possibility of achieving lower grinding forces and better surface finishing as result of a Yb:YAG picosecond pulsed laser treatment performed exclusively on the silicon nitride workpiece before the grinding process. Laser surface texturing has also been studied on sintered SiAlON- Si_3N_4 , which is often used to produce cutting tools, through a Ti:Sapphire femtosecond pulsed laser in order to reduce the contact area between the tool and the workpiece and to decrease the cutting forces [55].

The decomposition of silicon carbide under laser radiation is an important aspect when this material undergoes a laser treatment [56–60]. Choi et al. [61] studied the phase separation mechanism of a single-crystal 4H-SiC exposed to a femtosecond pulsed laser beam in an argon atmosphere, with the aim of exploiting the phenomenon to form multilayered graphene. In their study, after the first laser pulse, the structure was different from that obtained by Suess et al., who used a nanosecond pulsed laser [50] in air, as a polycrystalline silicon layer formed between the upper graphitic carbon layer and the SiC substrate. The decomposition of a SiC surface exposed to a continuous wave fibre-based laser was observed in air when the temperature exceeds 1427 °C, and the decomposition rate was observed to increase as the laser power increased [62]. The local carbonisation that takes place in the production of graphene on monocrystalline SiC is of particular interest for SiC, as a semiconductor for microelectronic applications and a laser treatment

is a promising technique to substitute the thermal process. For instance, a common thermal treatment is performed in an argon flow at a dwell temperature of between 1500°C and 2000°C for 15 min. The pressure could vary from approximately 1 bar (when the Si-face is treated) up to 9 bar (when the C-face is treated) [63].

Furthermore, silicon carbide is an interesting material in power electronics and sensor applications because of its semiconductor behaviour, accompanied by the possibility of working in harsh conditions, i.e. where silicon cannot be used [64–67]. Femtosecond pulsed lasers are promising for such applications, in particular for the micromachining of 4H-SiC and 6H-SiC (the two SiC polytypes most used in electronics) to obtain high-precision structures. Zhang et al. [68] investigated the use of a femtosecond pulsed laser with the aim of realising grooves on a 4H-SiC surface in air. They found that, by increasing the laser power and reducing the numerical aperture (NA), material removal increased. Additionally, they observed that surface roughness (which should be at a minimum) increased as the laser power increased and decreased with the number of scan repetitions. Furthermore, they reported that working in air caused the formation of SiO₂ micrometric particles in the grooves, thereby lowering the quality of the process, and the treated areas showed the presence of amorphous silicon and carbon phases in addition to the amorphous SiC induced by the treatment. The use of a femtosecond pulsed laser has proved to be beneficial as an assisting technique to accelerate the Inductively Coupled Plasma (ICP) etching rate when it is performed as a pre-treatment on 6H-SiC [69]. This result was attributed to the laser-induced bond-breaking effect that produces SiC amorphisation and its conversion to SiO₂, which can easily be etched. In addition, Meng et al. [70] proposed a femtosecond pulsed laser treatment to improve the machinability of single-crystal 4H-SiC, whereby LIPSS were formed in the treated surface areas.

With reference to the use of a laser as micromachining tool, the use of a UV nanosecond laser has been reported for the manufacturing of a 4H-SiC sensor. It proved to be effective in the release of cantilever beams, but some issues arose in controlling the drilling depth due to the formation of carbon and silicon phases [71].

The high heat fluxes generated by electronic components require a good cooling strategy to preserve all the parts. Among the possible strategies, one involves the use of microchannel heat sinks[72]. Deng et al. [73] exploited laser ablation to produce microchannels on the surface of sintered SiC, and found that the channel shape (triangular or trapezoidal) was influenced to a great extent by the laser processing parameters. This study emphasised the importance of a laser texturing strategy to achieve higher precision in the manufacturing of microchannels. The precision of this technique could be useful in improving the thermal exchange of SiC heat sinks through the manufacturing of complex geometry of channels.

According to the literature presented in this section, laser texturing can find many applications, as a stand-alone solution or as an assisting technology, when hard and brittle materials like silicon carbide and silicon nitride are treated. Several applications have been presented from different fields to provide an overview on what has been done to date, but it is difficult to identify recurring trends because, generally, few discussions were available on the motivation for the chosen laser parameters. Ultrashort lasers, however, can be considered the most promising technology when high precision machining is required.

3.3. Ceramic coatings

Ceramic materials are known to be resistant to high temperatures and they are utilised to coat components that have to withstand high thermal loads, such as gas turbines, space vehicles and engines. Among the various deposition techniques, thermal plasma spraying is frequently used to produce ceramic coatings on substrates, due to its cost-effectiveness and efficiency [74]. However, this technique does not allow a good control of the coating microstructure and it is usually associated with such defects as poor adhesion, voids and inclusions. A laser can be used before the deposition to prepare metal substrates [75–78] in order to remove contaminants and for surface roughening in order to enhance mechanical anchoring and improve adhesion to the ceramic coating. This can also be done with a ceramic or CMC substrate. Indeed, Gatzen et al.[79] have recently reported that the laser texturing of an $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ composite can be an effective way of increasing the adhesion of a plasma-sprayed environmental barrier coating when no reactions between the substrate and the coating material occur and when mechanical interlocking is crucial, as described in the previous section. Fig. 8 shows the cross-sections of plasma spray coated $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ composites with two different surface textures (dot and mixed). In fig 8.c., it can be observed that, even if delamination occurs, the interlocking between the plasma-sprayed coating and the substrate was remarkable. This study suggests that this could be a suitable way to improve the performance of plasma-sprayed coatings on fibre-reinforced ceramics.

Laser texturing can also be taken into consideration to enhance the effectiveness of all the coating deposition processes, such as PVD [80], electroless plating, etc. For example, a laser texturing treatment on alumina substrates has been reported to improve the adhesion of a nickel coating deposited by means of electroless plating. This result was considered

promising to replace the traditional chemical surface preparation with laser texturing, in order to reduce the environmental drawbacks and increase the safety of workers [81].

Additionally, a laser enables coating densification and phase transformation in the post-treatment [78]. Densification can be achieved by reducing the porosity through the laser-induced re-melting of the top layer, thereby exploiting the thermal effect of the beam. This can be done by selecting the most appropriate laser parameters, without affecting the underlying layers in multicoating structures [82]. Performing a laser glazing treatment can enhance the properties of the thermal protective coating by improving the resistance to thermal shocks and increasing the density of the sprayed layers [83].

Titanium dioxide is one of the most interesting ceramic coatings because of its unique properties. Indeed, titanium dioxide is a well-known photocatalyst; when exposed to UV radiation, the TiO_2 surface shows super-hydrophilic behaviour and acts as a catalyst to promote redox reactions that can be exploited to remove contaminants and toxic products. As a result of its properties, it is applied as a coating material in many fields: air purification, water decontamination, NO_x removal, self-cleaning and anti-bacterial applications [84]. The surface area of catalysts is crucial to promote their effectiveness, and surface texturing can increase this value. Talbi et al. [85] investigated the laser texturing of a thin film of non-stoichiometric titanium oxide by applying a femtosecond pulsed laser, in the UV wavelength range, to assess the viability of the process for structuring large areas. Different nanostructures (Fig. 9), nanodots and LIPSS, with different orientations were produced by varying the number of pulses, and the authors attributed their formation to free-energy minimisation mechanisms. Periodic micro- and nano-structured regions were produced on 25 mm^2 areas through laser scanning at lower fluences than the ablation threshold to prevent local ablation. The authors observed a

higher periodicity and homogeneity of the morphology in the large laser-scanned area, compared to the nanostructures that formed by varying the number of pulses without moving the laser beam. They identified the reason for such a result as being the more uniform energy distribution achievable when applying laser scanning.

Furthermore, the laser texturing of a TiO_2 -containing coating may be of interest to inhibit bacteria growth in medical and food applications. The surface fouling phenomenon consists in the accumulation of the build-up of undesired material on the surface and when bacteria are the fouling agent, biofilms, which can be a source of detrimental contamination, can be formed on the surfaces [86]. Yusuf et al.[87] evaluated the effect of picosecond pulsed laser structuring on the antibacterial properties of plasma-sprayed TiO_2 -ZnO coatings, since both oxides provide a bactericidal effect. The laser-induced texture consisted of alternating depressions on the surface of the coating, which resulted in an increase in the specific area, thus improving the contact area between the material and bacteria, and the adhesion of the bacteria on the textured bioactive TiO_2 -ZnO coating, which in turn helped kill the cells and prevent biofilm growth.

Hard coatings are often used to extend the lifetime of cutting tools [88], and laser texturing can be a viable way of improving the coating performances. Pakula et al.[89] proposed the laser texturing of a CVD Al_2O_3 -TiN coating deposited onto a Sialon tool to increase abrasion resistance. The laser treatment resulted in the formation of a honeycomb microstructure and nanoripples that increased the tribological properties, without having any detrimental effects on the adhesion of the coating. Wahab et al. [90] also observed enhanced erosion resistance for Al_2O_3 - TiO_2 plasma sprayed coatings. The laser-induced texture consisted of grooves that resulted in a reduced coating loss, due to the prevention of the continuous propagation of cracks generated by the abrasive contact with the silica

slurry, which simulated a marine environment. Zhang et al. [91] applied a process that coupled plasma etching and femtosecond laser texturing to a TiAlN coating, before the deposition of a layer of tungsten sulphide, and they reported an enhancement in the wear and adhesion performances. Zhao et al. [92] also described an improvement in wear resistance. The authors applied laser texturing to a titanium surface in a nitrogen atmosphere in order to obtain a textured surface containing titanium nitride, but the laser-induced coating was not found to be uniform. Bobzin et al. [93] investigated the femtosecond pulsed laser texturing of three hard coatings – (Cr,Al)N, (Cr,Al)ON and nanolaminate CrN/AlN - deposited on steel via PVD. The laser wavelength absorption was reported to vary according to the coating composition and its architecture. Furthermore, when the pulse energy was too high, the hardness was found to be lower than that of the as-deposited coatings for all the samples. This was attributed to the thermal effect that induced amorphisation of the coating.

It is reasonable to expect that the use of laser on ceramic coatings and/or to prepare the surface of ceramic materials to be coated will experience a growth in the next years. The field of ceramic coatings, as described in this section, can dramatically benefit from the possibility of controlling the surface texture without affecting the underlying materials, even when thin coatings are treated.

3.4. Ceramic Matrix Composites (CMCs)

The machining of ceramic matrix composites (CMCs) is a challenging task because of the high level of hardness and the brittleness of their single phases. A first indication of the ease of machinability can be gathered from the ratio between the material hardness

and the fracture toughness. The higher the ratio value is, the higher the cutting forces and the tendency to induce brittle fractures. The most difficult members of the CMC family to machine are those containing SiC and Al_2O_3 [94]. For this reason, alternative options to traditional mechanical machining are of interest for CMCs and, in such a context, laser-based techniques are of great importance. Of these techniques, laser drilling has been found to be effective in the hole-making process, even when applied to super-hard ceramics like B_4C [95]. The complex architecture and the different phases of composite materials represent an additional challenge. Laser drilling on carbon-based and SiC-based CMCs has been studied extensively [9,10,96] to optimise the laser parameters and to obtain holes with precise tolerances and a good finishing. The studies mentioned above have identified laser drilling as a viable technology to overcome the issues related to mechanical drilling and to obtain high-quality holes in carbon-based and SiC-based CMCs, as long as an optimisation step is conducted to identify the appropriate parameters for getting the desired output. Moreover, mechanical drilling on ceramic reinforced composites presents a demanding challenge in terms of ensuring hole quality aspects such as delamination, surface finishing and roundness, while retaining a satisfactory tool life. Another CMC that has been the subject of laser drilling-oriented studies is particle-reinforced $\text{TiN}/\text{Al}_2\text{O}_3$ [97]. This material is applied to cutting tools, due to its wear resistance, but it is difficult to mechanically machine, and laser machining can be interesting, so it was studied looking for laser drilling process optimization.

Carbon fibre reinforced composites are used in the aerospace field to guarantee high performances in challenging environments. A key feature that must be taken into account when these materials are chosen to make space vehicles is their ablation resistance on re-entry. Laser technology has been used to assess this property by simulating the re-entry

thermal load on carbon-based matrix composites, but very few studies are available on the use of laser ablation as a surface modification technique for these materials . As far as ablation resistance is concerned, it is of interest that Hf-containing elements, added to the matrix of silicon carbide - carbon fibre composites, have been shown to provide enhanced laser ablation resistance [98,99].

To date, as already mentioned, only a few works have been conducted on the laser surface modification of ceramic matrix composites. Some works inherent to the surface modification of C/SiC and SiC/SiC composites are reported hereafter. The literature available on the surface texturing of oxide matrix composites has already been presented in the bioinert materials and ceramic coating sections.

Continuous carbon-based fibre ceramic composites, like C/SiC, show anisotropic wettability behaviour that is linked to the morphology of the fibre endings at the surfaces. Wu et al.[100] applied an excimer laser to produce v-shaped grooves parallel to fibres and perpendicular to fibres on the surface of a C/SiC composite, exploiting the laser thermal effect with the aim of studying the evolution of the water contact angle. Fig. 10 compares the laser ablated and the untreated surfaces. They found that the contact angle was lower after the laser treatment, and the anisotropic behaviour, observable between the two surfaces, was reduced. They also observed an increase in the oxygen content of the treated surface.

The surface morphology of C/SiC has been reported to be affected by the type of machining applied (grinding or laser ablation) [101]. In this work, a laser ablated surface was characterised by the formation of a microcracks-rich globular oxidised layer which showed a smaller amount of carbon and a higher content of oxygen than the ground

surface. Wu et al.[102], in a recent work, have identified the residual particles originating from laser ablation on the surface of C/SiC composites as being potentially beneficial for the control of surface wetting. They produced different structures by varying the laser parameters and the laser trace strategy. Among the various structures, they obtained a biomimetic one that resembled a lotus leaf.

In an effort to collect information on the laser ablation behaviour of C/SiC, Pan et al.[103] identified three different areas on the surface of laser-ablated C/SiC: a central region, where the temperature is high enough to ablate the SiC matrix and carbon fibres, a transition region, where the lower temperature allows the SiC particles to be redeposited and an outer region, where the temperature is low enough to permit the deposition of silica. The atmosphere surrounding C/SiC during laser ablation is relevant in determining the surface appearance. Wang et al.[104] studied the effect of the application of a supersonic airflow onto a laser ablated C/SiC surface, and they observed that the ablation rate increased due to the convection effect and the mechanical erosion induced by the airflow. The formation of silica can be avoided through the use of a non-reactive gas. Zhai et al. [105] reported that the formation of silica was not observed on the surface of a femtosecond laser ablated C/SiC after using argon as a shielding gas.

SiC/SiC composites are considered the most promising materials for the manufacturing of lightweight, high-performing, hot sections for turbine engines for aerospace applications to replace heavy weight alloys, as they result in fuel savings and a lower environmental impact [106]. In the mentioned applications, SiC/SiC composites may require to be integrated with other materials like metals and a textured surface might enhance the interlocking mechanism providing sounder joints and provide a better coating adhesion. Because of the issues related to the traditional machining of SiC/SiC

composites, it is expected that laser processing will be the standard route to structuring the surface of SiC/SiC turbines at a microscale [107]. Zhai et al. [107] utilised a femtosecond laser to produce microgrooves on the surface of a SiC/SiC composite, and they reported that the common defects that are typical of other processes were not found after an optimisation process. In particular, they highlighted the absence of fibre pullouts and edge collapses, which are generally associated with mechanical machining. Furthermore, common issues associated with laser processing conducted in air, such as SiC/SiC oxidation and a heat affected zone, were not evident after the optimisation process. Again, the use of a suitable shielding gas could prevent the occurrence of an oxidation reaction [105].

Although limited information is available on laser texturing of CMCs, the works presented in this section suggest that it could become a new standard for these difficult-to-machine materials. However, there is a strong need for further studies to collect more information and to develop a deeper understanding.

4. Summary and outlook

This work is intended to provide an overview of the recent and available literature about laser texturing techniques on ceramic material and ceramic composites. The aim has been to provide an updated state of the art that could be consulted by researchers in this field. Table 1 offers a summary of the applications of laser texturing on ceramics and CMCs presented in this review, listed in order of appearance and collected according to the application.

Different types of lasers applied to various ceramic materials have been discussed, focusing on relevant applications, such as biomedical, electronics and coatings. Most of the presented studies were application-driven, thus leaving room for research on the characterisation of the laser-ceramic/CMC material interaction, which is necessary to obtain a better understanding of the opportunities and limitations of each laser type.

The possibility of obtaining specific geometries with high precision on hard and brittle components, such as ceramics, is the one of the most interesting aspects of laser surface texturing. Femtosecond-pulsed lasers currently appear to be the most promising to achieve high-precision textures on ceramics, because of the nearly total absence of adverse thermal effects surrounding the ablated area.

It is worth pointing out that most of the cited references in the present work have been published over the last five years, thus identifying a significant increase in interest in the laser surface structuring topic.

As a final remark, future research should be addressed to the study of surface modifications of CMC materials, which, till now, have received very little attention .

Furthermore, the laser technology might replace traditional techniques, like acid-based etching, as it provides a more eco-friendly processing. Moreover, laser processing can guarantee the high reproducibility of the surface textures that is required for most applications.

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Figure captions:

Fig. 1. Nanosecond pulse laser-material interactions (on the left); femtosecond pulse laser- material interactions (on the right) [18].

Fig. 2. The growth of studies inherent to LIPSS over the years.

Fig. 3. a) LIPSS formed on fused silica and b) the layered system built on a fused silica substrate. (Adapted from [30]).

Fig. 4. Cell growth in function of the laser-formed grooves on treated alumina toughened zirconia (ATZ) compared to cell growth on unmodified ATZ. (Adapted from [34]).

Fig. 5. The surface of YSZ (on the left). the textured surface of the fs-pulsed laser modified YSZ (on the right). Adapted from [38].

Fig. 6. Alumina-zirconia acetabular cup textured by microsecond pulsed laser prior to (a) and after a thermal treatment in an oxidising environment (b) [41].

Fig. 7. The cross-section of the nanosecond pulsed laser treated SiC (on the left); the graphic scheme of the formed layers (on the right). (Adapted from [50]).

Fig. 8. Cross sections of different plasma sprayed coated laser-textured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ composites [79]: (a) yttria-coated dot-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (b) yttria-coated mixed-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (c) YSZ-coated dot-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (d) YSZ-coated mixed-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (e) $\text{Gd}_2\text{Zr}_2\text{O}_7$ -coated dot-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (f) $\text{Gd}_2\text{Zr}_2\text{O}_7$ -coated mixed-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$.

Fig. 9. Nanostructures on a non-stoichiometric TiO_x surface formed using different laser pulses numbers. a) 500 pulses, b) 1000 pulses, c) 5000 pulses and d) 10000 pulses. A UV femtosecond laser beam was applied [85].

Fig. 10. An untreated C/SiC fibre-parallel surface (a) and C/SiC fibre-perpendicular surface (b). Laser-induced v-shaped grooves on a C/SiC fibre-parallel surface (c) and C/SiC fibre-parallel surface (d) [100].

Table captions:

Table 1. Relevant laser surface modifications on ceramic and CMC materials reported in this review. All the listed materials are intended as bulk materials, unless otherwise specified.

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LIPSS formation				
surface-modified material	laser pulse	outcome	notes	ref.
SiC (coating)	fs-pulsed	Surface texturing (LIPSS)		[27]
Al ₂ O ₃ - ZrO ₂ - Nb	fs-pulsed	Surface texturing (LIPSS) Water wettability increased	The fluence was selected to prevent the ceramic phase from reaching ablation. The modification led to the selective formation of LIPSS on the metal phase	[28]
ZnO	fs-pulsed	Surface texturing (LIPSS) Enhanced sensitivity to NO ₂		[29]

Fused SiO ₂	ns-pulsed	Surface texturing (LIPSS)	The surface of a substrate was modified by exposing it to a confined ablation using a designed layered system	[30]
Surface texturing of bioinert ceramics and CMCs				
surface-modified material	laser pulse	outcome	notes	ref.
YSZ	fs-pulsed	Surface texturing Surface roughening		[32]
Al ₂ O ₃ - ZrO ₂	fs-pulsed	Surface texturing Cell growth guided by the laser-induced texture No chemical or phase changes		[33],[34]
Al ₂ O ₃	ps-pulsed	Surface texturing Enhanced cell proliferation		[35]

YSZ	ns-pulsed	Surface roughening		[36]
		No enhancement of the coating bond strength		
		Negligible conversion from cubic to monoclinic zirconia		
ZrO ₂	μs-pulsed	Surface roughening		[37]
		No enhancement of the coating bond strength		
ZrO ₂	fs-pulsed	Surface texturing		[38]
		Enhanced bond strength with brackets		
Al ₂ O ₃ - ZrO ₂	ns-pulsed	Surface texturing	The laser	[41]
		Roughness in the same range as the osteoblastic cell sizes	treatment was successfully applied to non planar real-size	

		acetabular cups for hip prosthesis		
Surface texturing of silicon carbide and silicon nitride				
surface-modified material	laser pulse	outcome	notes	ref.
SiC	ns-pulsed	Silica nanotextured layer on the surface Increase in the specific area Formation of an underlying nanometric graphite layer, which is detrimental for the mechanical joining properties		[50]
Si ₃ N ₄	ns-pulsed	Silica nanotextured layer on the surface Increase in the specific area		[51]

		Higher apparent shear strength of joints		
Si ₃ N ₄	ps-pulsed	Surface texturing prior to grinding Lower grinding forces Better finishing after grinding	Laser texturing was also performed on the tool using a femtosecond pulsed laser in [53].	[53], [54]
SiAlON-Si ₃ N ₄	fs-pulsed	Surface texturing prior to grinding Lower grinding forces		[55]
Monocrystalline 4H-SiC	fs-pulsed	Formation of multilayered graphene on the SiC surface	Argon atmosphere	[61]
Monocrystalline 4H-SiC	fs-pulsed	Surface texturing		[68]
Monocrystalline 6H-SiC	fs-pulsed	Higher etching rate for ICP	The bond breaking and silica formation obtained with the laser enhanced the ICP etching	[69]

Monocrystalline 4H-SiC	fs-pulsed	Surface texturing (LIPSS) Better machinability of the LIPPS- covered surface		[70]
Ceramic coatings				
Al ₂ O ₃ / Al ₂ O ₃	Not declared	Better interlocking between the CMC substrate and coatings		[77]
non- stoichiometric TiO ₂ (coating)	fs-pulsed	Surface texturing (LIPSS)		[85]
TiO ₂ - ZnO (coating)	ps-pulsed	Surface texturing Higher contact area with enhanced antibacterial properties		[87]
TiAlN (coating)	fs-pulsed	Surface texturing Enhanced adhesion of an upper WS layer	Laser texturing coupled with plasma etching	[91]

Titanium	undeclared	Formation of a structured TiN layer	Laser texturing carried out in a nitrogen atmosphere to promote TiN formation	[92]
		Better wear and corrosion resistance		
		Non-uniform TiN laser-induced layer		
Carbon-based CMCs				
surface-modified material	laser pulse	outcome	notes	ref.
C/SiC	Not declared	Surface texturing		[100]
		Reduction of the wettability anisotropy		
SiC/SiC	fs-pulsed	Surface texturing		[107]

Figure 1 (colour). Nanosecond pulse laser-material interactions (on the left); femtosecond pulse laser- material interactions (on the right) [18].

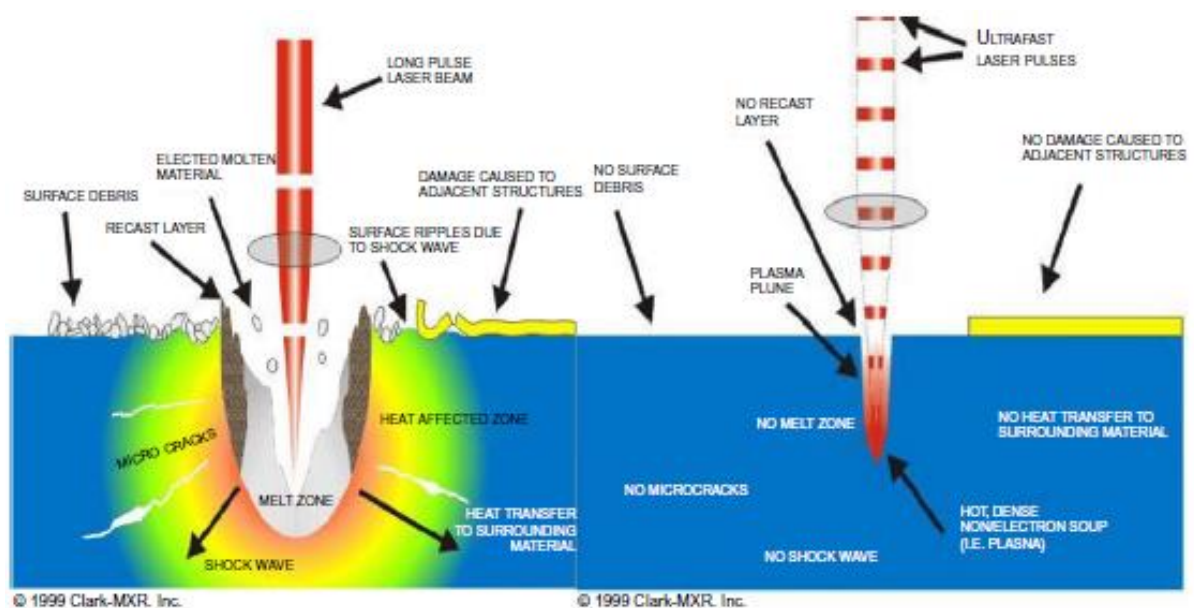


Figure 2 (colour). The growth of studies inherent to LIPSS over the years.

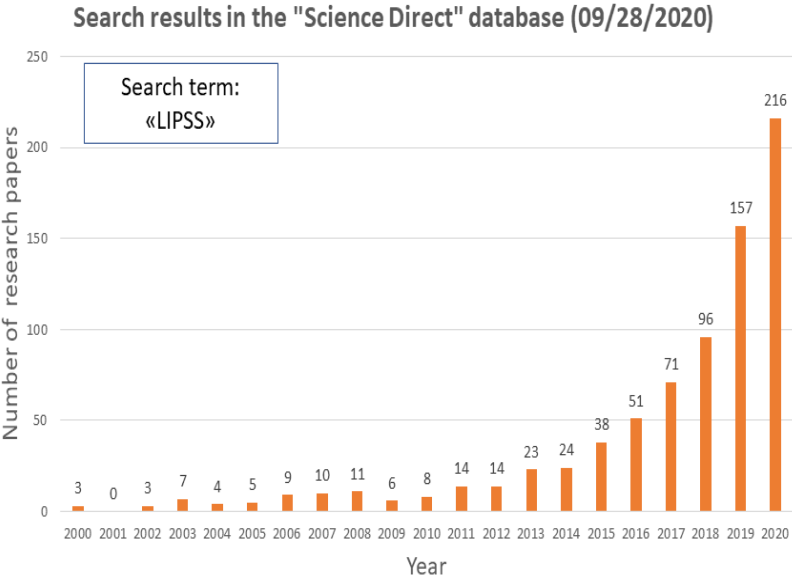


Figure 3 (colour). a) LIPSS formed on fused silica and b) the layered system built on a fused silica substrate. (Adapted from [30]).

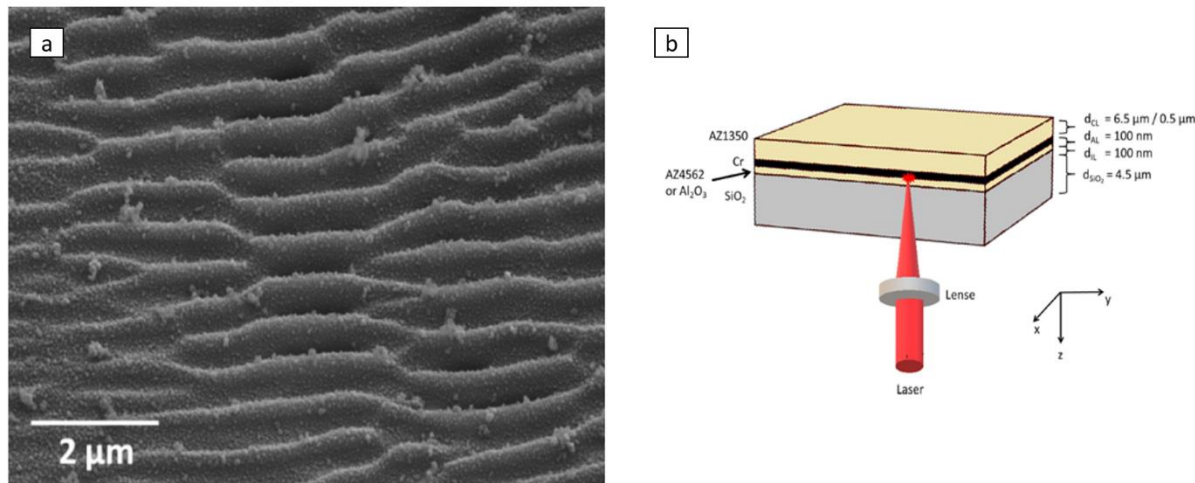


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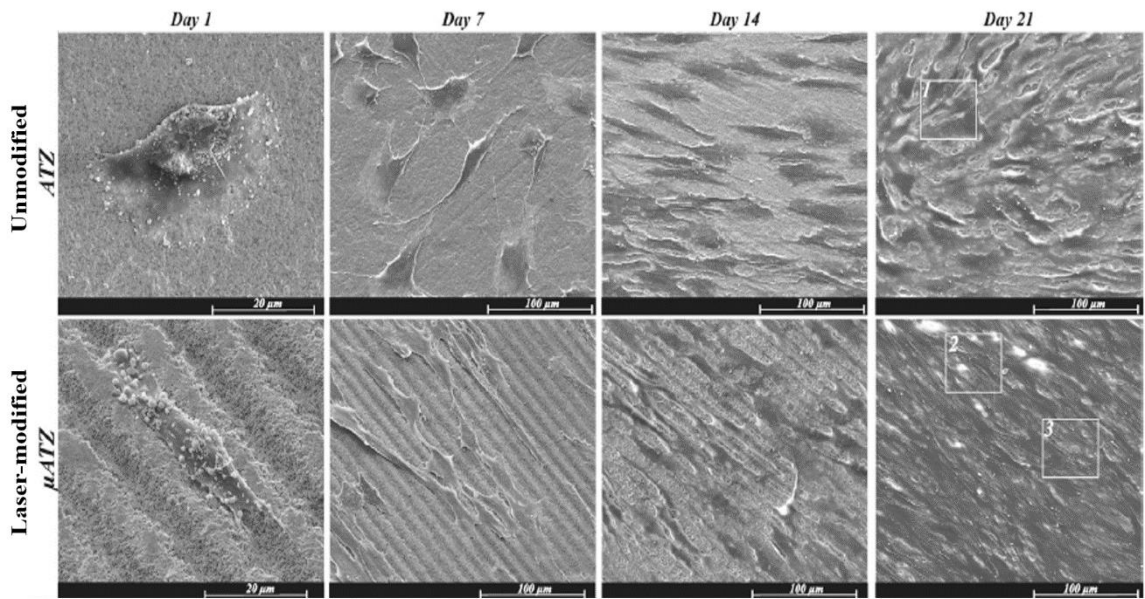


Figure 5. The surface of YSZ (on the left). the textured surface of the fs-pulsed laser modified YSZ (on the right). (Adapted from [38].)

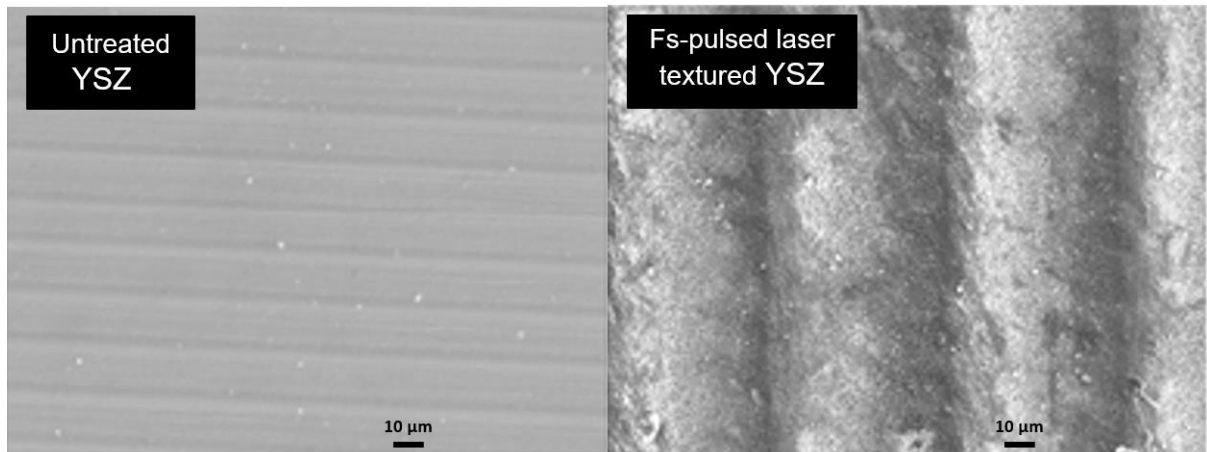


Figure 6 (colour). Alumina-zirconia full-scale acetabular cup textured by microsecond pulsed laser prior to (a) and after a thermal treatment in an oxidising environment (b) [41].

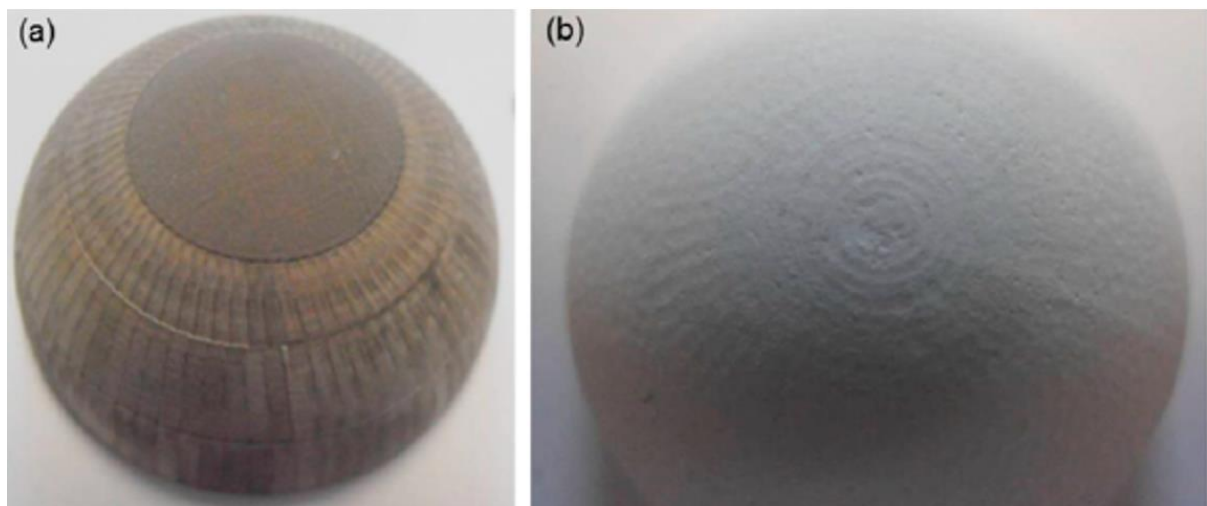


Figure 7 (colour). The cross-section of the nanosecond pulsed laser treated SiC (on the left); the graphic scheme of the formed layers (on the right). (Adapted from [50].)

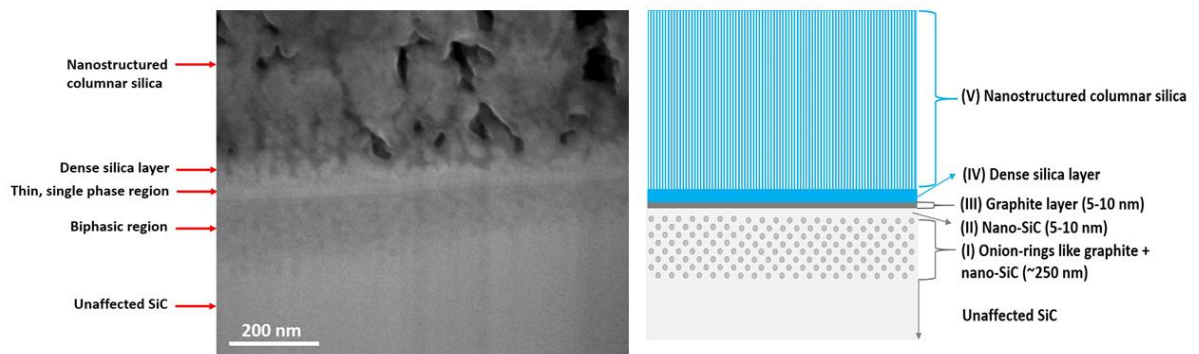


Figure 8. Cross sections of different plasma sprayed coated laser-textured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ composites [79]: (a) yttria-coated dot-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (b) yttria-coated mixed-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (c) YSZ-coated dot-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (d) YSZ-coated mixed-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (e) $\text{Gd}_2\text{Zr}_2\text{O}_7$ -coated dot-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$; (f) $\text{Gd}_2\text{Zr}_2\text{O}_7$ -coated mixed-structured $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$.

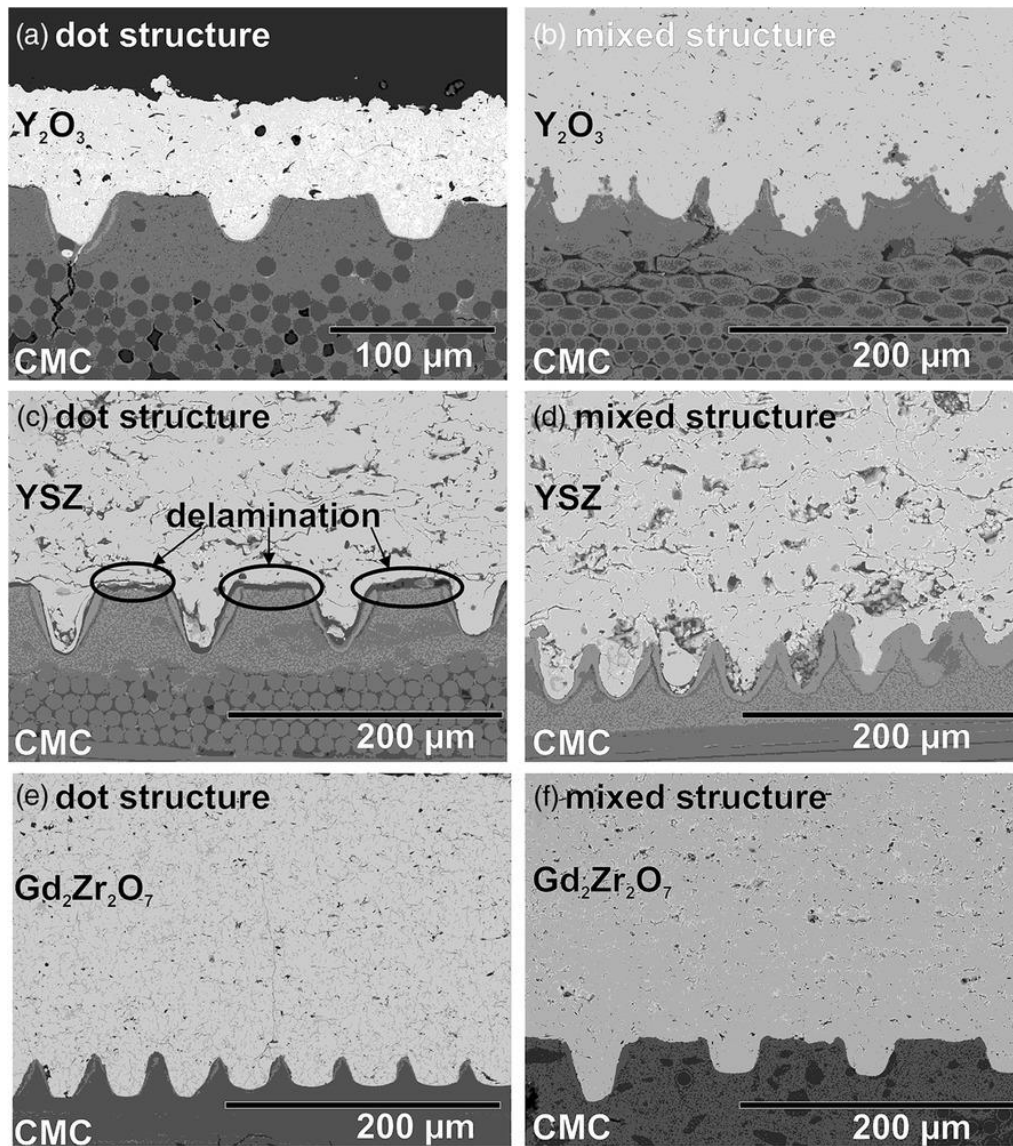


Figure 9. Nanostructures on a non-stoichiometric TiO_x surface formed using different laser pulses numbers. a) 500 pulses, b) 1000 pulses, c) 5000 pulses and d) 10000 pulses. A UV femtosecond laser beam was applied [85].

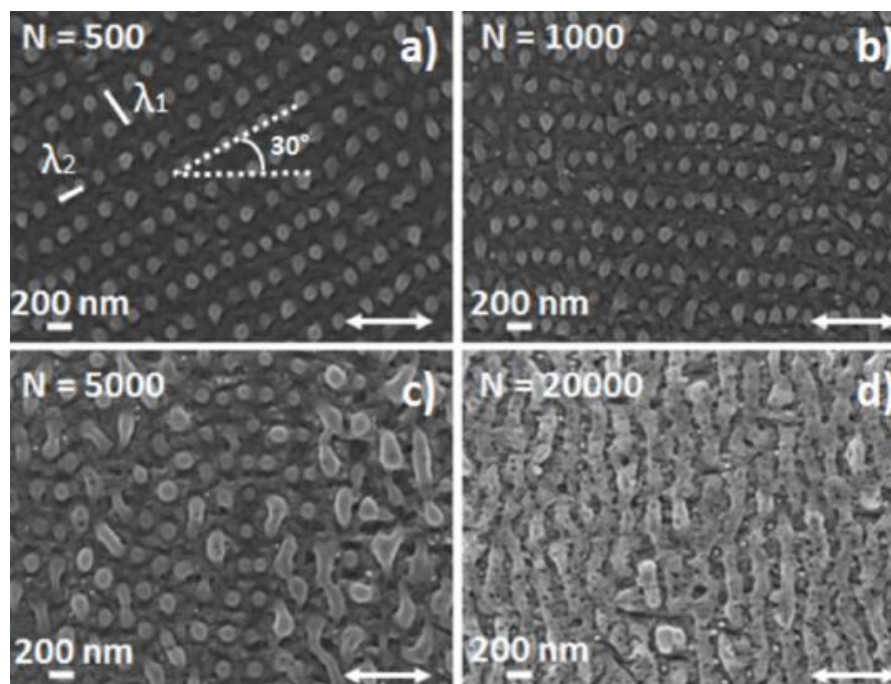


Figure 10 (color). An untreated C/SiC fibre-parallel surface (a) and C/SiC fibre-perpendicular surface (b). Laser-induced v-shaped grooves on a C/SiC fibre-parallel surface (c) and C/SiC fibre-parallel surface (d) [100].

