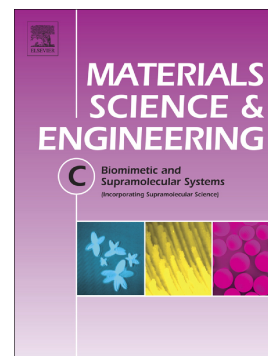


## Journal Pre-proof

Laser surface texturing of zirconia-based ceramics for dental applications: A review

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# Laser surface texturing of zirconia-based ceramics for dental applications: a review

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## Abstract

Laser surface texturing is widely explored for modifying the surface topography of various materials and thereby tuning their optical, tribological, biological, and other surface properties. In dentistry, improved osseointegration has been observed with laser textured titanium dental implants in clinical trials. Due to several limitations of titanium materials, dental implants made of zirconia-based ceramics are now considered as one of the best alternatives. Laser surface texturing of zirconia dental implants is therefore attracting increasing attention. However, due to the brittle nature of zirconia, as well as the metastable tetragonal  $ZrO_2$  phase, laser texturing in the case of zirconia is more challenging than in the case of titanium. Understanding these challenges requires different fields of expertise, including laser engineering, materials science, and dentistry. Even though much progress was made within each field of expertise, a comprehensive analysis of all the related factors is still missing. This review paper provides thus an overview of the common challenges and current status on the use of lasers for surface texturing of zirconia-based ceramics for dental applications, including texturing of zirconia implants for improving osseointegration, texturing of

zirconia abutments for reducing peri-implant inflammation, and texturing of zirconia restorations for improving restoration retention by bonding.

**Keywords:** Laser surface texturing; Zirconia-based ceramics; Dental implants; Zirconia restorations

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**Nomenclature**

ABA	Airborne particle abrasion
Al <sub>2</sub> O <sub>3</sub>	Aluminum oxide
ATZ	Alumina toughened zirconia
BIC	Bone-to-implant contact
<i>c</i>	Cubic
CaO	Calcium oxide
CCD	Charge-coupled device
CeO <sub>2</sub>	Cerium dioxide
Ce-TZP	Ceria-stabilized tetragonal zirconia polycrystal
CO <sub>2</sub>	Carbon dioxide
DLIP	Direct laser interference patterning
Er,Cr:YSGG	Erbium, chromium-doped yttrium, scandium, gallium and garnet
Er:YAG	Erbium-doped yttrium aluminum garnet
FLB	Focused laser beam
fs	Femtosecond
HSFL	High-spatial frequency LIPSS
LIPSS	Laser-induced periodic surface structures
LIPT	Laser induced phase transformation
LP	Laser patterned
LSFL	Low-spatial frequency LIPSS
LTD	Low temperature degradation
<i>m</i>	Monoclinic
MgAl <sub>2</sub> O <sub>4</sub>	Magnesium-aluminum oxide
MgO	Magnesium oxide
Mg-PSZ	Magnesia-partially stabilized zirconia
μs	Microsecond
ms	Millisecond
Nd:YAG	Neodymium-doped yttrium aluminum garnet
nm	Nanometer
ns	Nanosecond
ps	Picosecond
PSZ	Partially stabilized zirconia
s	Second
SEM	Scanning electron microscopy

<i>t</i>	Tetragonal
Ti	Titanium
TSC	Tribochemical silica coating
TZP	Tetragonal zirconia polycrystal
UV	Ultraviolet
WCA	Water contact angle
Yb	Ytterbium
8Y-FSZ	8 mol% Ytria-fully stabilized zirconia
Y <sub>2</sub> O <sub>3</sub>	Yttrium oxide
Y-PSZ	Ytria-partially stabilized zirconia
Y-TZP	Ytria-stabilized tetragonal zirconia polycrystal
3Y-TZP	3 mol% Ytria-stabilized tetragonal zirconia polycrystal
ZrN	Zirconium nitride
ZTA	Zirconia toughened alumina

## 1. Introduction

Its excellent biocompatibility, desirable physical and mechanical properties have made titanium the material of choice for dental implants for more than five decades [1-4]. The primary limitation of titanium as a dental implant material is its grayish color which can lead to an unsatisfactory esthetic appearance after implantation [5, 6]. The corrosion of titanium dental implants in the oral cavity may also cause undesirable effects, such as the reduction of fatigue life of the implant, local pain and swelling, and particle release induced osteolysis [7, 8]. Some patients even develop metal hypersensitivity issues with titanium dental implants [9-12]. Nowadays, zirconia-based ceramics are considered as the most promising alternatives to titanium in dentistry because of their tooth-like color, excellent biocompatibility and acceptable mechanical properties [13-15].

A sufficient fracture toughness and mechanical strength of the base material is a prerequisite for a dental prosthesis component. Owing to the transformation toughening mechanism, zirconia-based ceramics exhibit the best mechanical properties in terms of fracture toughness and mechanical strength among all oxide ceramics [16, 17]. A conventional dental prosthesis is composed of an implant, abutment, and restoration. In addition to mechanical properties, the different parts of prosthesis may require the material to possess additional specific merits. For the implant, the osseointegration between the implant surface and human bone is of vital importance [18-20]. This requires the implant material to have a good biocompatibility, which has been proven for zirconia-based ceramics [21-23]. For the abutment material, zirconia is considered superior to titanium because zirconia is less attractive to bacterial adhesion and concomitantly has less peri-implant inflammatory problems [24-28]. The outstanding

material properties of zirconia-based ceramics suggest a good potential for their application in dental implants. Several review papers on the history and current status of zirconia-based ceramics in dental applications can be found in literature [20, 29-33].

Besides the material properties, the surface condition of the dental implants also plays an important role [34-36]. Many *in vivo* studies using different animal models showed that surface modified zirconia implants have a much better osseointegration than non-modified ones [37-42]. In a recent review on the role of the implant surface modification on osseointegration, Liu et al. summarized the characteristics of different implant surface modification techniques and their influence on osseointegration [43]. More review papers on this topic are also available [44-50]. For zirconia restorations like crowns and bridges, durable adhesion to the dentin or abutment remains a challenge [51]. Surface modification is also needed to improve bond strength and eventually increase the clinical longevity of zirconia restorations.

Common zirconia implant surface modification methods include machining [52, 53], sandblasting [37, 54], chemical etching [54, 55], laser processing [56], coating [57, 58], etc. Compared to other methods, laser processing has started to attract increasing attention because of the following characteristics. First, there is no surface contamination onto the implant during surface processing because the laser treatment is a contact-free process. Second, laser processing can produce hierarchical surface structures with regular patterns and therefore control the wettability of the surface, which is believed to have a big influence on the cell adhesion behavior [59-61]. Third, laser processing, especially with ultrafast lasers, can be applied to any kind of material irrespective of its hardness and mechanical strength [62].



Laser processing for surface functionalization of dental implants has shown promising results in terms of improving osseointegration, reducing biofilm formation, and enhancing soft tissue attachment [63-70]. Review papers on this topic were mainly focused on titanium dental implants [71, 72]. However, the laser absorption mechanisms for ceramics and metals are fundamentally different. For metals, the laser energy is directly absorbed by free electrons which is a linear process, i.e. the absorbed laser energy is proportional to the laser intensity, while there are almost no free electrons in oxide ceramics. For zirconia-based ceramics, the laser absorption and subsequent material ablation can only be triggered with a much higher laser fluence that limits the laser source mainly to short or ultrashort pulsed lasers. Moreover, unlike titanium alloys, zirconia-based ceramics are brittle materials. Zirconia is a thermal insulator and is more susceptible to the mechanical shocks caused by laser generated high temperature gradients which can lead to the formation of thermal cracks and deteriorate the mechanical properties of the laser treated materials [73-75]. A careful evaluation of the influence of laser processing on the mechanical strength as well as long-term stability of zirconia-based ceramics is therefore indispensable. Thermal gradients are less critical when processing titanium implants and the main efforts were focused on the evaluation of biological response, especially the osseointegration, of laser processed implant surfaces [76-80].

In view of the above, an overall picture about laser surface texturing of zirconia-based ceramics ranging from laser-ceramic interaction mechanisms to the impact of laser texturing on surface topography and material properties, and the subsequent influence on the long-term stability of the laser processed materials as well as the functionality of the generated surfaces, is not yet available. Therefore, this review paper provides a

comprehensive overview of the current status on the use of lasers for surface processing of zirconia-based ceramics for dental applications. This review paper covers the following aspects: basics of pulsed laser–ceramic interaction mechanisms, brief introduction to zirconia-based ceramics, characteristics of laser generated surface textures, laser induced surface damages and their impact on mechanical strength and long-term stability, and experimental evaluation of laser textured functional surfaces.

## 2. Zirconia-based ceramics in dentistry

Pure zirconia has three temperature-dependent allotropes: monoclinic (*m*), tetragonal (*t*), and cubic (*c*) [81]. At ambient conditions, zirconia has a monoclinic crystal structure, which transforms to a tetragonal structure at 1170°C and to a cubic structure at 2370°C with a melting point at 2716°C [81]. The martensitic *t*-*m* transformation occurs upon cooling after the high-temperature sintering process and is accompanied by a volume expansion of approximately 4.5% which causes large internal stresses that can disintegrate the material by cracking [82]. To avoid this, stabilizing oxides such as CaO, MgO, Y<sub>2</sub>O<sub>3</sub>, or CeO<sub>2</sub> are alloyed with pure zirconia to allow the high-temperature *t* or *c* phases to be fully or partially retained at room temperature [81]. However, the *t* phase is metastable and has a tendency to transform to *m* phase under applied tensile stresses or in the presence of water [83]. In the case of stress induced *t*→*m* transformation, the ensuing volume expansion will exert a compressive stress field to the crack tip, which can hinder the propagation of cracks, resulting in an enhancement of the fracture toughness of the material. This mechanism is usually referred to as transformation toughening [16]. Spontaneous *t*→*m* transformation can also occur gradually over time in the presence of water, which is known as low temperature

degradation (LTD) or hydrothermal aging [83]. LTD could lead to a reduction of the mechanical properties of zirconia-based ceramics and is believed to be responsible for the catastrophic failure of around 400 femoral heads shortly after surgery in 2001 [84]. The failure of these femoral heads was identified as the result of accelerated aging of Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) in two Prozyr (SGAC Desmarquest, Evreux, France) product batches [84].

Based on their microstructure, zirconia-based ceramics can be classified into three categories [82, 85]: (a) TZP, e.g. 3Y-TZP; (b) partially stabilized zirconia (PSZ), e.g. Mg-PSZ and Y-PSZ; (c) zirconia containing ceramics like zirconia toughened alumina (ZTA) and alumina toughened zirconia (ATZ). Representative microstructures of these three categories are shown in Fig. 1.

### **2.1 3Y-TZP**

Among these three categories, 3Y-TZP, which contains 3 mol%  $Y_2O_3$ , exhibits the optimal mechanical properties with a flexural strength of 900-1200 MPa and a fracture toughness of 3-10  $MPa\ m^{1/2}$ , and is therefore most widely used in dentistry [31, 33]. The main possible drawback associated with 3Y-TZP is its sensitivity to LTD [84]. The consequences of LTD include surface roughening due to grain pull out, micro-cracking, and mechanical strength degradation [32].

### **2.2 Mg-PSZ and Y-PSZ**

Mg-PSZ is reported to have a better performance in terms of long-term stability with a much lower degree of LTD than 3Y-TZP [86]. Its mechanical properties are however inferior to those of 3Y-TZP, and Mg-PSZ was therefore not the first choice for dental applications during the early stage of zirconia ceramics development [87]. With the

addition of spinel particles, such as  $\text{MgAl}_2\text{O}_4$ , the mechanical properties of Mg-PSZ, especially the fracture toughness, can be higher than that of 3Y-TZP [88]. Together with the major advantage of being almost hydrothermally stable, its prospect in future dental applications may still be promising [87]. Y-PSZ with yttria content higher than 3 mol%, such as 4Y-, 5Y-, and 6Y-PSZ, are attracting increasing attention due to their highly translucent appearance, which makes them aesthetically superior to 3Y-TZP for dental restorations [89, 90]. Their mechanical properties are however inferior to 3Y-TZP. Therefore, they are currently not used for abutments and implants but mainly for solitary crowns [91-94].

### **2.3 ZTA and ATZ**

ZTA is composed of a minor  $t\text{-ZrO}_2$  phase fraction that is dispersed in an alumina matrix. A higher content of  $t\text{-ZrO}_2$  phase leads to a larger fracture toughness of the composite, while a lower content leads to a better hydrothermal aging resistance [95]. When the zirconia content is below the percolation threshold, which is 16 vol% or 22 wt%, LTD can be completely avoided, provided that no zirconia aggregates are formed [96]. ATZ, with alumina being the minor phase, also attracts much attention. ATZ exhibits a higher fracture toughness and especially strength than ZTA, but the LTD issue associated with the  $t\text{-ZrO}_2$  phase cannot be fully avoided [97]. Ce-TZP/ $\text{Al}_2\text{O}_3$ , with a typical composition of 10 mol%  $\text{CeO}_2$ , shows a much better resistance to LTD as well as better mechanical properties, especially the fracture toughness, than yttria-stabilized zirconia and its composites [85, 98-101]. Its prospect in dental application is under assessing with some promising results already available [102, 103].

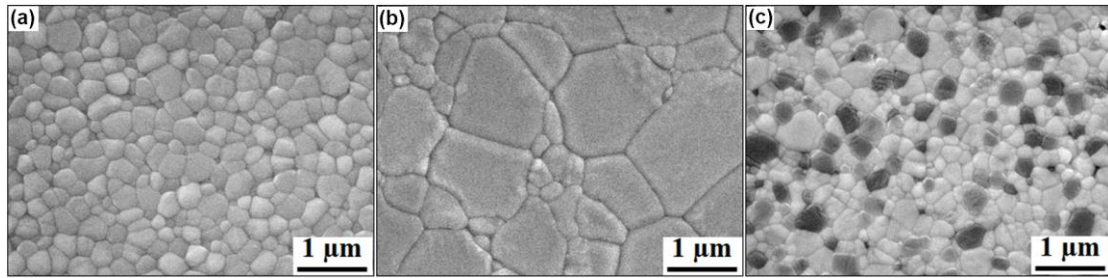


Fig. 1. Representative microstructures of three categories of zirconia-based ceramics: (a) Y-TZP. Adapted with permission from [91]. Copyright © 2016 The Academy of Dental Materials. Published by Elsevier Ltd., (b) Y-PSZ. Adapted with permission from [104]. Copyright © 2020 The Academy of Dental Materials. Published by Elsevier Inc., (c) ATZ based on Y-TZP. Adapted with permission from [105]. Copyright © 2016 Elsevier Ltd.

### 3. Laser–ceramic interaction mechanisms

#### 3.1 Long-pulsed laser

Zirconia is a wide band gap dielectric with a band gap of around 5.8 eV [106], which is much larger than the photon energy of common lasers. The electrons in zirconia valence band cannot be excited into the conduction band through single photon absorption. However, even for ideal dielectrics, the conduction band, which is empty at 0 Kelvin, is not totally free of electrons at ambient temperature. Color centers and impurities that always exist in industrial grade materials will contribute more free electrons and inter-band electrons with band gaps smaller than the photon energy. These free electrons and inter-band electrons are capable of absorbing photon energy through a linear process. For lasers with a pulse duration longer than a few tens of picoseconds, such as nanosecond and microsecond lasers, it is generally accepted that the laser absorption occurs by conduction band and small band gap inter-band electrons [107]. The conduction band and inter-band electrons absorb laser energy and transfer it to the lattice vibrations, causing the temperature to increase and eventually the removal

of material by melting and evaporation, and even phase explosion under high laser fluence [108].

### ***3.2 Femtosecond laser***

For ultrashort pulse lasers, typically the pico- and femtosecond lasers, the laser intensity can be high enough to trigger nonlinear absorptions, including multiphoton absorption and tunneling ionization, generating free electrons in the conduction band [109]. These free electrons can further absorb laser energy through free carrier absorption (inverse Bremsstrahlung) to gain energy and, after gaining enough energy, will collide with valence band electrons to generate more free electrons, causing a collisional (avalanche) ionization to happen.

Free electrons that are generated from multiphoton absorption and avalanche ionization processes transfer energy to nuclei by colliding. Considering the huge difference of the mass between electrons and nuclei it takes many picoseconds to reach electron-phonon equilibrium and heat the lattice [110]. Since the pulse duration is shorter than the electron-phonon relaxation time, when an ultrashort laser pulse touches the material surface, the electrons are excited almost immediately and the electron system is fully thermalized while the lattice system remains nearly cold at the end of the laser pulse. The electronic excitation in dielectrics will disturb the interatomic bonding and may lead to non-thermal phase transformations such as ultrafast solid-solid phase transitions [111]. The build-up of positively charged ions at the material surface, caused by emission of highly energetic electrons, can eventually result in material removal by Coulomb explosion, which is a non-thermal process [112]. Nevertheless, the contribution of Coulomb explosion to the total material removal in the laser ablation

process is very small [113]. The main material removal mechanisms are photomechanical spallation and phase explosion [113].

Compared to long-pulsed lasers, a major advantage of short-pulsed lasers is that the thermal side-effects, including thermal cracks and heat affected zone, are minimized during laser material processing. However, the price for a femtosecond laser system is much higher than for a longer pulsed laser system, such as for example a nanosecond laser. It should be noted that it is mainly the laser intensity and to a lower extent the laser wavelength, rather than the laser pulse duration, that determines the laser absorption mechanism. The reason for multiphoton absorption not to be the main absorption mechanism during nanosecond laser processing of wide band gap materials is the too low laser intensity in commonly available nanosecond laser systems to trigger this process.

## **4. Laser surface texturing of zirconia-based ceramics**

### ***4.1 Surface topography***

The surface topography plays a vital role in the osseointegration of the implant, the bacterial adhesion onto abutments, and the bond strength of restorations. A rougher implant surface is shown to have a better osseointegration compared to a smoother one [114]. Surface roughening of zirconia implants can be achieved by numerous methods, including sand blasting, acid etching, and laser processing [115-117]. Fig. 2 shows representative SEM images of zirconia-based ceramic surfaces after different surface treatment processes. A unique feature of laser texturing compared to other surface treatment methods is that it can produce micro-patterns with regular geometry instead

of random surface roughness, as shown in Fig. 2 (a), which is shown to have a favorable effect on osseointegration [118-121]. In laser surface texturing, the generated surfaces can exhibit hierarchical structures featured by the superposition of microscale textures, nanoscale roughness, and even laser-induced periodic surface structures (LIPSS).

Despite the advantages of laser processing over other surface treatment methods that have briefly been introduced in the introduction part, there are also challenges with laser processing of zirconia-based ceramics, especially for dental applications where a long service time in a harsh environment is expected. These include thermal cracking, which can reduce mechanical strength, and laser induced phase transformation (LIPT), which may impair the long-term stability of dental implants.

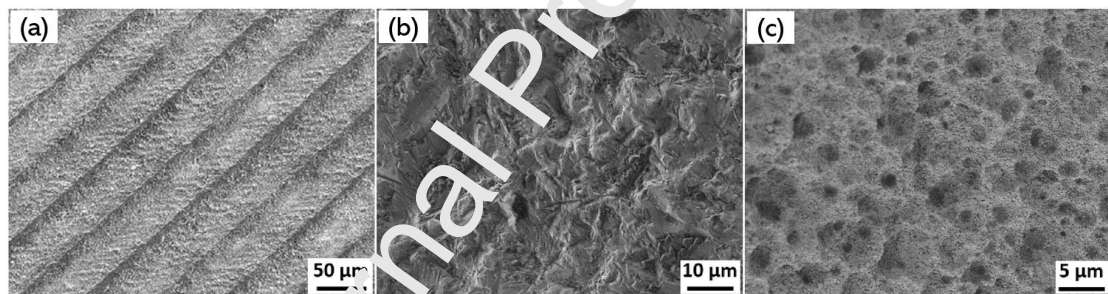


Fig. 2. Comparison of surface morphology after different surface treatment processes: (a) femtosecond laser surface texturing. Adapted with permission from [60]. Copyright © 2019 Elsevier Ltd and Techna Group S.r.l. (b) Sand blasting; (c) acid etching after sand blasting. Adapted with permission from [117]. Copyright © 2020 Elsevier Ltd.

#### 4.1.1 Microscale textures

The microscale texture is formed by the direct removal of material by spatially localized laser energy deposition, such as using focused laser beam (FLB) (Fig. 3. (a) and (b)) [122] or through direct laser interference patterning (DLIP) (Fig. 3. (c)) [123].

The topography and dimension of the textures produced by FLB is influenced by



several parameters, including laser spot size, laser power, scan speed, and scan strategies [61]. The smallest feature size is limited by the laser spot size, which typically ranges from several micrometers to tens of micrometers. For two-beam DLIP, the period of the textures is described by  $P = \lambda/2\sin(\theta)$  (Fig. 3. (d)), where  $\lambda$  is the laser wavelength, and  $\theta$  is the half-angle between interference beams [124]. The feature size of the textures produced by the DLIP method is not determined by the laser spot size but by the laser wavelength and the angle between the interference beams, and therefore smaller scale surface structures can be achieved. Besides two-beam DLIP, which can produce groove textures, multi-beam DLIP, which can produce more complex surface textures, is also possible [125].

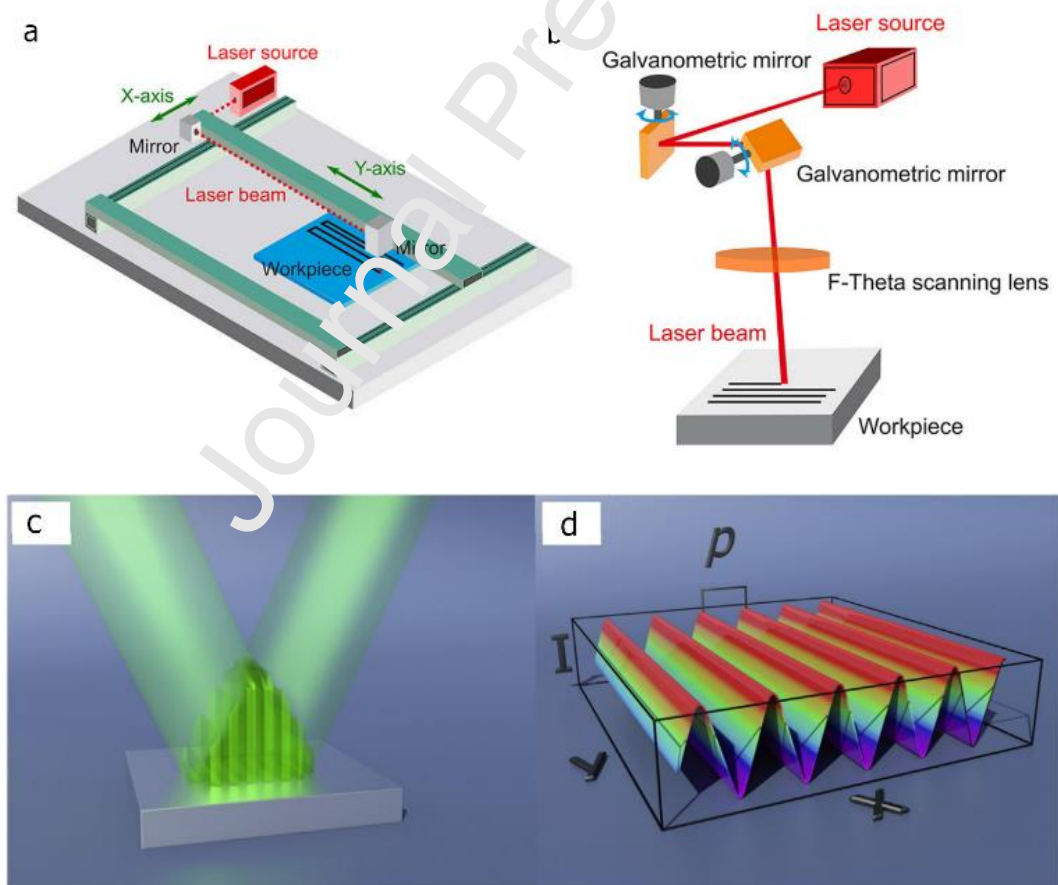
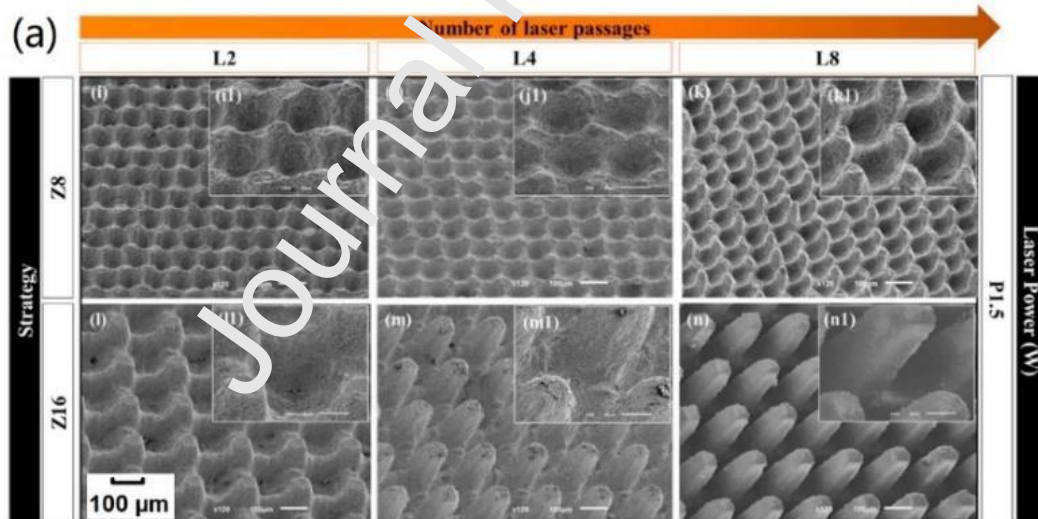


Fig. 3. (a) FLB texturing with a motion platform; (b) FLB texturing with a scanning system. Reproduced with permission from [126]. Copyright © 2018 Riveiro, Maçon, del Val, Comesaña and Pou. (c) Two-beam DLIP; (d) intensity distribution for two

overlapping laser beams. Reproduced with permission from [127]. Copyright © 2016 Elsevier Ltd.

Roitero et al. [128] investigated the influence of the number of pulses and fluence per pulse on the laser interference patterned surface quality and topography of 3Y-TZP using a nanosecond laser with an output laser wavelength of 355 nm. They reported that the best surface quality with minimum material damage was achieved under a low number of pulses with high laser fluence, while deep patterns were generated with high number of pulses and high laser fluence. Limited by the contrast of the laser energy distribution in the interference patterns as well as the feature size of the structures that can be created, it is difficult to produce high aspect ratio surface textures with the DLIP method, while there is no such limitation for texturing with FLB. For a direct comparison, Fig. 4 shows the surface textures produced by these two approaches.



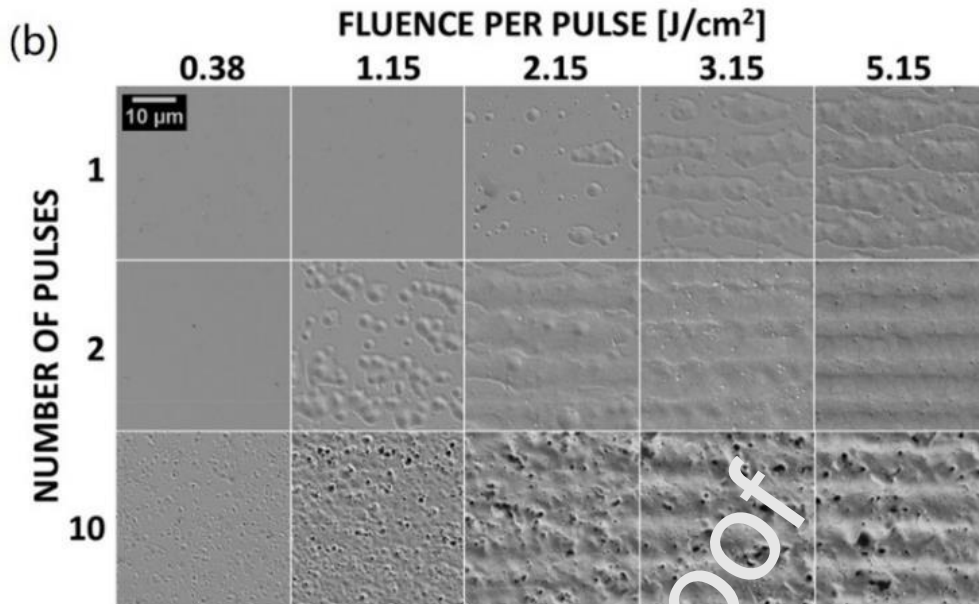


Fig. 4. SEM micrographs of zirconia (3Y-TZP) surfaces produced by laser texturing with: (a) FLB. Reproduced with permission from [61]. Copyright © 2019 Elsevier. (b) DLIP. Reproduced with permission from [123]. Copyright © 2016 The Academy of Dental Materials. Published by Elsevier Ltd.

#### 4.1.2 LIPSS

The formation mechanisms of LIPSS are more complex. Existing theories include the interaction of incident laser light with surface electromagnetic waves [129-131], particularly with the laser excited surface plasmon polaritons [132, 133], for low-spatial frequency LIPSS (LSFL) (spatial period  $\Lambda > \lambda/2$ ), and ultrafast laser induced material self-organization that is related to Marangoni effect for high-spatial frequency LIPSS (HSFL) (spatial period  $\Lambda < \lambda/2$ ) [134, 135]. Temporal beam shaping using an interferometer and time-resolved study by pump-probe experiment are two common approaches for investigating the LIPSS formation mechanisms [136-138].

Example of LSFL generated on 3Y-TZP is shown in Fig. 5 [139]. The spatial period is around 730 nm, which is comparable to the laser wavelength  $\lambda = 795$  nm. Fig. 5 (b) shows the cross-section of LSFL. The periodic ablation profile indicates the

non-uniform laser energy deposition due to the interaction of incident light with surface electromagnetic waves. The spatial period of LIPSS may also be influenced by laser pulse duration. Masayuki et al. [140] observed an increase of the spatial period from around 900 nm to 1050 nm when the pulse duration was increased from 77 fs to 327 fs with a Ti:Sapphire laser having a wavelength of 810 nm.

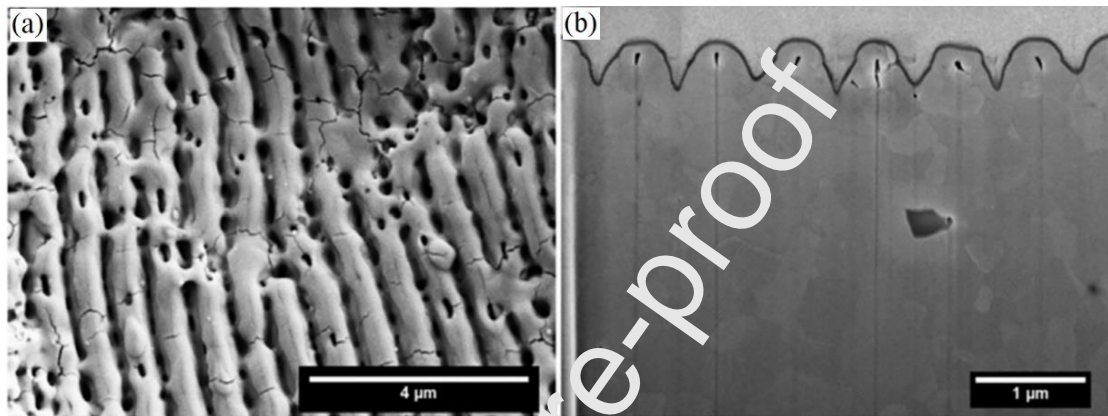


Fig. 5. (a) LSFL on 3Y-TZP by a Ti:Sapphire laser with a pulse duration of 120 fs and wavelength  $\lambda = 795$  nm; (b) cross section of the LSFL. Adapted with permission from [139]. Copyright © 2017 Elsevier Ltd.

## 4.2 Mechanical properties and microstructure

### 4.2.1 Thermal cracks and mechanical properties

Cracking is an intrinsic tendency of brittle materials under thermal shock loading during laser micromachining [73-75, 141, 142], which is influenced by the laser parameters and can be minimized through process optimization, such as increasing the scan speed while reducing the pulse energy to avoid excessive energy deposition per unit area [105]. It was shown that the cracking problem is more severe for long-pulsed laser processing than for short- and ultrashort-pulsed lasers [143]. A good compromise to achieve a high performance while maintaining a good processing efficiency is therefore to use a long pulse laser for rough machining so that a high material removal

rate can be achieved, and a short-pulsed laser to perform the post-processing (Fig. 6) [143].

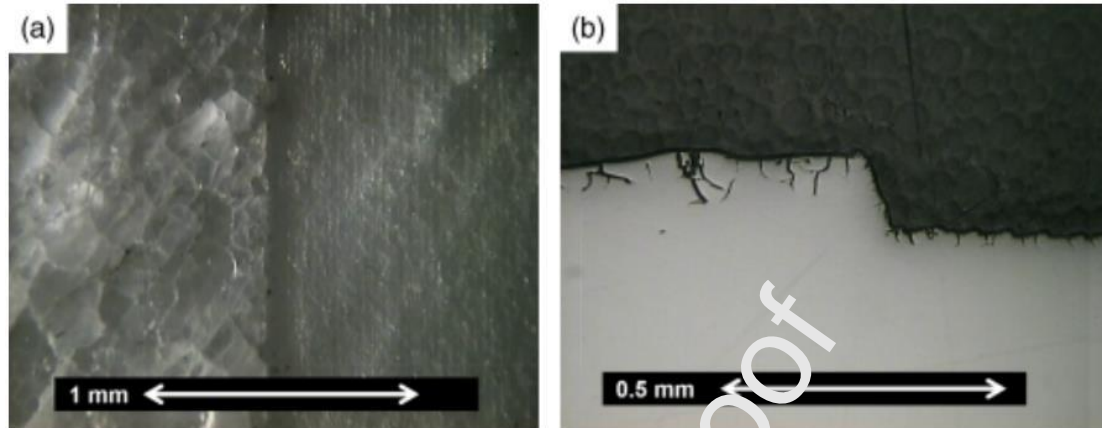


Fig. 6. Nanosecond laser postprocessing (on the right) of a ms-laser cut (on the left) 3Y-TZP surface: (a) top view; (b) cross-section. A smoother surface with smaller cracks was achieved with ns-laser postprocessing. Adapted with permission from [143]. Copyright © 2008 The American Ceramic Society.

In laser surface texturing where only a small amount of material is removed, the heat affected zone is confined to a thin layer at the top of the material surface (Fig. 7 (a) and (c)) [144]. The thermal cracks that can be formed are very small, normally limited to a few micrometers in depth (Fig. 7 (b)), and will not extend into the bulk. It is claimed that the mechanical properties of the bulk material will not much be influenced by these small cracks [144-146]. However, due to the relevant research studies are very limited, the influence of microcracks on mechanical properties needs to be further examined. Besides, in the aforementioned research, only static load condition was considered. Since the fatigue property of a material is very sensitive to its pre-existing defects, the influence of microcracks on the fatigue behavior of the laser textured material should not be overlooked.



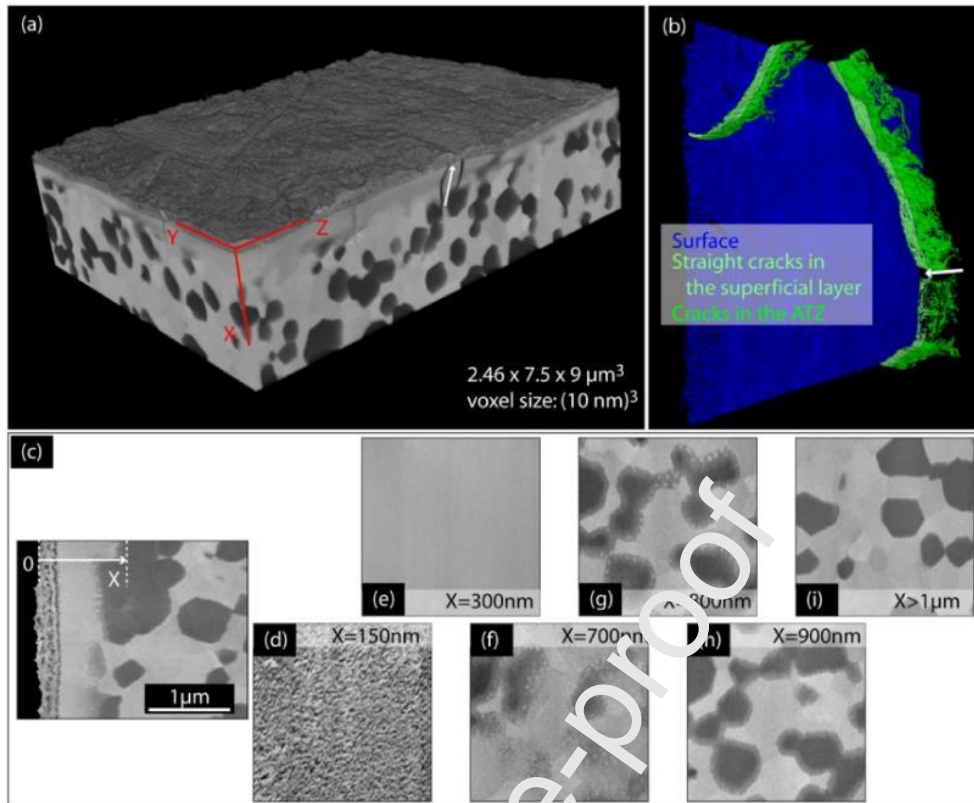


Fig. 7. (a) 3D FIB reconstruction of the sub-surface of a laser textured ATZ surface; (b) crack network extracted from (a) (the arrows in (a) and (b) point to the same location); (c) cross section extracted from (a); (d)-(h) sections parallel to the surface (orthogonal to (c)), showing the evolution of the different phases with depth; the sections cover the depth indicated by the 2 dashed lines in (c). Zirconia grains appear in white, alumina in grey. Reproduced with permission from [144]. Copyright © 2020 Elsevier Ltd.

As mentioned in the previous section, the depth of the textures produced by DLIP is relatively small. The influence of the textures on the total area of the cross-section of the material can be neglected. However, it can still influence the mechanical strength of the bulk material. Roitero et al. [147] reported a minor decrease of the mechanical properties in terms of biaxial strength and hardness of the laser surface treated 3Y-TZP (Fig. 8). They attributed the reduction of the mechanical properties to the pre-existing defects close to the surface, which were enlarged due to the laser irradiation, rather than to the laser affected layer, which was too small, less than 1  $\mu\text{m}$  in thickness, to be able to affect the bulk mechanical properties. A contradictory result was reported by Daniel et

al. [148], who claimed a significant improvement of the flexural strength up to 50% after DLIP of 8Y-FSZ and attributed this behavior to laser generated high compressive stress together with grain refinement on the surface of the material. However, these results may not be directly comparable, since neither the composition and microstructure of the materials, nor the laser parameters, which were used in these experiments were identical.

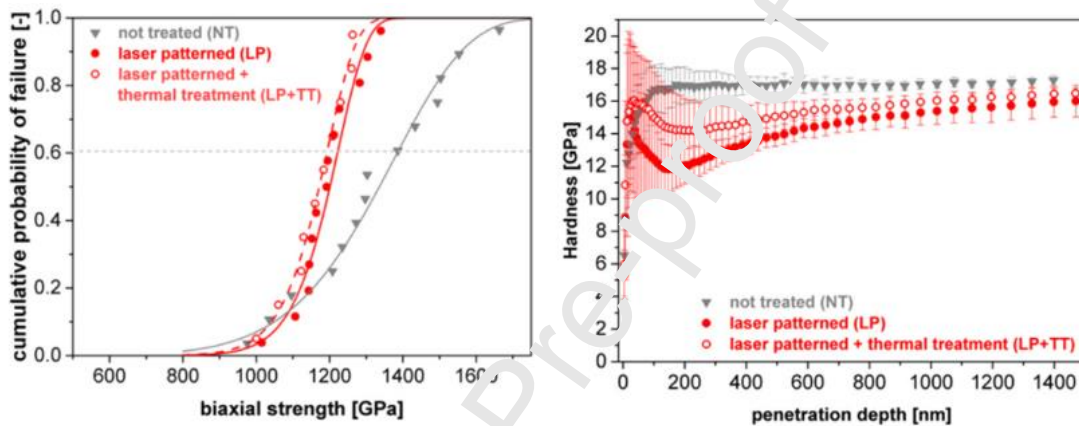


Fig. 8. Weibull distributions and nanoindentation tests results of not treated (NT, grey triangles) and laser patterned before (LP, hollow red circles) and after thermal treatment (LP+TT, red circles) 8Y-TZP samples. Reproduced with permission from [147]. Copyright © 2018 Elsevier Ltd.

For laser surface texturing with FLB, the laser ablation depth can be much larger than that produced by DLIP. The mechanical properties of materials are expected to be influenced more by FLB processing than DLIP. Several research works [61, 149] reported a decrease in flexural strength for FLB laser textured samples, and there is a positive correlation between the reduction in flexural strength and the laser ablation depth (Fig. 9). A possible explanation is that the highly roughened surface with deep features can provide many stress concentration points upon loading; therefore, crack initiation and propagation will be easier compared to a smoother surface. As a result, the flexural strength is lowered after laser processing. This suggests that in designing

surface textures for real applications, especially with a large feature depth, the influence of those textures on the mechanical properties of the products needs to be taken into account.

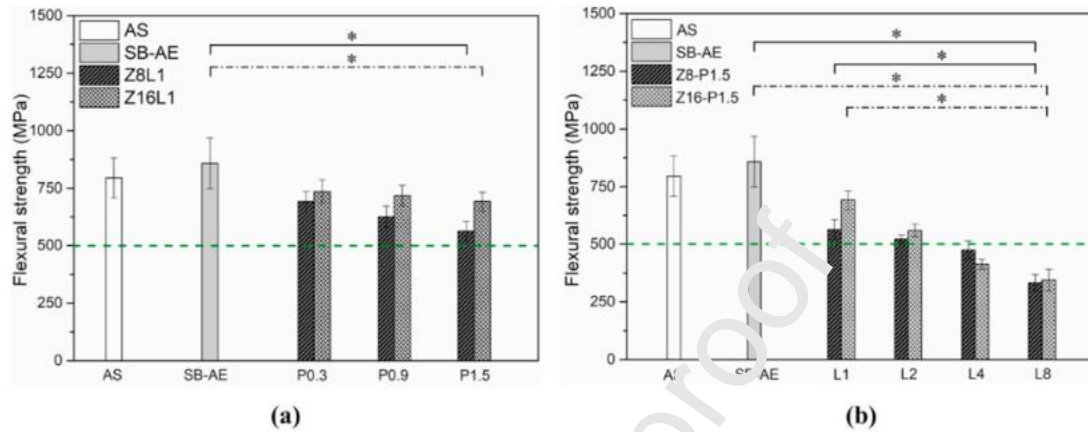


Fig. 9. Average flexural strength data for both laser strategies (Z8 and Z16, the SEM images of the textures produced with different laser strategies are shown in Fig. 4), as a function of (a) laser power (laser passages: L1), and (b) number of laser passages (laser power: P1.5). The asterisk (\*) indicates statistically significant differences ( $p < 0.05$ ). Reproduced with permission from [61]. Copyright © 2019 Elsevier B.V.

#### 4.2.2 LIPT and LTD

Besides the topography modification, laser surface texturing can also lead to local material property changes such as formation of a recast layer, grain refinement, micro-crack formation, introduction of residual stresses, and also LIPT. Even though these alterations might not immediately reduce the mechanical strength of the bulk material, they might influence the long-term stability, especially LTD, of the material and therefore should not be overlooked.

Gremillard et al. [144] tested the hydrothermal aging behavior of 20 wt% ATZ after long-pulsed laser (pulse duration 0.4  $\mu$ s) surface treatment. They found that the laser treatment had no significant influence on aging at high temperature (above 100°C), while the laser treated materials (LE2 and LE3) showed a slightly faster aging rate at



body temperature (37°C) compared to as received (AR) and sintered after laser treated (LE1) materials (Fig. 10). They concluded, however, that the hydrothermal aging behavior of ATZ was not much influenced by laser treatment.

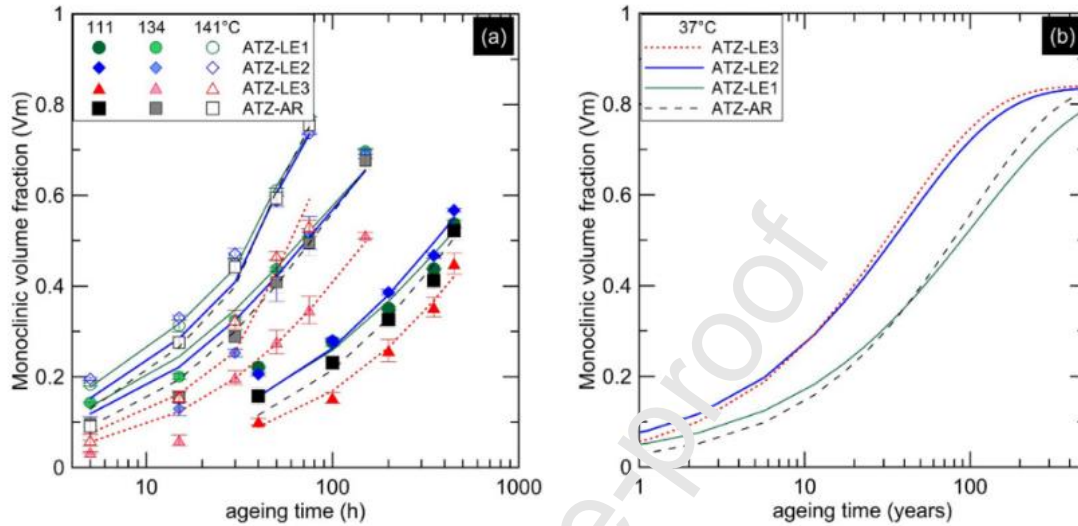


Fig. 10. Aging kinetics of ATZ: (a) measured at 111, 134 and 141°C and (b) extrapolated at 37°C. ATZ-AR: as-received (sintered), ATZ-LE1: sintered after laser treatment, ATZ-LE2 and ATZ-LE3: laser treatment with varying scan speed of 400 mm/s and 50 mm/s after sintering, respectively. Reproduced with permission from [144]. Copyright © 2020 Elsevier Ltd.

Silva et al. compared the phase transformation and LTD of 3Y-TZP subjected to Nd:YAG nanosecond laser surface treatment and sandblasting followed by acid etching [61, 149, 150]. They reported that the monoclinic content after laser surface treatment was lower than after sandblasting. The aging rate after laser treatment, even though higher than for pristine material, was also lower than after sandblasting and acid etching. A recent study using a femtosecond laser for the surface treatment reported a similar result [151]. Mona et al. [117] reported a significant reduction of the bending moment, from 4530 to 3970 Nmm, of laser grooved commercial 3Y-TZP implants (Z-systems<sup>®</sup>, Oensingen, Switzerland) after artificial aging.

An in-depth analysis of the LIPT and LTD behaviour of 3Y-TZP after nanosecond laser DLIP and the impact of an additional thermal treatment was performed by Roitero et al. [145, 146]. The LTD kinetics at 131°C are shown in Fig. 11, indicating that the laser treated material was more susceptible to LTD but with a lower aging rate than the untreated material. After annealing of the laser treated material, with the aim of reversing  $m\text{-ZrO}_2$  to  $t\text{-ZrO}_2$  as well as releasing residual stresses, aging initiation was delayed compared to the pristine material. The explanation, according to the authors, is:

- 1) Laser treatment will induce  $t \rightarrow m$  transformation, increasing the  $m\text{-ZrO}_2$  after laser treatment compared to the pristine material and resulting in an overall higher degree of LTD.
- 2) Laser treatment can introduce compressive residual stress, due to the presence of monoclinic twins, which could hinder the LTD process, leading to a lower aging rate.
- 3) Annealing after laser treatment can retard the initiation of  $m\text{-ZrO}_2$  due to the existence of a textured (ferroelastic domains) fine grained  $t\text{-ZrO}_2$  surface, but it will not reduce the aging rate.

Therefore, they suggested that even though laser treatment of 3Y-TZP could decrease their resistance to LTD, this could be remedied by an annealing treatment at 1200°C for 1 h afterwards. Some other studies also reported a beneficial effect of heat treatment after laser surface texturing on the improvement of flexural strength and suppression of LTD of 3Y-TZP [149, 150].

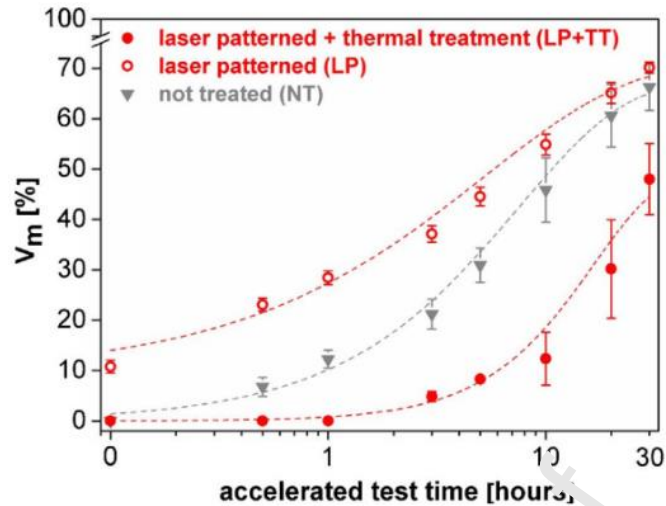


Fig. 11. Kinetics of LTD in vapor at 131°C. Evolution of monoclinic volume fraction with time of accelerated test of not treated (NT, grey triangles), laser patterned (LP, hollow red circles) and laser patterned and thermal treated (LP+TT, filled red circles) 3Y-TZP. Reproduced with permission from [145]. Copyright © 2017 Elsevier Ltd.

### 4.3 Wettability

Wettability is influenced by both surface topography and surface free energy. According to Young's equation [152], a higher surface free energy of a material indicates a smaller water contact angle. Zirconia-based ceramics, which are held together by a mixed ionic-covalent bonding, have a high surface free energy, and normally they exhibit a hydrophilic nature [153]. In contrast, materials that are mainly composed of van der Waals-type bonding, such as polymers and molecular crystals, have a hydrophobic tendency with a lower surface free energy [153].

The well-known Wenzel model [154] predicts that the wetting properties will be amplified by surface roughness, which means a hydrophilic surface will become more hydrophilic and a hydrophobic one will become more hydrophobic when the surface roughness is increased. This behavior was well demonstrated on 3Y-TZP by Moura et al. [150], who reported that the water contact angle (WCA) was reduced from  $46.9 \pm 5^\circ$  to

$36.4 \pm 1^\circ$  before and after laser surface texturing. Similar results were also obtained by Faria et al. [61] except that the exact WCA values were different, with  $21.3 \pm 9^\circ$  for a smooth surface and ranged from 0 to  $13.2^\circ$  after laser surface texturing under different laser processing parameters.

Lawrence et al. [155-158] investigated the wettability of Mg-PSZ subjected to a laser surface treatment with a defocused  $\text{CO}_2$  laser beam. Instead of creating certain surface textures by material removal, the material surface mainly underwent a melting and resolidification process without drastic surface topography change. They found that the wettability of laser treated surfaces was also reduced and attributed the enhancement of the hydrophilicity mainly to the increase in surface energy due to a change in the material microstructure. Surface oxygen might also influence the wetting property to some degree, but surface topography did not play an important role.

A more recent work [159] using a high pressure nitrogen gas assisted  $\text{CO}_2$  laser surface treatment of 3Y-TZP showed different results that cannot be explained by the Wenzel model. The author reported that the initial hydrophilic surface with a WCA of  $51.1 \pm 5^\circ$  turned hydrophobic with a WCA of  $121.4 \pm 5^\circ$  after laser treatment. According to the authors, there were two reasons that were responsible for this seemingly unusual behavior. First, the surface free energy after laser treatment was reduced due to the formation of ZrN due to the nitrogen environment during the laser surface treatment process. Second, the surface layer became porous with micro-cavity formation that could trap air bubbles after laser treatment and turned the droplet from a Wenzel state to a Cassie dominated state. Therefore, the Wenzel model failed to describe this situation

and the Cassie–Baxter equation [160] should be adopted. Fig. 12 shows the schematics of the three wetting models.

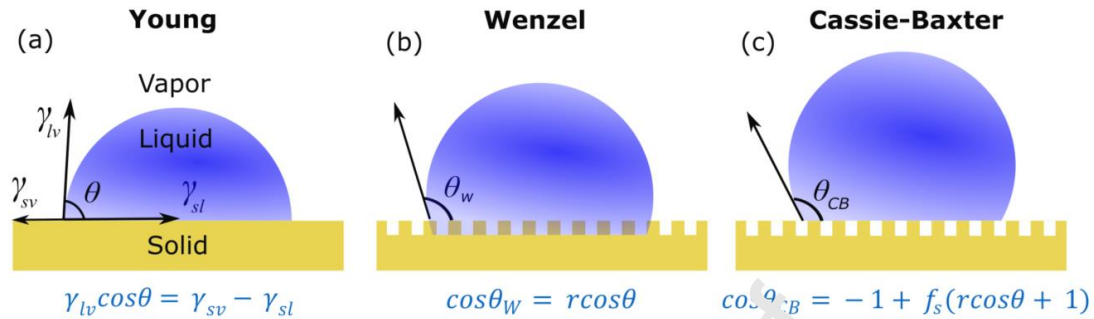


Fig. 12. Wetting models of (a) Young's model, (b) Wenzel's model,  $r$  is the ratio of the true surface area over the apparent one, and (c) Cassie–Baxter's model,  $f_s$  is the fraction of the solid area on the contact area.

Another research by Ji et al. [161] also realized the hydrophilic to hydrophobic transition by specially designed hierarchical micro-grooves machined by a picosecond laser rather than relying on randomly formed porous surface structures. They achieved WCAs ranging from  $< 60^\circ$  to  $> 120^\circ$  for different groove settings, as illustrated in Fig. 13. This suggests that it is possible to tune the wettability of the material surface in a more deterministic manner and also to a wider range than merely “amplifying” the wettability by solely modifying the surface topography without changing its surface chemistry. This might be useful for dental applications where a hydrophilic implant surface is required for better osseointegration, whereas a hydrophobic abutment surface is preferred to prevent bacterial adhesion. Nevertheless, the introduction of hydrophobicity by texturing is at the cost of increasing the surface roughness, which is shown to have a negative effect on preventing bacterial adhesion [162]. Therefore, the effectiveness of this concept is uncertain and needs to be further evaluated.

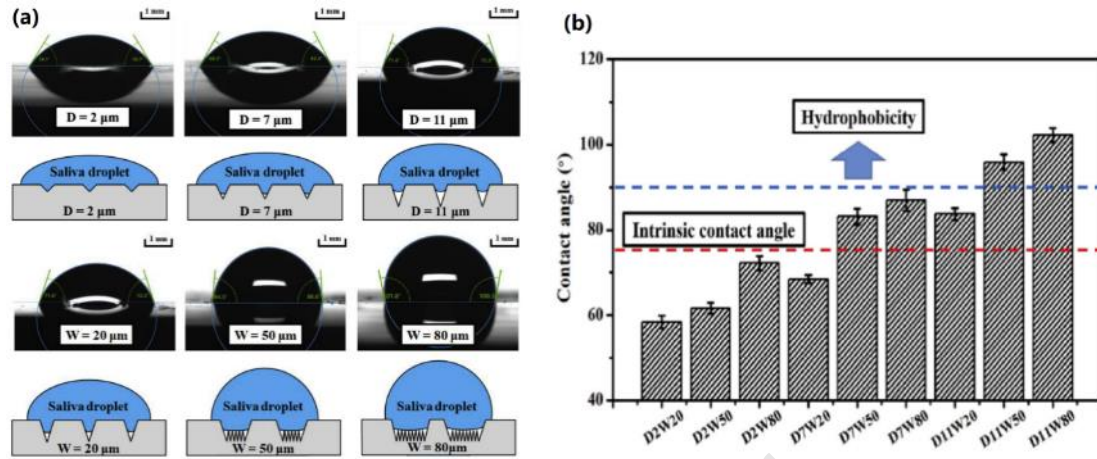


Fig. 13. The variation of wettability of laser textured surface with different groove widths: (a) CCD camera captured droplet photographs and the corresponding schematics; (b) the evolution of obtained contact angle with different surface textures. Adapted with permission from [161]. Copyright © 2019 Elsevier Ltd and Techna Group S.r.l.

In addition to surface topography modification, changing the surface chemistry and concomitant surface free energy, will also lead to a change in surface wettability. A common method to make the surface of zirconia-based ceramics hydrophobic is the silanization process [163-165]. The mechanism of silanization is to cover the surface with organofunctional groups which can reduce the surface free energy and therefore enhance the surface hydrophobicity [166]. Superhydrophobic (WCA > 150°) surfaces can be generated on zirconia-based ceramics by silanization after laser surface texturing with optimized surface topographies [164, 165].

It is a common phenomenon that the surface wettability may change with time due to the wetting state transition from a Cassie to a Wenzel state [167] or due to the surface free energy change caused by contamination [168]. This phenomenon was also reported for zirconia-based ceramics by Pu et al. [163], who showed that an initial hydrophilic surface produced by laser surface texturing gradually transformed to a hydrophobic one after several days of exposing to ambient air condition. Ultraviolet (UV) light radiation

is commonly used to remove contaminations, such as hydrocarbons from titanium dental implants, and hence to reactivate their biological activity [169-172]. This process is known as photo-functionalization [173], which can also be used to treat zirconia-based ceramics. Plenty of research has reported that after UV light irradiation, zirconia surfaces regained hydrophilicity and showed a better bioactivity, in terms of improved cell attachment and proliferation, or an enhanced osseointegration indicated by a larger bone-implant contact and bone volume [174-176].

## **5. Functionality of laser textured surfaces**

### ***5.1 Osseointegration of implants***

Osseointegration of an implant is considered to be correlated with its surface wettability. In general, a hydrophilic surface tends to enhance the initial cell adhesion, proliferation, and bone mineralization, and therefore shows a better response in terms of osseointegration than a hydrophobic one [179-181]. The influence of surface wettability on the interaction with bone cells is illustrated in Fig. 14 [182]. A comprehensive review about the impact of implant surface wettability on biological response can be found in literature [182, 183], and the influence of multiscale surface roughness on cell behavior was also reviewed elsewhere [184-186].



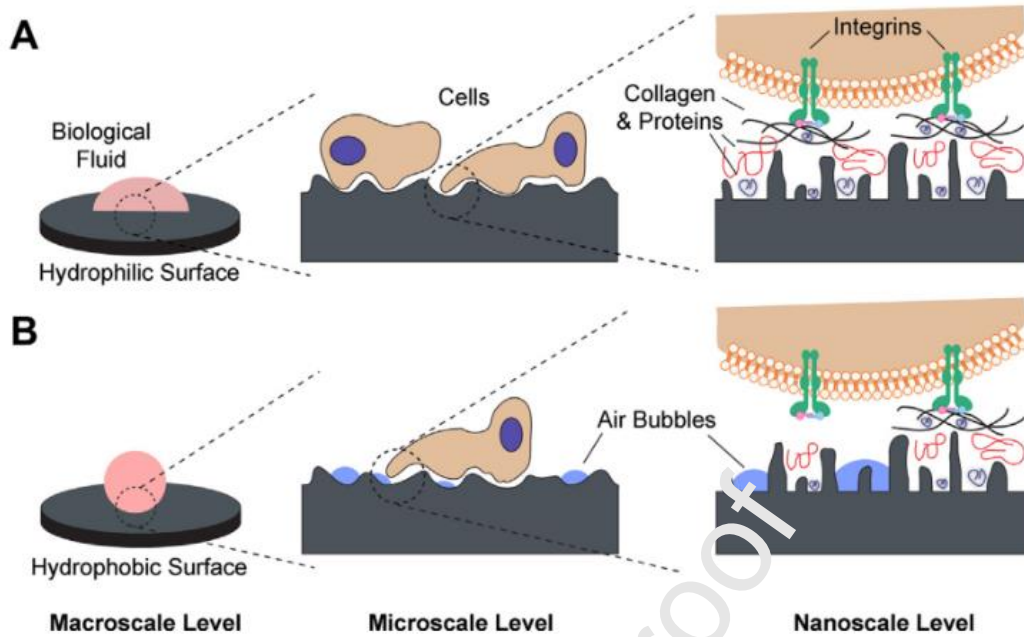


Fig. 14. Schematic of the cell and substrate interactions with (A) hydrophilic and (B) hydrophobic surfaces at different length scales. (A) Biological fluids prefer to spread at a hydrophilic surface, providing more area for protein adsorption and interaction with cell receptors. (B) A hydrophobic surface shows limited fluid spreading. Air bubbles can be trapped between biological fluids and substrate, resulting in reduced contact area between cell and surface, and therefore in less protein adsorption. Reproduced with permission from [132]. Copyright © 2014 Acta Materialia Inc. Published by Elsevier Ltd.

### 5.1.1 *In vitro*

It is well known that the surface topography of implants can also influence their biological response through modulating cell behaviour at the tissue-implant interface [187, 188]. By designing regularly patterned surfaces, directional cell alignment, migration, and proliferation can be achieved [186, 189]. Cell responses to laser textured zirconia-based ceramics with different patterns, such as grooves [60, 190, 191], pits [139], and grids [60, 192, 193], have been reported. Fig. 15 shows representative SEM images of mesenchymal stem cell morphologies that were cultured on a laser textured 20 wt% ATZ surface with regularly spaced micro-grooves [190]. For the laser textured



surface, the cells tended to arrange along the groove direction, while they appeared to be randomly distributed on the smooth surface.

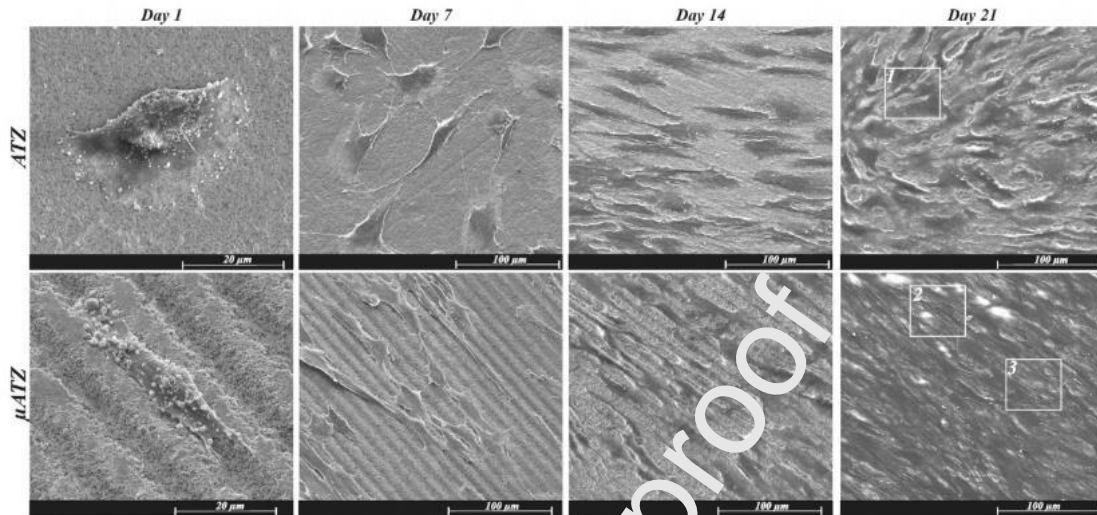


Fig. 15. SEM images of the hMSC morphology adhering to an ATZ and laser grooved ATZ after 1, 7, 14 and 21 days of culture. Reproduced with permission from [190]. Copyright © 2017 Elsevier B.V.

In addition to guiding cell growth, metabolic activity and osteogenic differentiation was also reported to be enhanced on ordered surface patterns [60, 120, 121, 190]. This is supposed to be clinically beneficial for reducing implant healing time and accelerating bone formation [194].

### 5.1.2 *In vivo*

Most of the *in vivo* studies using animal models found some benefits of laser surface texturing of zirconia implants on the improvement of osseointegration [119, 195-198]. Delgado Ruiz et al. [119, 198] compared the performance of laser micro-grooved 3Y-TZP dental implants with sandblasted zirconia implants and acid-etched titanium implants. They found that the presence of micro-grooves increased the number of transverse collagen fibers, and the blood vessels and bone cells were found to be able to

penetrate into the microgrooves. As a result, the bone-to-implant contact (BIC) and bone density were increased for micro-grooved zirconia implants.

Yasuno et al. [196] investigated the influence of micro-groove direction and size on osseointegration and found that 3Y-TZP implants with larger groove depth and width showed better osseointegration. In addition, implants with grooves that were vertical to the thread direction were found to perform better than horizontal ones. The BIC values were  $64.9 \pm 5.3\%$  and  $49.0 \pm 2.8\%$  for vertical and horizontal grooves with a large depth, and they were  $39.8 \pm 12.1\%$  and  $17.5 \pm 11\%$  for vertical and horizontal grooves with a small depth, respectively.

Masatsugu et al. [195] evaluated the influence of laser texturing on osseointegration of implants with different material compositions. In this research, Y-TZP and Ce-TZP/ $\text{Al}_2\text{O}_3$  implants were laser grooved by a nanosecond-pulsed laser and implanted into a rat femur. For Y-TZP implants, the laser grooved implants showed an increased BIC compared to the control group, which were sandblasted followed by acid etching. Regarding the Ce-TZP/ $\text{Al}_2\text{O}_3$  implants, the laser grooved implants performed worse than the control group with a lower BIC. They concluded that in addition to surface topography, surface chemistry may also play an important role in influencing bone formation around zirconia implants. This is reasonable since osseointegration is closely related to the wettability of the implants, which is influenced by both surface topography and surface chemistry, as discussed in previous section.

## ***5.2 Bacterial adhesion and Soft tissue integration of abutments***

### **5.2.1 Bacterial adhesion**

Peri-implant inflammation, which is caused by subgingival biofilm formation, is a major factor responsible for alveolar bone loss and may eventually lead to implant failure [199, 200]. Reducing bacterial adhesion or enhancing soft tissue attachment to the abutment are two potential approaches to prevent biofilm formation [28].

Surface roughness, surface free energy, and material composition are the three main factors that can influence the initial bacterial adhesion on abutment surfaces [162]. It is generally considered that there is a threshold value of surface roughness of 0.2  $\mu\text{m}$ , above which bacterial adhesion and biofilm formation will increase due to increased surface area [201, 202]. In terms of surface free energy, a low free energy surface, with a surface energy between 20 and 50 mN/m, showed the lowest bacterial adhesion [203]. From the material perspective, zirconia abutments were shown to have less risk of bacterial adhesion compared to their titanium counterparts [28].

Surface wettability can also influence the bacterial adhesion behavior. Many research studies showed that bacteria prefer to adhere onto a surface with moderate wettability [204-206]. Superhydrophobic and superhydrophilic surfaces tend to inhibit bacterial adhesion [207, 208]. However, the relationship between surface wettability and bacterial adhesion is complex; it is influenced by many factors such as bacteria type, surface charge, surface topography, and chemical composition, and contradictory results are often reported [209, 210].

In principle, by increasing surface roughness, it is possible to induce a higher degree of hydrophobicity as has been discussed in a previous section. However, since surface roughness and hydrophobicity exert an opposite influence on bacterial adhesion, it is yet to be proven that laser texturing induced hydrophobicity is beneficial to reduce bacterial adhesion. Besides the overall surface properties, including surface roughness and hydrophobicity which do not provide comprehensive information about the microscale characteristic of the surface, the relative length scale between the surface texture and bacterial size is also considered to play an important role on surface anti-bacterial properties. It is reported that LIPSS, which have comparable or even smaller feature size than bacteria, could effectively reduce the bacterial adhesion and prevent biofilm formation on metal surfaces [63, 211]. Since LIPSS can also be created on zirconia-based ceramic surfaces with ultrafast lasers, it might be promising to reduce bacterial adhesion by ultrafast laser processing.

Abutment surface modification through other methods is also possible, for example by using coatings of antibacterial polymers and polydopamine [212, 213]. Recently, Madeira et al. [214] presented a hybrid process that combines laser surface texturing with powder deposition and subsequent laser sintering to incorporate gold nanoparticles and silver microparticles into the 3Y-TZP surface and to form an antibacterial layer. They expected that the slow release of gold and silver particles would act as bactericide. Fig. 16 shows a SEM image of the antibacterial layer, whereas Fig. 17 (a) shows a schematic of the antibacterial design solution.

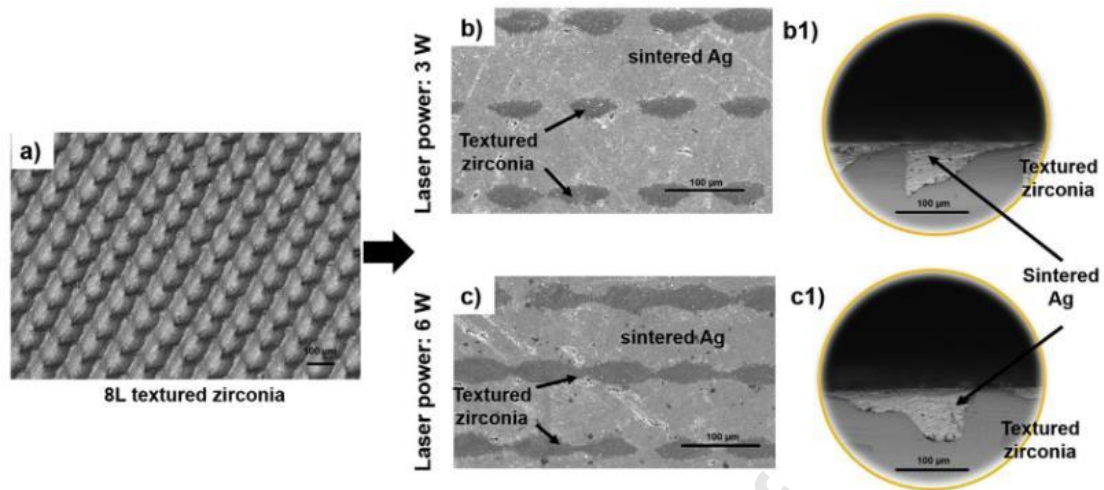


Fig. 16. SEM images of (a) zirconia texture; (b) and (c) after Ag sintering; (b1) and (c1) cross-section views. Reproduced with permission from [214]. Copyright © 2019 Elsevier Ltd and Techna Group S.r.l.

### 5.2.2 Soft tissue integration

An alternative way to prevent biofilm formation is to enhance the soft tissue attachment to the abutment, as illustrated in Fig. 17 (o). This can be achieved through modification of the abutment surface characteristics, including surface topography, surface free energy, and surface chemistry [201], to promote adhesion, proliferation, and differentiation of human gingival fibroblasts, which have been identified as the main cells of peri-implant soft tissues [215].

In terms of surface topography modification, microgrooved surfaces by laser texturing have shown an effective improvement of soft tissue attachment to the abutment surface and were widely reported for application in titanium implants [216-219]. However, research on the performance of laser microgrooved zirconia abutment surfaces, especially *in vivo*, is very limited.

A recent study [220] by Madeira et al. investigated the bond strength between artificial soft tissue and laser micro-grooved 3Y-TZP surfaces. They found that the presence of

micro-grooves could increase the bond strength between artificial soft tissue and the zirconia disks. However, the static bond strength test may not be able to represent the real dynamic behaviour of the interaction between human gingival fibroblasts and the zirconia abutment surface, and therefore further *in vivo* evaluation is necessary to reach a conclusion.

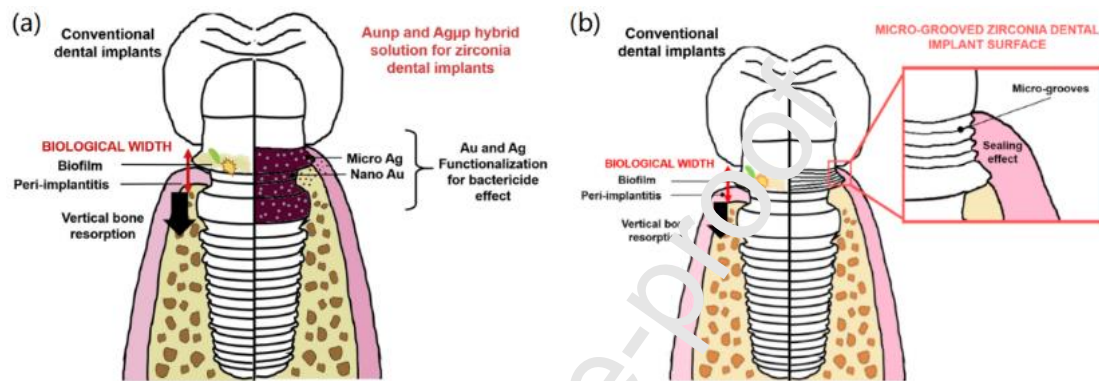


Fig. 17. Schematic for a (a) antibacterial design solution. Reproduced with permission from [214]. Copyright © 2019 Elsevier Ltd and Techna Group S.r.l. (b) soft tissue attachment enhancement design solution. Reproduced with permission from [220]. Copyright © 2020 Elsevier Ltd and Techna Group S.r.l.

### 5.3 Bonding of restorations

Bonding of zirconia restorations to tooth substrate using resin-based composite cements, such as bonding a zirconia crown to dentin, is often required in dental practices. A reliable bond of composite cement to zirconia ceramics is therefore of great importance for the long-term survival of the prosthesis [221]. Unlike silica-based ceramics, which can be hydrofluoric acid etched followed by silanization to achieve a durable bond, zirconia-based ceramics are chemically inert materials and are difficult to be acid etched [222]. Alternative solutions often rely on the increase of surface roughness to allow for micromechanical interlocking, for example through airborne

particle abrasion (ABA), also called sandblasting, with  $\text{Al}_2\text{O}_3$  particles or by laser surface texturing [223, 224].

The most commonly used lasers for surface treatment of zirconia ceramics for improving bond strength include  $\text{CO}_2$ , Er:YAG, Er,Cr:YSGG, and Nd:YAG lasers [225]. These lasers are normally designed for surgical purposes in dentistry, and therefore sometimes called “dental lasers” with the following common features: long pulse duration, typically longer than several hundred microseconds; low laser power, in the order of several watts; and relatively long wavelength, in the infrared range for the purpose of better absorption by human tissue. However, these lasers are not well suited for surface texturing of zirconia-based ceramics, which require a higher laser power for effective material removal as well as a shorter pulse duration for minimizing heat affected zones.

With long pulse duration and relatively low laser power, hardly any material is removed by laser ablation. Instead, the zirconia ceramics are mainly subjected to melting and resolidification, during which a drastic change in surface roughness, especially micro- and nanoscale roughness, is often not achieved. Sometimes there is even a polishing effect with long pulse laser treatments of originally rough surfaces. This makes the results of laser surface treatment of zirconia ceramics, with the aim of improving bond strength, highly dependent on the laser processing parameters as well as the original surface conditions of the material to be processed. Therefore, even though a considerable amount of research showed some positive effects towards an increased bond strength after laser surface treatment using different dental lasers, including  $\text{CO}_2$  laser [226-236], Er:YAG laser [226, 232, 236-238], Er,Cr:YSGG laser [233, 239, 240],



and Nd:YAG laser [234, 237, 239, 241-244], conflicting results are frequently reported [245-254].

High power lasers with much shorter pulse duration, such as nano-, pico- and femtosecond lasers, are recently attracting increasing attention for surface treatment of zirconia ceramics in order to improve their bonding receptiveness for composite cements. The advantages of a short over a longer pulsed laser, as discussed in the previous section, are the much higher peak power and reduced heat affected zone. Microscale material removal with minimized collateral damage at the periphery of the laser spot is possible, which makes surface roughening of zirconia ceramics at the microscale effective. Therefore, enhanced bond strength of composite cements to laser treated zirconia can be realized.

Kara et al. [255] compared the influence of different laser types on surface roughening and bond strength enhancement for two kinds of zirconia ceramics (Zirkonzahn and Zirkonzahn Prettau, Zirkonzahn Worldwide). They reported that a femtosecond laser showed a clear advantage over Nd:YAG and Er:YAG lasers in terms of increasing surface roughness and bond strength. For femtosecond laser treated samples, the average surface roughness and bond strength were around 1  $\mu\text{m}$  and 52 MPa, respectively, with no clear difference between the two ceramic materials; surface roughness ranged from 0.46 to 0.78  $\mu\text{m}$  and bond strength from 40 to 43 MPa for the other two types of laser treated samples.

Some studies [256-258] compared the performance of a femtosecond laser treatment with other surface modification methods. Prieto et al. [256] reported that femtosecond laser treated Y-TZP revealed the best shear bond strength (10.8 MPa) among all the



groups, which signified its superiority over ABA (8.1 MPa) and tribochemical silica coating (TSC) (9.5 MPa) methods. Similar results were reported by Ruja et al. [257]. Besides, they found that an ultrashort pulse laser treatment did not induce  $t \rightarrow m$  phase transformation in Y-TZP, while phase transformation was observed for ABA and TSC methods. Although these researches suggested femtosecond laser surface treatment performed better than ABA and TSC in terms of improving bond strength, no significant difference was found between these three methods in the study of García-Sanz et al. [258]. Since the principle for enhancing bond strength is surface roughening to allow for micromechanical interlocking, the selection of the right laser processing parameters, which directly determines the produced surface topography and microscale surface roughness, will be critical for achieving desirable outcomes.

Several research studies investigated the influence of laser processing parameters as well as the generated surface topographies on bond strength. Yucel et al. and Akpinar et al. reported that texturing by an inclined laser beam showed a better result in terms of bond strength than a vertical beam [259, 260]. A smaller groove distance and a higher laser power led to a higher bond strength [261]. A projection surface was shown to be superior to a recessed one [262].

Several papers also reported comparable results to femtosecond laser texturing using nanosecond or sub-nanosecond lasers, which are much cheaper than femtosecond lasers. Akay et al. [263] used a sub-nanosecond UV laser to process Y-TZP ceramic; different surface textures were produced, including holes, grooves, and grids. All textured samples showed a significantly higher flexural bond strength than non-treated samples.

Iwaguro et al. [264] investigated the bonding properties of a nanosecond laser textured microslit surface of two different zirconia ceramics. They reported that laser texturing was effective in enhancing the bond strength of composite cements to 3Y-TZP, while it did not function well for Ce-TZP/Al<sub>2</sub>O<sub>3</sub>. In addition, laser texturing did not show statistical benefits for bonding veneering porcelain to both of these two zirconia ceramics. In a most recent publication of the same group [265], Shimoe et al. investigated the influence of the microslit width on the bond strength of acrylic resin to the same two zirconia ceramics. They reported that the bond strength of the laser textured groups was significantly higher than that of the ABA group for both 3Y-TZP and Ce-TZP/Al<sub>2</sub>O<sub>3</sub>, while the microslit width did not have any influence on the bond strength. Henriques et al. [266] also investigated the bond strength of veneering porcelain to zirconia. They found that the bond strength to laser textured surfaces was significantly higher than that to the ABA treated surfaces, which is different from the results obtained by Iwaguro et al. [264]. The surface textures generated by a laser were hole arrays with different diameters. However, thermal cracks were found to occur on the sidewall of the holes, which may be harmful to the mechanical properties of the material. Therefore, Henriques et al. adopted an alternative way of laser surface texturing to overcome this problem [267], i.e. by texturing the green zirconia compact before sintering. The bond strength to zirconia was much larger after laser texturing and sintering than after sandblasting. Besides, laser textured surfaces followed by sintering and then sandblasting could further increase bond strength.

Besides early bond strength, durable adhesion of composite cements to zirconia ceramics is also crucial for the longevity of dental prostheses. Bond durability studies to laser textured zirconia ceramics are however scarce. In the case of surface treatment

with dental lasers, available data do not give much positive results [246, 252, 268]. Instead, the use of short- and ultrashort-pulsed lasers for zirconia surface texturing tends to result in a better performance than the existing methods employed in dentistry [257, 264, 265, 269]. Even though most reports show an appreciable reduction in bond strength after cyclic loading, at least comparable values to ABA zirconia can be guaranteed. However, due to the limited amount of published data, confirmation by further research is necessary.

Despite the fact that research efforts on laser texturing of zirconia ceramics to enhance bond strength are increasing, all of the currently available studies were conducted in the laboratory. To the best of the authors' knowledge there are no published *in vivo* studies available yet. A prerequisite to use lasers for surface treatment is that the shape of the surface to be treated should be as simple as possible, for example a flat or a cylindrical surface or at least a surface of known geometry. This is due to the necessity to be able to control the laser path during the laser surface texturing process as compared to the commonly used ABA and ICC methods, which are not sensitive to the direction the surfaces are processed. For laser surface texturing, in most cases, the laser beam direction should always be nearly parallel to the surface norm. However, this is difficult to fulfill if the prosthesis has a very complex geometry; therefore, uniform surface textures may not easily be achieved, which then compromises the effectiveness of the designed function. In this context, further research evaluating the effect of the laser beam incidence angle and defocusing during laser texturing will help to improve the laser process for complex shape applications.

## 6. Conclusions and outlook

Laser surface texturing is extensively explored in various areas for different applications, including tuning optical properties, tribological properties, wettability, and biological properties. In dentistry, laser surface texturing of titanium dental implants has long been studied and promising results in clinical trials have been shown. For zirconia dental implants, the use of laser surface texturing for improving functionality is still in the early stage of laboratory testing with limited *in vivo* studies available using animal models. Considering the distinct differences of the material properties of titanium and zirconia, which lead to different laser absorption mechanisms and material responses, many remaining questions need to be clarified before shifting the experiences gained on titanium to zirconia. These questions include:

- Thermal cracking is a common problem in laser processing of zirconia ceramics. How to suppress or avoid thermal cracking?
- What is the mechanism of laser induced  $t \rightarrow m$  phase transformation of zirconia ceramics? How will it influence the long-term stability of zirconia implants?
- How will the laser textured multiscale surface roughness change the wettability of the zirconia surface and influence its biological response?

In this review, the current status regarding the use of laser surface texturing of zirconia-based ceramics for dental implants, covering the above concerns, was examined. Some concluding remarks can be summarized as follows:

- 1) The laser absorption mechanism and brittle nature of zirconia-based ceramics suggest that a shorter pulsed laser, which can achieve a much higher laser

intensity together with a smaller heat affected zone, is preferred for surface texturing. Dental lasers normally have low laser power, long wavelength, and long pulse duration, and their effectiveness for texturing of zirconia-based ceramics is questionable.

- 2) Thermal cracks generated by laser texturing will reduce the mechanical strength of the bulk material and therefore should be taken into consideration when designing surface textures for certain functions. Thermal damage to the zirconia material surface can be minimized or eliminated by several approaches, such as optimizing the laser processing parameters, using shorter pulsed lasers, or applying heat treatments after laser surface texturing.
- 3) Most of the research suggested LPT is not severe in laser surface texturing of zirconia ceramics. However, the kinetics of LTD may change after laser processing, which could influence the long-term stability of the dental zirconia implants. Judicious heat treatments afterwards can eliminate the negative influence of laser processing on LTD.
- 4) Wettability of laser textured zirconia surface is influenced by both surface topography and surface free energy. The zirconia surface is intrinsically hydrophilic, and it will normally become more hydrophilic after surface roughening. However, with properly designed surface textures, it is possible to make the surface hydrophobic due to the wetting transition from a Wenzel to a Cassie state. An initial hydrophilic surface can also change to hydrophobic due to surface contamination, which is common during storage. Therefore, UV laser

irradiation can be applied to reactivate the biological activity of the zirconia implants before implantation.

- 5) Due to the only limited *in vivo* studies on the performance of laser surface textured zirconia implants, the real benefits of laser surface texturing on an improved osseointegration cannot be concluded yet.
- 6) Given that zirconia abutments are generally considered superior to titanium ones in the prevention of bacterial adhesion, there are possible ways for further improvement, such as reducing bacterial adhesion by surface alloying with antibacterial particles and enhancing soft tissue attachment by laser grooving.
- 7) Laser surface texturing for improving the bond strength between zirconia ceramics and composite cements is a promising technique. To this aim, short and ultrashort pulsed lasers, such as nano-, pico- and femtosecond lasers, are much better than dental lasers. Even though many positive results have been reported with dental laser surface treatments, contradictory results are common. The bond strength is also highly dependent on the topography of the laser textured surface, which should be designed carefully. The bond durability to laser textured surface seems better than for other common surface treatment methods. However, the available data are very limited and a concrete conclusion cannot be drawn.

In summary, the current literature search results already suggest that laser surface texturing can be beneficial for dental zirconia implants in several aspects, including improving their osseointegration, reducing bacterial adhesion on abutments, and enhancing the retention of zirconia restorations. Since the essence of laser texturing is

to enhance surface functions by the introduction of surface features with defined dimensions, the shape and the scale of the features are therefore of vital importance to the performance of the textured surfaces. For implants, the optimal shape and scale of the features should have some connection with the size of the human cells that have direct contact with the implant surface; regarding restorations, they are supposed to be influenced by the bond strength of the resin cements. However, systematic research on the influence of the shape and scale of the features on the performance of laser textured surfaces is still lacking, requiring further research and especially *in vivo* evaluation and clinical evidence.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Journal Pre-proof

**Highlights:**

- Short pulse lasers are preferred over longer pulse lasers in processing zirconia ceramics
- Thermal damage should be taken into account in laser texturing zirconia implants
- Heat treatment can eliminate the negative effect of laser induced phase transformation
- Laser texturing can modify wettability thus influencing osseointegration of implants
- Laser texturing of abutment and restoration for enhanced functionality are reviewed