

High-Precision Ultrashort-Pulsed Laser Machining of Dental Ceramic Implants

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Abstract

A novel approach for machining of cylindrical hard materials and arbitrary shapes is presented. Alumina-toughened zirconia dental implants with complex geometry are manufactured with femtosecond quasi-tangential laser ablation. This rapid prototyping approach for small-scale production decreases the development-time cycle tremendously and trumps conventional approaches. Moreover, a competitive parameter study for radial and tangential ablation with single and multi-pulse is presented. A process achieving an ablation rate of $1 \text{ mm}^3 \text{ min}^{-1}$ with a surface roughness R_a of $0.2 \mu\text{m}$ is introduced. The meta-stable tetragonal phase of the ceramic persists and is assessed via Raman spectroscopy. The small heat-affected zone is subsequently ablated with a radial laser process step. Hence, high-precision dental implants with a mean error of smaller $5 \mu\text{m}$ over the complete contour are shown.

Keywords: Dental Implant, Laser Manufacturing, ATZ Ceramic, Ultrashort Pulses, Raman Spectroscopy, Precision Machining

1. Introduction

Today, technical ceramics are used for a broad spectrum of applications. The high hardness, corrosion resistance, thermal stability and biocompatibility are some of the desired properties. Here, the use of ceramics for bio
5 applications is addressed in the context of dental implants. For many years

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these implants have been made out of metals like steel, titanium and alloys thereof [1]. However, corrosion and deterioration without wear enables titanium ions to diffuse, which possibly lead to inflammation [2]. Recent advances in material science make the creation of ceramic compounds with optimized physical properties possible [3]. These ceramics are often based on zirconia (ZrO_2) and alumina (Al_2O_3) with possible additives [4]. Especially, for dental application an alumina-toughened zirconia (ATZ) with additional yttria (Y_2O_3) is applicable. The degradation is minimal at body temperature condition [5, 6], inhibiting inflammation [7]. Moreover, this ceramic is electrically insulating and a poor thermal conductor and therefore well suited for bio applications. The characteristic mechanical features of ATZ ceramics are a high fatigue strength, a Young's modulus of 160 GPa, ultimate tensile strength of 2 GPa and hardness of 1400 Vickers.

Therefore, sintered ceramics are highly difficult to machine properly with conventional processes. The standard process chain for dental implants is to produce a diamond grinding wheel for the adjacent target geometry and grind the sintered workpiece. Hence, a change in the geometry requires a new grinding tool. The tool wear, even for diamond or Borazon tools, is high and the tool has to be conditioned on regular basis. Conditioning processes for ultrahard tools via laser ablation have been shown [8, 9]. However, the production of complete implants in the scope of rapid prototyping with ultrashort-pulsed laser ablation has hitherto not been investigated. Laser machining in general is attributed a high potential for application in various fields [10]. The limitations of the ultrashort-pulsed laser sources in the beginning were resolved and stable sources with high average power and repetition rate are available [11]. The main challenge at the moment is the lack of decent computer aided manufacturing (CAM) routines to achieve penetration in industry. In contrast to conventional manufacturing techniques, the principals of the ultrashort-pulsed ablation processes are still a matter of fundamental research. Especially, for insulators the well-established two-temperature model has to be expanded and more complex non-linear excitation modes for band gap materials implemented [12, 13]. Recently, some advances point to a correlation between the threshold and damage mechanism with different ablation phenomena [14]. Most models concerning ultrashort-pulsed ablation are implemented on a microscopic level. However, the prediction of the ablation behavior on multi-pulse ablation in a feasible timescale for macroscopic ablation is not viable.

Following, if the laser parameters for a certain material have been deter-

mined experimentally, the beam path and hatching can be computed. Commonly, laser processes are carried out with the incident beam orthogonal to the surface of the specimen. In case of single step cutting processes, the laser is steered on a $2D$ plane. If the strategy concerns more than one ablation layer, a $2.5D$ process with certain layer thickness is addressed. Prominent examples are cutting, milling and drilling. In case of ceramics these processes have been shown in literature over the last decades. More specifically, cutting of alumina with femtosecond-laser pulses and cutting speed up to $143 \mu\text{m s}^{-1}$ has been reported [15, 16]. Moreover, machining of yttria tetragonal zirconia polycrystalline ceramic with an ablation rate of up to 1.35 mm min^{-1} and a surface roughness of $R_a = 2.8 \mu\text{m}$ was shown [17]. In comparison to metals, the ablation characteristics of ceramics show a pronounced dependence in terms of heat-affected zone on the number of applied laser pulses per area [18]. The reported studies on orthogonal laser machining point directly to the problem in terms of surface quality and geometrical precision. A layered ablation process accumulates the inherent statistic deviations of the laser process over each layer and strongly depends on material inhomogeneity, which leads to an increased surface roughness in comparison to the pristine surface. Figure 1 shows the two strategies of orthogonal and tangential incidence angle. Ablation under grazing incidence has been proposed for dia-

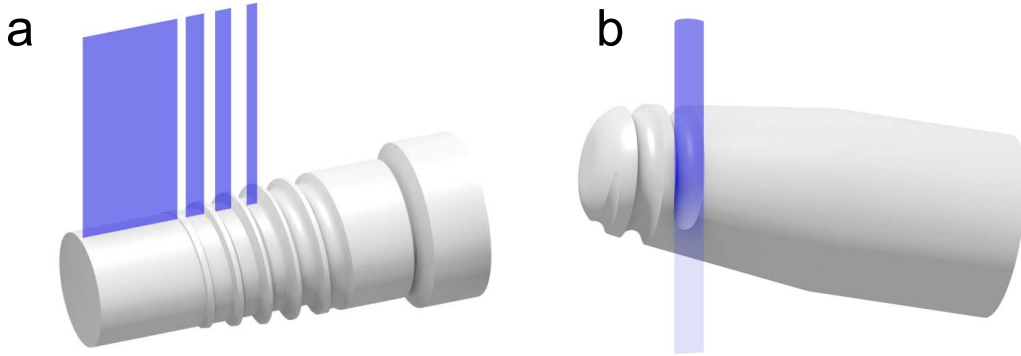


Figure 1: (a) A helical groove is ablated with a radial process triggering the Laser on the envelope. In contrast the groove geometry of quasi-tangential ablation tilts the workpiece into the slope (b).

mond polishing [19]. The laser is steered under oblique incidence $\theta_i > 75^\circ$ over the surface with a energy density slightly above the threshold. Hence, the surface roughness can be decreased and the process is self limiting. In

case of cylindrical workpieces the process is translated to quasi-tangential ablation conditions, shown in figure 1b. This has been successfully used for the manufacturing of ultrahard cutting tools with high precision [20].

70 To the authors best knowledge, complex 3D shapes have not been machined on sintered ceramics with quasi-tangential irradiation conditions. Recently, a CAM tool for quasi-tangential laser manufacturing has been deployed [21]. The complex hatch and path calculation for arbitrary shapes can be computed for synchronous 7-axis laser machining [22]. Moreover,
75 combined orthogonal and quasi-tangential processes can be implemented for optimized laser manufacturing.

2. Material and methods

2.1. Experimental Configuration

The ablation setup consisted of five high-precision axes and two optical
80 axes, as illustrated in figure 2. The femtosecond laser acted as source and was guided via modifying optics into the scanhead. A beam expander was used to adapt the beam diameter and alter the focal spot radius. Furthermore, wave plates allowed to control the polarization state and direction. The whole setup was built with controllers from Aerotech Inc. and controlled with Aerotech's A3200 software. All axes could be operated and
85 programmed synchronously to make combined motion of the mechanical and optical system possible. In case of seven-axis processing, programming the motion commands manually would be uttermost demanding. Consequently, a CAM tool set was developed and realized. Briefly, the CAD file can be
90 imported and with a prior experimentally attained parameter set the axes movement and laser hatches determined [21].

2.2. Material

A technical alumina-toughened ceramic was used throughout this study. The composition contained 76% ZrO_2 , 20% Al_2O_3 and 4% Y_2O_3 . Yttria is
95 added to stabilize the meta-stable tetragonal phase of zirconia. The tetragonal to monoclinic phase transition can be shifted to higher temperatures of about 1000°C. ATZ cylinders with 5 mm diameter were obtained from Metoxit. This compound is used specifically for bio application with high load subjected to wear. The radial parameter study was carried out on the
100 same material using a 100 mm diameter disc.

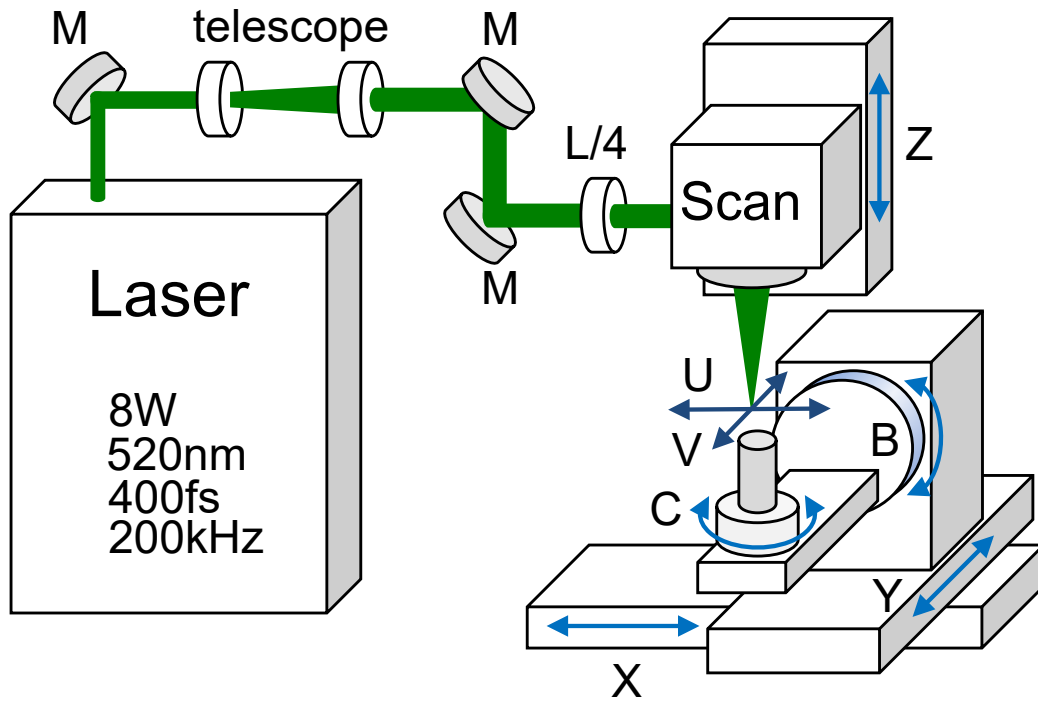


Figure 2: Experimental setup for synchronous 7-axis laser ablation facilitating a ultrashort-pulsed laser source. The axes are three linear stages for XYZ, a swivel axis B, rotational axis C and two dynamic galvo scanner axes UV.

2.3. Measurement methods

Optical microscopes were used for fast inspection after laser processing. The measurement of the ablation volume, depth and surface roughness were determined with a Leica DCM3D confocal 3D microscope. Implants were
105 measured utilizing an Alicona Infinite Focus focus-shifting 3D microscope equipped with a Real3D rotational axis. Surface roughness was measured on a length of 1.5 mm with 0.8 mm cutoff wavelength. Flat samples for the radial ablation study were measured parallel and normal to the laser hatches. Therefore, the influence of the pulse and line overlap was specified to optimize
110 the laser parameters. The implants roughness was measured on the bottom of the helical groove structure.

A PhenomWorld ProX scanning electron microscope (SEM) was used for high-magnification imaging and inspection of the surface. For the non-conducting ceramic specimen the low-vacuum mode was applied.

115 Geometric deviations from the CAD design to the implant were assessed with a Zoller Venturion 450 measurement device. This illuminates the sample with collimated light and the shadow cast by the sample is detected by a large scale detector. A rotational axis enables the measurement over the whole circumference. The Zoller pilot software was used for evaluation of the
120 measurement. An accuracy of 1 μm is given by the manufacturer as ultimate resolution.

Raman spectroscopy was carried out with a WITec alpha300R and three laser sources. Pretests had shown the best signal-noise ratio for the ATZ ceramic to be with green excitation. Therefore, all measurements were carried out with 532 nm wavelength, a spot size of 1 μm and 10 mW average
125 power. The relevant Raman shift for alumina and zirconia were found in literature [23, 24]. However, the interest from this measurement was solely the possible tetragonal to monoclinic phase change of zirconia. Hence, the grating was set to 1800 cm^{-1} with the spectral center at 430 nm for high resolution in the range of 120 to 700 cm^{-1} . Each spectrum was measured three
130 times at the same spot and integrated over at least 5s. The measurement data was filtered to remove possible cosmic rays (CRR) and smoothed by Savitzky-Golay.

3. Results and Discussion

3.1. Parameter Study

Two distinct strategies for high-precision laser manufacturing are used in the experiments. Figure 3 shows the two principal ways for ablation. The laser beam is steered over planar surfaces with normal incidence and certain pulse overlap l_p and scan overlap l_b . In the case of rotational specimen, a tangential process can be thought of additionally. In this case, the spot is a projection on the curved surface. In similar manner a pulse and beam overlap

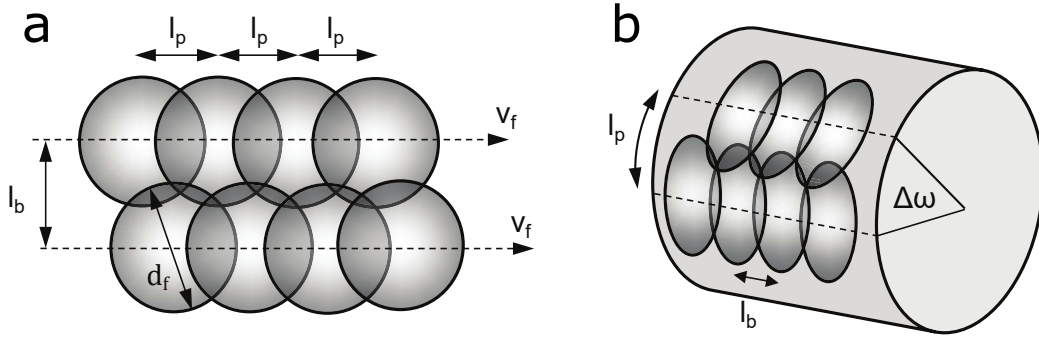


Figure 3: Ablation strategies for orthogonal and quasi-tangential ablation. The parameters pulse overlap l_p , line overlap l_b , focal radius d_s and feed rate v_s are denoted.

can be defined with a rotational angle of $\Delta\omega$ leading to the distance l_b on the convex cylindrical area. Both strategies are different in their characteristics. Radial ablation is more efficient taking into account the coupling to the surface with the whole beam. For layered 2.5D ablation the deviations in each layer accumulate and therefore a higher surface roughness and deviation to design is expected. In contrast the quasi-tangential process suffers from low absorption due to the shallow beam incidence angle. This strategy has the advantage of being self limiting and the deviations solely depend on the spot diameter and position accuracy of the axes.

3.1.1. Threshold Fluence

In case of a Gaussian laser pulse the threshold energy density can be determined experimentally by measurement of the fluence-dependent ablation craters. If BeerLambert's absorption law is taken into account, a logarithmic dependence of the crater depth evolves. The threshold fluence can then be derived from the semi-logarithmic Liu plot [25] and least-square curve fitting,

see equation 2. The Liu plot is defined with the function of D^2 over pulse energy E_p . Starting with the squared ablation crater and adjacent fluence

$$D^2 = 2w_0^2 \ln \left(\frac{F}{F_{th}} \right). \quad (1)$$

Incorporating the Gaussian beam radius w_0 at $1/e^2$, the experimentally applied peak fluence F in ratio to the threshold F_{th} . Rewriting the equation, the following fitting function can be identified with the energy-dependent ablation diameter:

$$D^2 = \alpha \ln E_p + \beta \quad (2)$$

Moreover, the focal spot diameter can be estimated with good agreement from the slope and determined by $w_0 = \sqrt{\alpha/2}$. The threshold fluence follows after translating equation 2 to fluence with the fitted w_0 and extrapolating to the intersection with the abscissa. Measurement data of five experiments and the fitting results for α and β are depicted in figure 4. This resulted to a threshold fluence of 1.63 J cm^{-2} with a focal laser spot of $d_{foc} \approx 16 \mu\text{m}$ in good agreement with the measurements.

3.1.2. Parameter Study

For the ablation of complex geometries, the single-pulse ablation threshold gives a rough starting point. A recently published model points to an efficient ablation region between 5 to 10 times the single-pulse ablation threshold [26]. In case of complex shaped geometries, the parameters chosen should be fast with superior surface quality. Hence, a broad parameter range has been experimentally investigated due to limited references of ATZ ceramics. Figure 5 sums up the attained parameters in a ternary contour plot. The interdependence of the arguments lead to:

$$\begin{aligned} F &= \frac{P}{w_0^2 \pi f_{rep}} \\ X_p &= 1 - \frac{v_F}{d_{foc} f_{rep}} \\ X_b &= 1 - \frac{l_b}{d_{foc}} \end{aligned} \quad (3)$$

Within this study, the repetition rate f_{rep} was limited by the Laser system to 200 kHz and the focal spot set to $d_{foc} \approx 16 \mu\text{m}$. Therefore, the overlap percentage depends solely on l_p and l_b . All parameters have been normalized and spread between $[0, 1]$. Accordingly, the fluence between $[1.3, 10.4] \text{ J cm}^{-2}$, l_p $[1.25, 5] \mu\text{m}$ and l_b $[2.5, 10] \mu\text{m}$ was investigated. The attained ablation rate

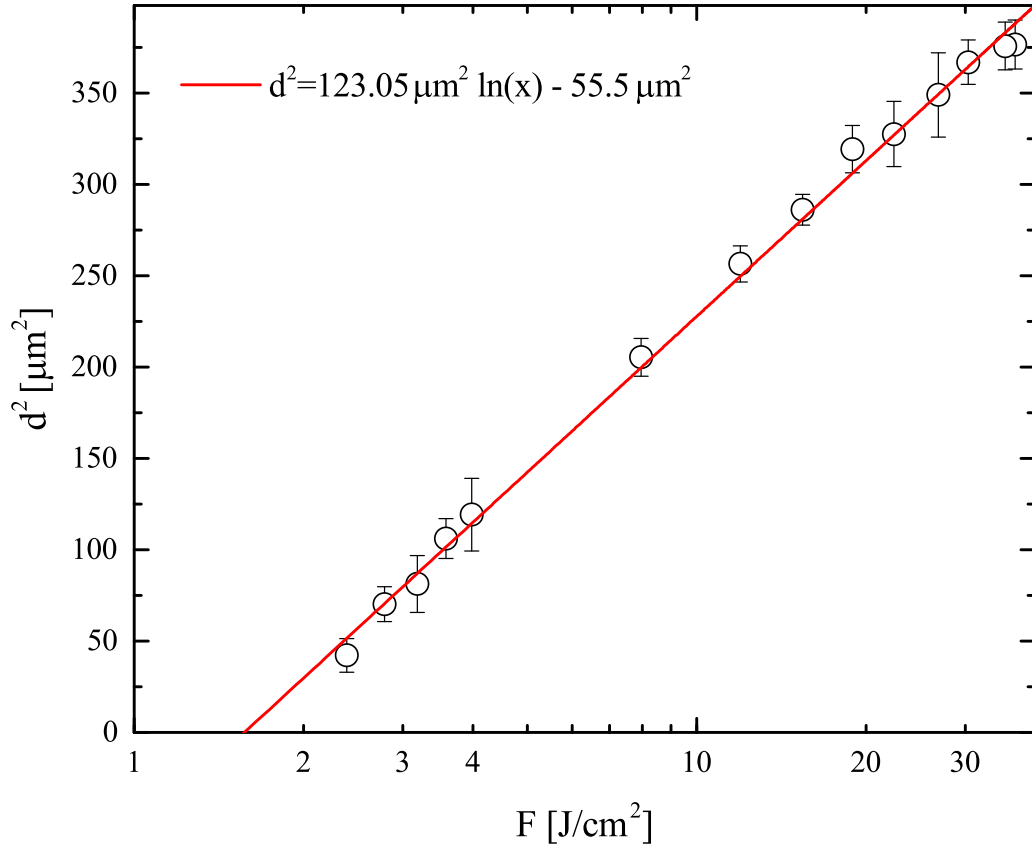


Figure 4: Squared diameter of ablation craters from the single pulse ablation study. Each experiment has been repeated five times and in red a LSQ fit to equation 2 is given.

Table 1: Experimentally attained ablation parameters for radial P1 and P2 and tangential P1T and P2T processes.(mention projection for tangential)

Parameter	P1r	P2r	P1t	P2t
P [W]	0.5	2	8	8
F [J cm ⁻²]	2.5	10.4	41.8	41.8
l _z [μm]	1.3	7.2	7.5	15
Q [mm ³ min ⁻¹]	0.18	0.96	0.32	1.28
R _{aH} [μm]	0.27	0.58	0.13	0.18
R _{aV} [μm]	0.64	1.16	-	-

165 $\dot{Q}$ and adjacent surface roughness R_a are depicted in dependence of the fluence, beam and pulse overlap.

Clearly, a trade-off was distinguishable between surface quality and maximal ablation rate. The green marked areas pointed the region of parameters best for fast precise ablation. In the scope of fast manufacturing two parameter settings for the radial and tangential processes were chosen. Table 1 presents the parameters for the production of the dental implants. Additionally, the optical measured surface roughness is shown in horizontal (R_{aH}) and vertical R_{aV} direction. This pointed to the dependence of the roughness on the pulse and beam overlap. The latter strongly altered the ablation rate and a quasi-optimum taking the roughness into account was chosen.

3.2. Dental Implant

In the context of rapid prototyping, a defined geometry of a ceramic implant was manufactured. Figure 6 depicts the involved steps for the production in case of the quasi-tangential strategy. A five-millimeter raw cylinder was used and the envelope of the implant ablated. The neck was finished after the envelope was machined; compare figure 6b, and therefore the roughening and finishing parameters set used. In case of radial production the hatching was directly carried out for the design geometry. When only a radial strategy was followed, the radial P1r was applied taking into account the accumulation of errors for each ablated layer.

3.2.1. Surface Condition

The surface was imaged qualitatively with the SEM. A comparison of the attained topology with varying technologies and processes is depicted

190 in figure 7. The conventionally manufactured dental implant was inspected
 after grinding 7a and subsequent sandblasting with an etch step 7b. The
 grinded surface revealed the grooves from the diamond tool with an overlap
 per revolution of $5\text{ }\mu\text{m}$. After sandblasting and etching the surface appeared
 smoother and smeared out. This is corroborated by the geometrical precision
 195 and roughness shown in table 2. Subsequently, the laser-manufactured
 surfaces are depicted. Figure 7c shows the bottom of the implant, compare
 figure 3c, after the radial processes P1r and P2r. There are no obvious tracks
 and the surface appears homogeneously. In contrast the introduced quasi-
 tangential process, figure 7d, revealed cracks at the surface. Moreover, a
 200 polishing process was tested with the parameters P1t from table 1 except a
 layer feed l_z of zero. Apparently, steering the laser along the final envelope
 reduced the surface roughness due to local melting of small debris particles.
 The cracks at the surface opened wider and a deeper HAZ can be assumed.
 The energy input from the process seemed to produce a heat gradient leading
 205 to stress and therefore cracks. A potential phase transition was ruled out
 by Raman-spectroscopy studies. Following the quasi-tangential ablation a
 radial cleaning process was established to remove this HAZ. In addition to
 the parameter set P1r, the power was increased to 1 W leading $12\text{ }\mu\text{m}$ ablation
 depth with three layers. This increased the ablation rate and therefore the
 210 production time was decreased. Figure 7f shows the transition from the
 process strategy and the cracks could be successfully removed.

Cross sections were prepared by breaking the ceramic implant. Follow-
 ing the cleavage was embedded, diamond grinded removing approximately
 $300\text{ }\mu\text{m}$ and polished. Figure 8 depicts the cross section of the laser pro-
 215 cessing steps. The radial process revealed a smooth transition and neither
 dissolution nor HAZ was detectable. In the bottom structure of the groove
 the discretized layered ablation was observable. The quasi-tangential pro-
 cessing of the helical groove with P1t and P2t clearly revealed HAZ, shown
 in figure 8b. Alumina appeared darker and seemed to dissolve approaching
 220 the surface. In case of the quasi-tangential polishing process the affected
 depth increased and more cracks could be observed, see 8c.

The thermal expansion coefficients of alumina and zirconia were similar,
 so solely a temperature gradient introduced cracking could be ruled out.
 Two possible scenarios appeared feasible with this observation. Either the
 225 zirconia was subjected to a phase transition, increasing the volume by about
 10 % from tetragonal to monoclinic, or the alumina dissolution generated
 stress. The particle-like structure smeared out and seemed to accumulate

around the boundary to zirconia. Taking into account the reported smaller threshold fluence of alumina this would be feasible [16]. Therefore, Raman spectroscopy was carried out to detect potential phase transformations of the ATZ ceramic, as discussed in the next section.

3.2.2. Raman Spectroscopy Study

The characteristic spectra for adjacent phases of zirconia were found in literature. First principle calculations have been carried out [24] in strong agreement to experimentally attained spectra [23]. Here, the data was analyzed by a least-square fit (LSQ) to the spectral data and a Lorentz peak shape was applied following

$$I = I_0 + \frac{1}{\pi} \frac{2Aw}{4(k - k_c)^2 + w^2}. \quad (4)$$

A constant offset I_0 was taken into account and the peak height A , width w and location k_c fitted. Figure 9 depicts the measured spectra in solid black and the applied Lorentz peaks for each of the five peaks. The peak positions clearly revealed a tetragonal phase with the characteristic inelastically scattered energies depending on the phonon modes. Successively, the yttria-stabilized ATZ ceramic was studied with respect to the applied processes. The monoclinic phase is more complex allowing more phonon modes and therefore peaks in the Raman spectrum. A quantitative study was not applicable due to strongly differing phonon scattering probabilities. However, Raman spectroscopy revealed the existent phases. Figure 10 shows the measured Raman spectra for different processes and the raw material.

The green vertical bands mark the region of the tetragonal phase and the reddish striped bands the most prominent monoclinic peaks. The spectra were normalized and shifted top-down for clarity. Inspection of the mechanically grinded ATZ (red) revealed a majority of the tetragonal configuration. Some fraction was detectable for the monoclinic phase with a small fraction comparable to the raw material (black). The sandblasted and etched implant (pink) clearly was subjected to a tetragonal to monoclinic phase transition. Even the most prominent tetragonal peaks at $(147.9 \pm 0.2) \text{ cm}^{-1}$ and $(261.69 \pm 0.15) \text{ cm}^{-1}$ vanished. Laser-machined ATZ did not show any sign of the monoclinic phase. Moreover, the ultrashort-pulsed ablation reduced the amount of the monoclinic fraction. This corroborated the picture of alumina dissolution on the boundaries leading to stress and consequent cracks at the surface.

3.2.3. Geometric Precision

The introduced production chain for complex shaped dental implants was evaluated in terms of geometric deviations and surface quality. Figure 11a depicts the red measurement in terms of precision and the target contour is illustrated in black with a 10 μm green tolerance band. The mean deviation $\bar{\xi}$ of this quasi-tangential machined dental implants was 4 μm with a maximum deviation $\hat{\xi}$ of 15 μm . The biggest deviation appeared on steep slopes, where the taper angle plays a role. However, the precision was reached from the pristine workpiece without feedback measurements. Hence, the self-limiting quasi-tangential process uttermost pointed to high precision manufacturing capabilities. The accuracy could be further increased with inline or an iterative measurement approach [27].

Table 2 shows the surface quality in terms of roughness and deviations for the discussed production processes. Moreover, the production time for the

Table 2: Comparison of different technologies and process strategies in terms of surface roughness $R_{a,z}$, maximal deviations $\hat{\xi}$ and $\bar{\xi}$ the mean deviation to design.

	R_a [μm]	R_z [μm]	$\hat{\xi}$ [μm]	$\bar{\xi}$ [μm]
grinded	0.18	0.91	27	7
sandblast and etch	0.5	2.85	57	13
radial neck P1r, P2r	0.37	1.86	52	18
radial groove	0.71	3.72	-	-
tang P1t	0.38	1.97	-	-
tang P2t	0.24	1.1	15	4

finished specimen is of strong interest for industrial application. A manufacturing time of 2.5 h was needed for the radial laser machining facilitating P1r and P2r. In comparison the quasi-tangential process was separated in the three steps depicted in figure 6 with the settings P1t and P2t from table 1. The manufacturing of the envelope from a 5 mm raw cylinder took 49 min. Subsequently, the ablation of the varying helical groove was carried out in 13 min followed by finishing with 15 min. Totally, the production time of the dental implant depicted in figure 11 is 77 min. Apparently, the longest processing step was the removal of the excess material from the raw cylinder. This would be the highest gain in terms of production time and high laser power could be used. However, multiple process steps could be implemented with high power roughing followed by finishing with parameters fulfilling the required surface quality. Moreover, the complete process could be translated

to higher feed-rate and scanning speed, if a high repetition rate high power
285 ultrashort-pulsed laser system would be at hand.

4. Conclusions

Detailed parameter studies on single-pulse and multi-pulse ablation with
a femtosecond laser have been reported on ATZ. This material is commer-
cially used for dental implants and hard to machine. In comparison to the
290 conventionally manufactured implant, the laser manufacturing process could
clearly compete and high precision implants manufactures. Moreover, tak-
ing into account the total time for geometrical modifications, the introduced
quasi-tangential process was highly flexible. Hence, an industrial application
was presented for rapid prototype production of complex shaped geometries
295 on a ceramic workpiece.

The impact of the laser process on the material was tackled with a qual-
itative SEM study corroborated by Raman spectroscopy. A laser induced
phase transition of zirconia could be ruled out. However, the alumina phase
showed dissolution and migration possibly altering the mechanical properties.
300

High precision manufacturing was presented with a mean deviation of
4 μm over the whole contour. Moreover, a superior surface quality with
R_a = 0.24 μm reached. The combination of radial and tangential processes
showed the high potential for a competitive manufacturing time in com-
parison to the conventional grinding process. Scaling of the presented pro-
cesses is feasible and, especially, facilitating a high power and repetition rate
305 ultrashort-pulsed laser systems would tremendously shorten the manufactur-
ing time.

Acknowledgments

310 The authors want to thank the Swiss National Fund [FuSSiT/169654]
and the Swiss Commission of Technology and Innovation for the financial
support. N.A. wants to personally thank Prof. A. Otto for hosting and
discussion during a research stay at the TU Vienna.

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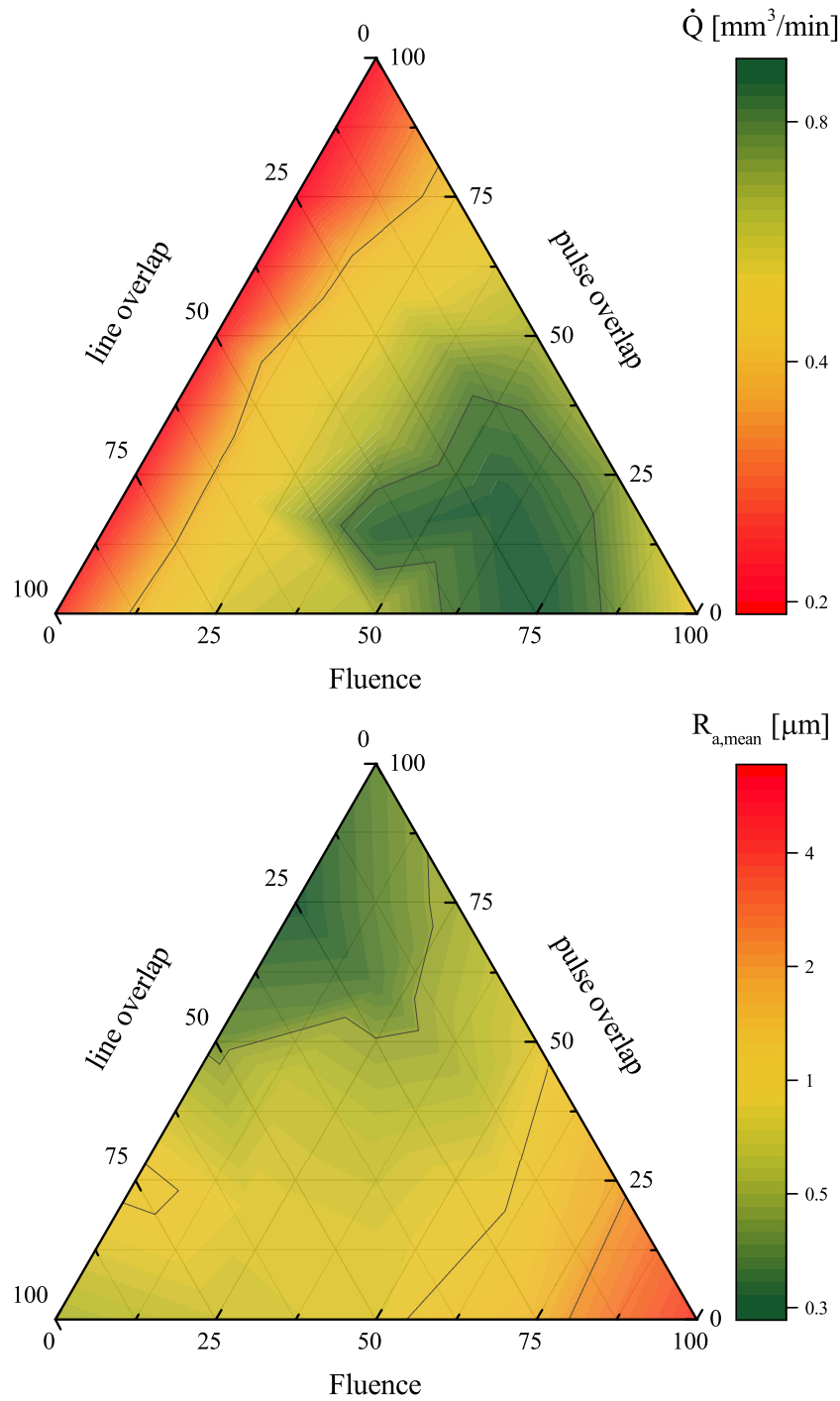


Figure 5: The ablation rate $\dot{Q}$ and surface roughness R_a are shown dependent on the normalized parameters fluence, line and pulse overlap. The colour map is inverted to show the regions of interest, contour lines separate the data limits and the grid is guide to the eyes.

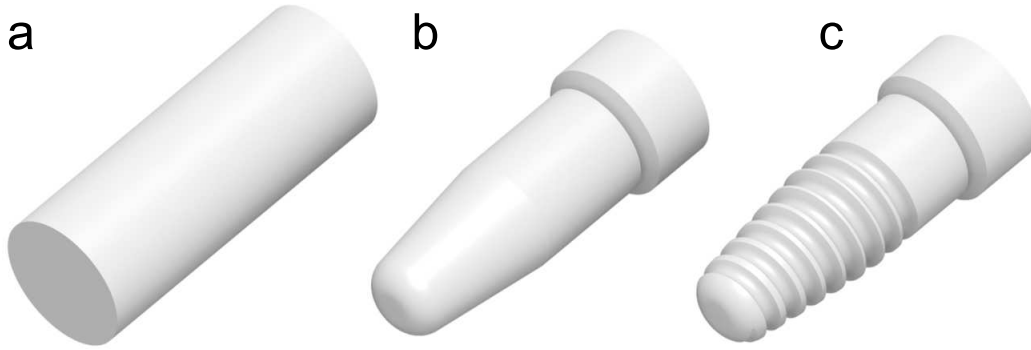


Figure 6: Steps for laser manufacturing. Starting with the raw cylinder (a) the envelope is manufactured (b). Following the helical groove is ablated (c).

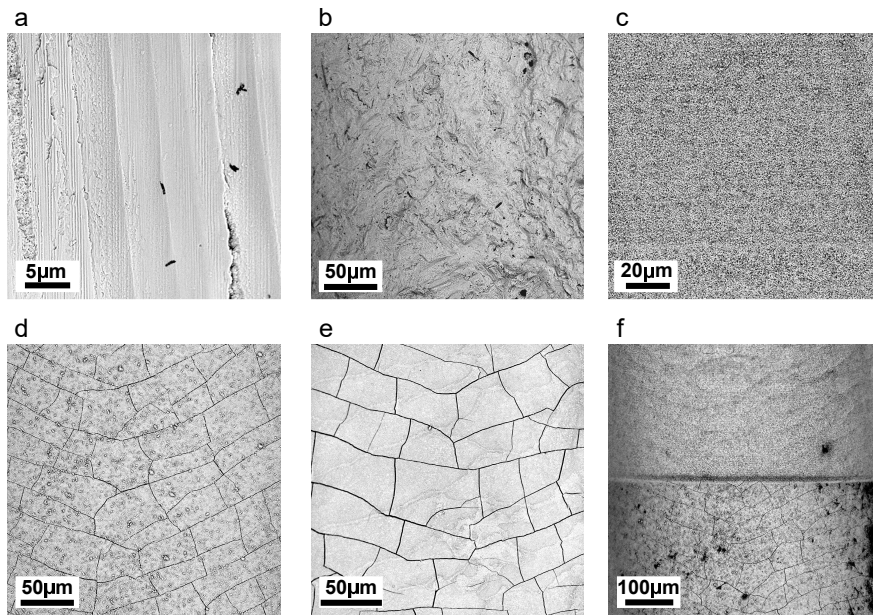


Figure 7: Comparison of processes concerning topography. In (a) the mechanically grinded surface is shown followed in (b) by sandblasting and etching. The SEM picture in (c) depicts the radial machined surface with P2r and in (d) the tangential ablation with P2t. In (e) a laser polished surface presented and sub-figure (f) depicts a combined tangential and radial surface.

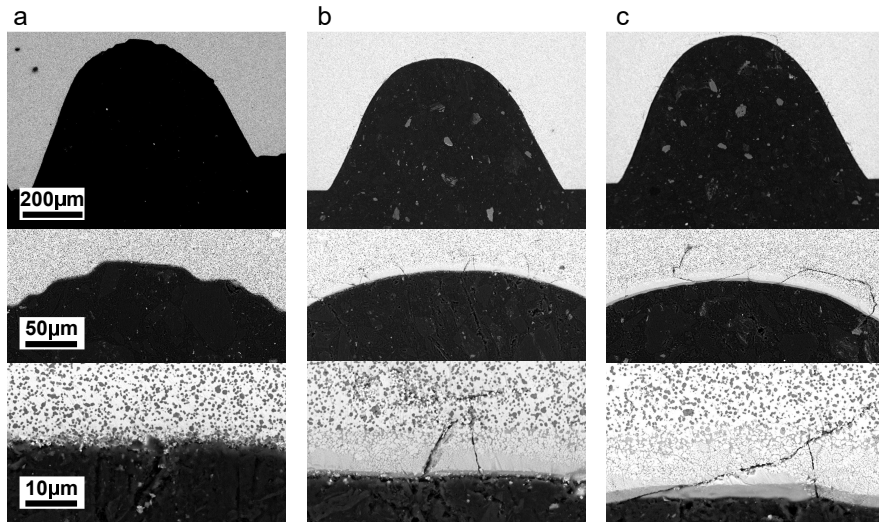


Figure 8: Diamond grinded and polished cross-section of the dental implant showing the radial (a), tangential (b) and polishing (c) process. The scale persists in each adjacent rows. In (b) and (c) a distinguishable HAZ appears with blackish Al_2O_3 dissolved in zirconia within $10\text{ }\mu\text{m}$ leading to cracks.

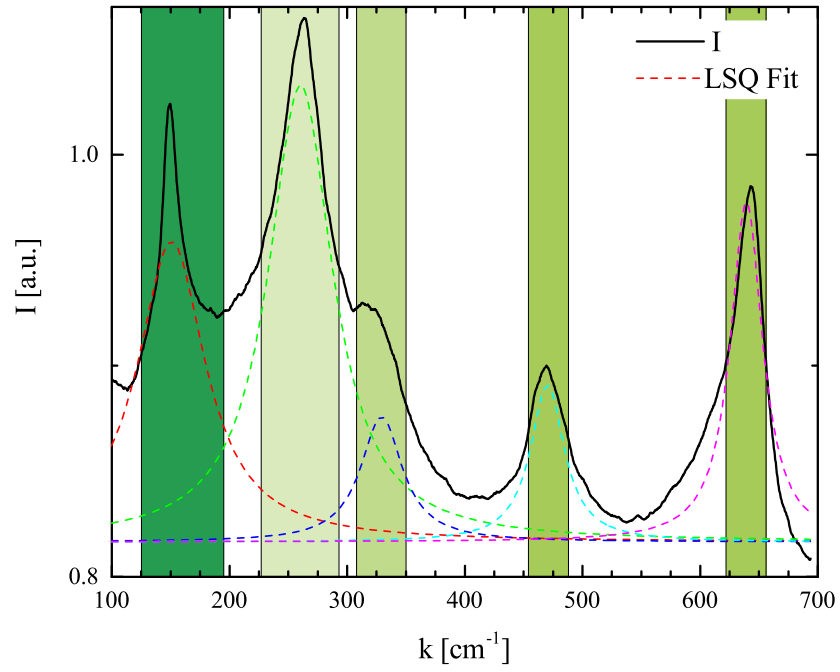


Figure 9: Raman spectrum for tetragonal zirconia. The LSQ peaks are shown with the fitted width marked in background color.

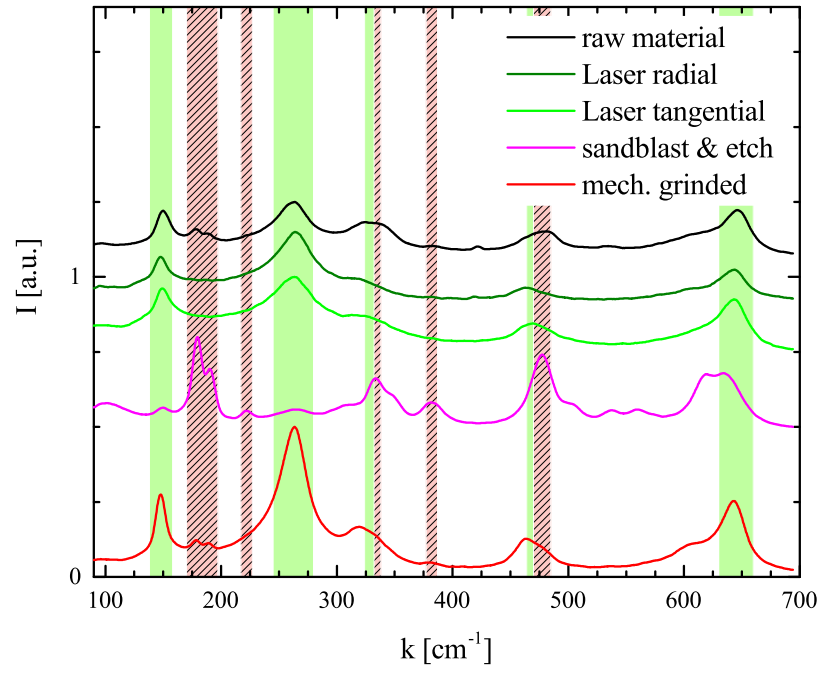


Figure 10: Raman spectra for ATZ ceramic implant manufactured with different technologies. In green the characteristic peaks for a tetragonal modification are shown and red hatched the monoclinic peaks accordingly.

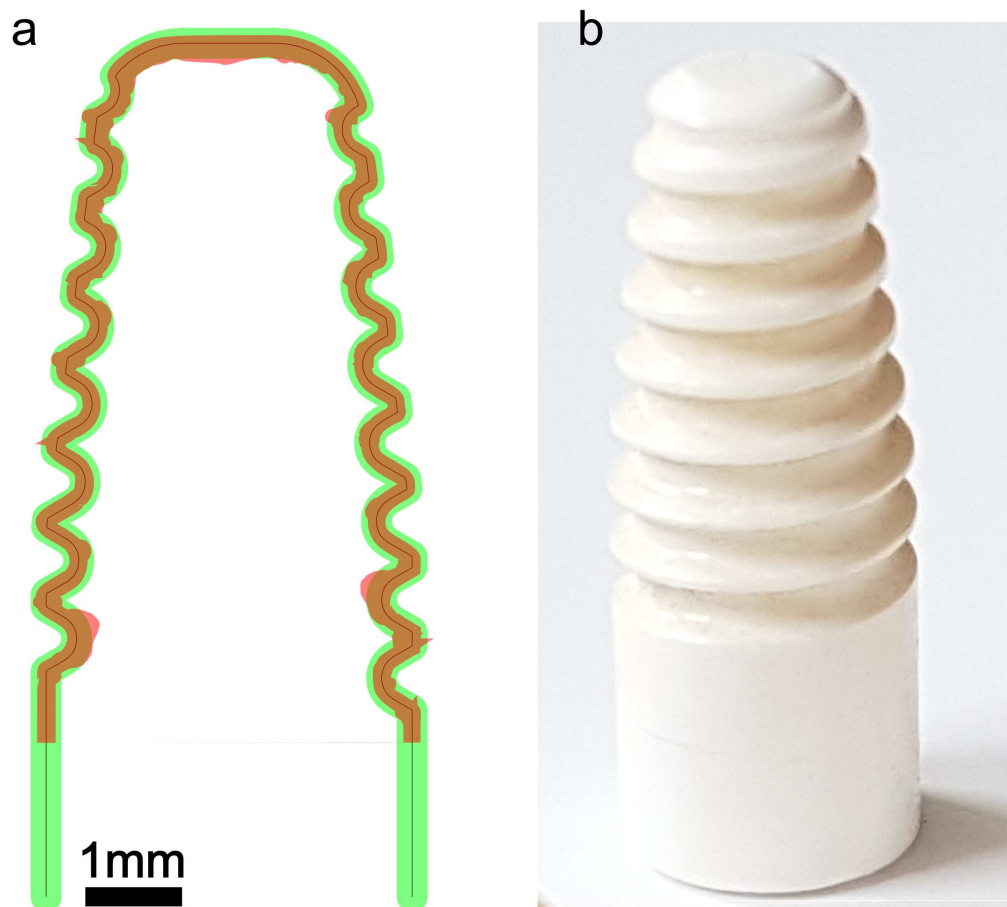


Figure 11: Dental implant with deviation ξ , the tolerance band shows $\pm 10\mu m$.