**LOW TEMPERATURE DEGRADATION OF LASER PATTERNED 3Y-TZP: ENHANCEMENT OF RESISTANCE AFTER THERMAL TREATMENT**

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1. **INTRODUCTION**

Tetragonal Zirconia Polycristal stabilized with 3 mol. % Y2O3 (3Y-TZP) is being increasingly used in dentistry applications, both as prosthesis and as implants, due to an excellent combination of biocompatibility, mechanical performance and aesthetics [1].

There is an increasing interest in the modification of topography and functionalization of these materials with the aim to improve the biological response or increase the adhesion to other materials, like enamels or dental resins. Each application may require a different kind of topography, in terms of geometry, regularity and scale-size (generally, the desired features are in the micro- and nano-scale [2]). For instance, if low bacterial adhesion is desired, a reduced roughness would be the preferred choice [3]. On the other hand, grinding, sandblasting or acid etching are considered valid techniques to introduce a relatively high roughness capable to enhance cells adhesion [4].

However, these techniques are not able to control precisely the topography of the surface, just the average roughness. In this context, laser-based techniques allow the production of accurate and regular geometries and are very interesting for patterning with periodical or directional characteristics, as for cell-guidance applications [REF Rom] [5]. Compared to the other mentioned techniques, laser patterning is highly reproducible, fast, relatively easy to implement and low-contaminating, belonging to the non-contact techniques [6]. All these are highly desirable characteristics for biomedical applications.

Among available laser patterning techniques, Direct Laser Interference Patterning (DLIP) exploits the interference of at least two laser beams to produce a periodical pattern on the surface to be treated. Interfering beams create an inhomogeneous intensity distribution on the surface of the sample. The high energy pulse delivered at maximum intensity position locally melts, evaporates and ablates the substrate. The pattern is thus engraved at the same time all over the exposed surface, being faster if compared to other laser-based technique that need to scan the focused laser beam along the desired geometry. Regular patterns, like series of lines and matrix of dots, can be produced depending on the optical setup and number of laser beams. A more detailed description of the technique and the achievable geometries can be found in [7] and [8].

Laser pulse melts locally the substrate and capillary forces generated thanks to temperature difference on the surface cause material flow and pattern formation [9]. Due to the shortness of the laser pulse and the low thermal conductivity of 3Y-TZP [10], a very steep thermal gradient is established on the treated surface, which results in thermal shock. This produces recrystallization in form of columnar grains growing perpendicularly to the surface and intergranular microcracking, down to 1 µm depth. The high thermal load induces also *t → m* phase transformation, texturization of *t*-phase and residual stresses and strains. Furthermore, the highly energetic laser irradiation activates color centers (mostly electrons trapped in charged oxygen vacancies). The total and local chemical composition of the surface is not altered by the laser exposure. All these modifications are homogeneously distributed along the topography and affect the first micrometer of material below the treated surface. Further details about type and distribution of collateral damages after laser treatment can be found in [REF].

One big concern for the long term integrity of zirconia ceramics (particularly for 3Y-TZP) is Low Temperature Degradation (LTD), also known as hydrothermal degradation or aging [11]. This is the progressive transformation of the metastable *t*-phase to *m*-phase, triggered by the contact with water molecules. Phase transformation starts on the surface where water derived species diffuse inside the lattice and destabilize the tetragonal structure. After surface saturation is reached, the transformation front propagates towards the bulk, resulting in microcracking of the material and consequent loss of structural integrity [[1] E. Jiménez-Piqué, A. Ramos, J. a. Muñoz-Tabares, A. Hatton, F. Soldera, F. Mücklich, M. Anglada, Focused ion beam tomography of zirconia degraded under hydrothermal conditions, J. Eur. Ceram. Soc. 32 (2012) 2129–2136. doi:10.1016/j.jeurceramsoc.2012.02.011.; [1] J.A. Muñoz-Tabares, E. Jimenez-Pique, M. Anglada, Subsurface evaluation of hydrothermal degradation of zirconia, Acta Mater. 59 (2011) 473–484. doi:10.1016/j.actamat.2010.09.047.] .. Microstructural features that have a strong influence on LTD resistance are those that govern *t*-phase stability: density, grains size, amount and distribution of stabilizer and residual stresses [12]. Any surface treatment capable of altering the microstructure of the material below is therefore able to influence the resistance to LTD, positively or negatively. For instance, it has been demonstrated that grinding [13,14], sandblasting [14] and air-borne particle abrasion [15] are able to increase the resistance to LTD of 3Y-TZP while soft polishing [16,17] and acid etching [18] can have a negative effect. The introduction of nano-grains, grains partitioning and texture (i.e. ferroelastic domain switching) makes the *t*-phase more stable, like in grinding and sandblasting. Also compressive residual stresses have a beneficial effect on LTD resistance, acting as a constraint and stabilizing the *t*-phase. This is the case of air-borne particle abrasion [15] and rough polishing [16]. On the contrary, it has been demonstrated that tensile residual stresses reduce LTD resistance of 3Y-TZP [16,17,19].

Laser pattering induces several microstuctural modifications that may affect the LTD resistance [9]. These features are mainly shallow microcraking, grains elongation, surface texture, *t → m* transformation and possibly residual stresses, which have been proven as possible causes of modification in LTD resistance of zirconia materials [12,20].

Therefore, in this work we explore the sensitivity to LTD of laser patterned 3Y-TZP, as treated and after a thermal treatment. The thermal treatment is done to relieve residual stresses and to revert *m*-phase. at date there has been no report on the LTD resistance of laser patterned 3Y-TZP.

1. **MATERIALS AND METHODS**
   1. *Material processing*

Commercially available powder of Tetragonal Polycrystalline Zirconia stabilized with 3% molar Y2O3 (TZ-3YSB-E, Tosoh, Tokyo, Japan) was cold-isostatic pressed at 200 MPa and then sintered at 1450°C for two hours (3°C/min heating rate). The rods were cut into discs of approximately 9 mm diameter and 2mm thickness. The surface of the samples was ground and polished with diamond suspensions of 30 – 6 – 3 μm particle size with a final step of colloidal silica. The measured final density was 6.03 ± 0.02 g/cm3 (99.67% of theoretical density) with a grain size of 0.31 ± 0.08 μm (intercept distance). The obtained material has biomedical grade, according to ISO 13356:2013 [1]. These samples were then split into two groups: the first group did not undergo any further modification while the other discs were laser patterned with DLIP. The samples that did not undergo any further treatment were labelled Not Treated (NT) and served as reference material. The discs that were laser-treated were labelled Laser Patterned (LP) and were further divided into two groups: one group (LP) did not undergo any further treatment after patterning while the other discs (LP+TT) were annealed after the laser treatment The annealing treatment was performed in an air furnace at 1200°C during 1 hour, with the purpose of eliminating residual stresses and revert the monoclinic phase to tetragonal (further details about the effect of the thermal treatment on LP samples will be given in section 3.2).

* 1. *Laser patterning*

A Q-switched Nd:YAG laser (Spectra Physics Quanta-Ray PRO210) with a fundamental wavelength of 1064nm was employed in the DLIP setup. The output wavelengths of 532 nm and 355 nm obtained by second and third harmonic generation were used for patterning of zirconia discs surface. The repetition rate and the pulse duration of the laser were 10 Hz and 10 ns, respectively. All samples were treated with one single pulse and with a fluence of 4 J/cm2 for 532 nm and 3.5 J/cm2 for 355 nm. An optical setup with two interfering beams allows producing a striped pattern consisting of alternating valleys and peaks with a peak-to-peak distance (i.e. periodicity) of 10 µm. The two-beam interference results in a plane sinusoidal intensity distribution *I(x,y)* on the surface of the sample. It can be described by:

(1)

where *Io* is the intensity of the laser beam before splitting, *λ* is the laser wavelength and *α* is the half angle between the interfering beams. Further details about the technique and the setup employed can be found in [21] and [22].

* 1. *Accelerated LTD tests and LTD kinetics*

LTD of the samples was evaluated performing accelerated tests in an autoclave in water steam under 2 bar at 131°C up to 30 h. The *t → m* transformation was followed measuring the monoclinic content as a function of test time by X-ray diffraction (XRD) with Bragg-Brentano symmetric geometry. XRD spectra were recorded on a diffractometer (D8-Advance, Bruker) using Cu K*α* radiation (40 kV and 30 mA) in an angle range of 20° ≤ 2θ ≤ 70° at a scan rate of 1 s/step and a scan size of 0.02°. Monoclinic phase content was then calculated using the equation proposed by Toraya (REF):

(2)

where *Vm* is the monoclinic volume fraction and *Im* and *It* represent the integrated intensity of the tetragonal (111) and monoclinic (-111) and (111) peaks, respectively.

Isothermal LTD kinetics is then evaluated by plotting the monoclinic volume fraction as a function of test time. This water-mediated *t → m* transformation generally has a sigmoidal trend that can be fitted with Mehl – Avrami – Johnson (MAJ) equation [11]. This model describes a “nucleation and growth” process and can be expressed in the following form [17]:

(3)

where *Vm min* is the minimum and initial monoclinic volume fraction, *Vm max* is the maximum monoclinic volume fraction reached, *b* and n are adjustable parameters (b depends temperature and is related to the activation energy of the process while *n* is a constant also known as MAJ exponent) and *t* is the aging time [23].

* 1. *Determination of degraded layer depth and microstructure*

Focused Ion Beam (FIB, Carl Zeiss Neon 40) was employed to prepare cross-sections to follow the propagation of the transformation inside the volume with FESEM. From the same volume thin lamellas of material were also lift-out and deposited on a Copper grid using FIB. They were characterized with Scanning Transmission Electron Microscopy (STEM, Carl Zeiss Neon 40 operating at 30 kV) and Transmission Electron Microscopy (TEM, JEOL JEM 2100 operating at 200 kV) to reach a higher resolution. LP samples and LP+TT samples were observed before aging and after 5 hours of accelerated test.

1. **RESULTS**
   1. *Accelerated test and LTD kinetics*

Samples treated with different wavelengths (532 and 355nm) show very similar kinetics. Due to the very similar kinetics observed (fig. 2B) and the comparable damage produced by the laser treatments [REF] further investigation has been conducted on the samples treated with green laser (532 nm) only, that from now on will be referred to as LP.

The evolution of the XRD spectra with time during the accelerated LTD test in water steam at 131°C is shown in fig. 2A for LP samples and in fig. 2B for LP+TT samples. The intensity of the monoclinic peaks (-111)*m*, (111)*m* and (002)*m* increase with time at the expense of the tetragonal peaks (111)*t*, (002)*t* and (020)*t*. The tetragonal phase is transformed isothermally into monoclinic phase, i.e. both materials suffer of LTD. However, *t → m* transformation is retarded in LP+TT samples since monoclinic peaks appear later.

A more detailed analysis of the spectra in fig. 2 also reveals that:

* the monoclinic phase is strongly textured. The intensity ratio of most intense monoclinic peaks is *I(111)m/I(-111)m* = 0.2 for LP samples and *I(111)m/I(-111)m* = 0.15 for LP+TT samples, while for untextured monoclinic it is *I(111)m/I(-111)m* = 0.68 [24];
* in fig. 2A (LP) after 10 hours of test a hump on the left of the principal tetragonal peak can be observed. It becomes more evident as degradation progresses and the intensity of the overlapping tetragonal peak decreases. This feature can be attributed to the presence of some cubic phase retained after the sintering step that is not susceptible to transform to monoclinic.



Fig.2

The LTD kinetics at 131°C is depicted in fig. 3 for NT, LP and LP+TT. LP samples have the lowest resistance to LTD, showing that the laser treatment has a negative effect on the long term stability of 3Y-TZP. On the contrary, LP+TT samples show a higher resistance to LTD, compared to both LP and NT samples. The annealing treatment is therefore beneficial for the long term stability of laser patterned 3Y-TZP.



Fig.3

Comparing LP with NT, two main differences can be enlightened in the laser patterned curves: the higher initial monoclinic volume and the flatter slope in the fast transformation region, i.e. the lower transformation rate. Right after patterning (at time 0) the LP material is prevalently tetragonal with an initial amount of monoclinic phase *Vm0* comprised between 8 and 10 %, caused by the local high thermal stresses suffered during the laser treatment [REF]. Afterwards, the *t → m* transformation proceeds with a lower speed than in the NT samples. In fact, after 30 hours of test the difference in monoclinic fraction between LP and NT is very small, being *Vm* ≈ 69 ± 2 % for LP and *Vm* ≈ 66 ± 5 % for NT.

After the annealing treatment (at time t=0) the LP+TT material is fully tetragonal. The monoclinic volume fraction starts to increase after 10 hours of accelerated test, showing a long incubation period, and then increases with a sigmoidal trend. The transformation is thus delayed and results in an overall deceleration if compared to LP and NT sample. However, a more detailed observation of the curves reveals various features that can be responsible for this different behavior. Comparing LP+TT to LP kinetics, the main differences are the lower initial monoclinic volume fraction and the steeper slope in the “fast transformation region”, i.e. a higher transformation rate. Therefore, the annealing treatment delays but not slows down the LTD kinetics of laser patterned samples. Furthermore, it is interesting to compare the LP+TT kinetics with the NT since both materials has the same *Vm0* ≈ 0% (or at least below the detection limit of XRD) and almost the same slope. However, the kinetics is delayed, in this case due to the presence of a longer incubation period. In fact, the LP+TT curve resembles the NT curve shifted forward in time.

In order to understand the origin of the increment in LTD resistance after the annealing treatment it was necessary to analyze in detail the microstructure of LP+TT samples and then to compare the different microstructures effect on LTD kinetics.

* 1. *Annealing treatment effect on microstructure*

In order to investigate the role of the different damages induced by laser treatment on the LTD behavior an annealing treatment (in an air furnace at 1200°C during 1 hour) was performed on the LP samples with the purpose of eliminating residual stresses and revert the monoclinic phase to tetragonal. This thermal treatment is commonly employed for two main purposes: to reveal the surface grains for grain size measurement, i.e. thermal etching, and to perform a stress relief treatment [13,16,17]. The thermal treatment does not alter significantly the striped topography and the interconnected intergranular microcracks that cover the treated surface are still present (fig. 4A). On the other hand, other microstructural modifications are introduced by annealing and are schematized in fig. 6:

* Grain boundary etching on the surface (fig. 4 …, …), due to diffusion from grain boundary towards the bulk, resulting in rounding of the surface grains;
* tip blunting of microcracks (fig. 4 …, …). The intergranular microcracks produced during laser treatment remain unaltered in length, with a penetration depth in the order of ≈ 1 µm as for LP samples. The tip is rounded due to the same mechanism as grain boundary etching.
* monoclinic phase reversion. As depicted in the XRD spectrum in fig.4… , after annealing the material is fully tetragonal and no monoclinic peaks can be detected. In the STEM images in fig. 4… there is no evidence of monoclinic twins, confirming the XRD observation. Monoclinic phase produced upon laser treatment has transformed back to tetragonal.
* narrowing of the main tetragonal peak. The FWHM of the (111)t peak of the LP sample is 0.12° and decreases to 0.10° after annealing (fig. 4..). This can be attributed to residual stresses relief, which is also observed in the more homogeneous appearance of the grains in the STEM images (fig. 4…).
* texturization??? of t-phase (t(002) and t(020) peaks intensity ratio different from normal)`Thermal treatment maintains the texture of the t-phase as generated by the laser
* F-centers deactivation. The reddish coloration of the surface related to the activation of F-centers in 3Y-TZP upon laser treatment [REF] fades away and the surface of the samples turns white again.



Fig.4

3.3. *microstructural features of LTD propagation*

In fig. 5 the FIB-cross sections of LP and LP+TT samples degraded at different times are displayed. It is possible to observe how the transformation proceeds from the surface towards the bulk. The transformed layer is homogeneously thick and is characterized by transformed grains and microcracking (see fig. 5B, C, F). Again, it appears clearly that LTD is retarded in annealed samples. At time 0 no transformation is appreciable with this technique in both materials. However, after 5 hours of test a 2 µm thick layer can be distinguished in LP samples while LP+TT still has no trace of transformation.

Fig. 5

For a more detailed analysis of the microstructure of degraded samples, FIB-cut lamellas of LP and LP+TT 3Y-TZP observed with STEM are displayed in fig.4. At time 0 there is no evidence of monoclinic phase in the LP+TT samples while some twinning can be distinguished in the LP samples, being coherent with XRD quantifications. In LP the monoclinic phase is concentrated around the microcracks that depart from the treated surface (as enlightened in fig. 6A,E). These monoclinic lamellas are a consequence of the highly localized thermal stresses arising during laser treatment. After 5 hours of accelerated test, in the LP+TT samples there is still no trace of transformation while in LP samples the degraded layer becomes homogeneously thick, with twins inside the transformed grains and intergranular microcracks (fig. 6B, F).



Fig. 6

A closer look at the surface grains of LP after 5 hours of accelerated test allows to distinguish some of the finest features of the *t → m* transformation (fig.7). In fig. 7A surface uplifts are visible on the laser treated surface due to twinning in the monoclinic phase below (fig. 7B).

Microcracks are evident both in the BF and DF STEM images in fig.7. The widest microcracks are intergranular and orthogonal to the treated surface and are concentrated in the first micron below the surface. They are present also in the LP sample at time 0 (fig. 6A, E) and are produced by the laser treatment due to rapid cooling [REF]. The parallel microcracks are homogeneously distributed inside the transformed volume and are due to the LTD of the material [13,25], appearing after some time at hydrothermal conditions. Some small transgranular microcracks, inside the first layer of grains, can also be observed.



Fig. 7

1. **DISCUSSION**

DLIP is a useful and effective tool to produce a regular micrometric-scale pattern on the surface of 3Y-TZP [9,26]. However, it introduces some collateral damage in the first µm of material below the surface: the steep thermal gradient and high thermal stresses induced by laser pulse produce directional grain growth, microcracking, *t → m* phase transformation, *t-*phase texturization and residual stresses, as described in [REF]. Highly energetic laser-material interaction also activates color centers.

These microstructural features influence the resistance to LTD of 3Y-TZP [20]. Results of the accelerated tests conducted at 131°C in water vapor show that the LTD is anticipated by laser patterning and retarded by the following thermal treatment (see kinetics curves in fig. 3). However, a more detailed analysis reveals that the changes in kinetics behavior are more complex, since the duration of the initial incubation period and the transformation rate may originate from different microstructural features. In the following paragraphs we will try to relate the different damages caused by DLIP to the observed kinetics modifications.

* 1. *laser patterning: effect on LTD of 3Y-TZP (LP samples)*

Laser patterning decreases the resistance to LTD of 3Y-TZP (see kinetics curve in fig. 3). However, it is interesting to observe that this change in the kinetics stems from the combination of two apparently contradictory factors: an increase in the *Vm0* and a decrease in the transformation rate (i.e. the curve slope) in the fast transformation region.

The higher initialmonoclinic fraction (*Vm0*  9%) corresponds to the monoclinic phase formed during the cooling step right after the laser pulse: high thermal stresses induce microcracking and, as a consequence, a *t → m* transformation at the crack tip which also produces twinning inside the grains [REF].

The reduction of the transformation rate can be attributed to the existence of residual stresses [16,19] and texture in the *t-*phase [13,14,27]. In order to elucidate which of these two mechanisms plays the main role in retarding LTD, a thermal treatment at 1200°C for 1 hour was done to relief residual stresses [13,14,16,17,27] without changing main microstructural features of the material. This treatment leaves unaltered the topography, microcracks, and columnar grains, ruling them out of further considerations as responsible in the decrease of LTD resistance. Texture in the *t*-phase is maintained but deserves particular attention and will be discussed later in the following section.

After the thermal treatment, the degradation rate was similar to conventional zirconia, suggesting that residual stresses play a major role on the variation of transformation rate. Similar studies have been performed to assess the role of residual stresses on LTD resistance for surface treatments like grinding [13,14,16], sandblasting [14] and airborne-particle abrasion [15]. These studies agree that residual stresses affect the kinetics of degradation. It has been demonstrated in [19] that tensile stresses favor the *t → m* transformation while compressive stresses can decrease the driving force for transformation, thanks to their constraint effect. For instance, Deville *et al.* [16] showed that a small amount of compressive residual stresses can increase the resistance to LTD of 3Y-TZP.

In LP samples the presence of residual stresses can be detected in the widening of XRD peaks and in the deformed crystalline structure observed in TEM images [REF], but precise quantification is difficult because they are localized very close to the surface of the material. The presence of monoclinic twins around crack tips is known to be a source of compressive stress in the surrounding tetragonal matrix [14], so it could be the origin of such residual stresses that cause the deceleration in the propagation of the transformation front.

The STEM image of the transformed layer in the FIB-cut lamella of LP sample after 5h of accelerated test (fig. 6B, F) shows that the *m*-phase in the transformed grains is twinned by self-accommodating variants causing micro-cracking and surface uplifts (see fig. 7A, B), as previously reported in [24] for not treated 3Y-TZP. Therefore, the transformation morphology and propagation resemble strongly that of not treated 3Y-TZP and the variation in transformation rate may then be attributed to a deceleration of the transformation front attributed to residual stresses. Similar observations have been recently reported in a paper by Cotič *et al.* [15] on 3Y-TZP abraded with airborne particles, where they showed that LTD progressed with different velocities depending locally on the microstructure of the material. Transformation rate was slower in the volume affected by surface treatment (mainly due to recrystallization, residual compressive stresses and possibly texturization) and reached the same speed as in not treated 3Y-TZP when passing through the not affected bulk material.

Directional grain growth does not to influence significantly the LTD kinetics. Columnar grains, being slightly larger in size than normal equiaxed grains, may have a destabilizing effect on the *t*-phase [12]. However, since the thermal treatment does not cause recrystallization, their role on the deterioration of LTD resistance of LP samples has to be secondary.

* 1. *annealing post laser patterning: effect on LTD kinetics(LP+TT samples)*

The annealing treatment increases the resistance to LTD of laser patterned 3Y-TZP (see kinetics curve in fig. 3).The annealing treatment was performed on LP samples relieving residual stresses and reverting monoclinic phase to tetragonal in order to assess their role on LTD kinetics. Experimental results showed that the thermal treatment does not alter the surface topography produced by laser patterning, nor causes recrystallization or cracks closure. The main differences observed are the *m → t* transformation, stress relief, surface grains rounding, cracks tip blunting and deactivation of color centers. Texture in the *t*-phase was preserved after thermal treatment, and even increased. In fact, it was possible to detect it with XRD also in Bragg Brentano configuration. This larger amount of textured *t*-phase can be attributed to the reversion of *m* *→ t* phase [REF].

The kinetics curve after thermal treatment has *Vm0* = 0% with a long incubation time and a curve slope similar to that of not treated 3Y-TZP.

The higher LTD resistance of LP+TT comes from the longer incubation time. This first step of nucleation and growth of monoclinic phase takes place on the surface of the material, where the contact with water molecules triggers transformation. The initial period of incubation, during which the nuclei of the *m*-phase are forming and growing until reaching the critical size, is longer for a material with a tetragonal structure free of residual stresses and crystal-lattice deformation [20]. For the LP+TT samples, the nucleation of the monoclinic phase can be retarded due to the existence of texture in the tetragonal phase. If the ferroelastic domains are smaller than the grain size, they are known to hinder *t → m* transformation making 3Y-TZP highly resistant to LTD as demonstrated by Jue *et al.* in [27]. This has been observed for other surface treatments like grinding [13] and sandblasting [14] where it was reported that this combination of temperature and time does not modify the textured state of 3Y-TZP. In this work we observed that texture was preserved after thermal treatment, and even increased. This larger amount of textured *t*-phase can be attributed to the reversion of *m* *→ t* phase [REF]. Therefore, we believe that texture has an important role in retarding transformation (especially after the annealing treatment) but may not play a significant role in the variation of transformation rate. In LP samples, although presenting texture as well, monoclinic phase was already present suppressing the incubation period. In this case the existence of texture did not improve performance.

Another contribution to the retardation of LTD may come from the shallow network of microcracks on the surface. The cracks could hinder the lateral propagation of transformation on the surface, avoiding transmission of stresses from a transformed grain to neighboring untransformed grains. Degradation is an autocatalytic phenomenon and the microcracks net can accommodate the deformations without generating stress. Again, in LP samples this beneficial action cannot be appreciated because of the reciprocal distribution of monoclinic phase and microcracks. The m-phase is in fact concentrated around microcracks tips below the first layer of grains, where the accommodating effect of open microcracks cannot be appreciated.

Once the degradation front is well below the surface, it propagates with the same kinetincs as a NT sample. This can be attributed to stress relief and restored microstructure, as discussed in previous section.

1. **CONCLUSIONS**

Laser patterning decreases the resistance to LTD of 3Y-TZP. The presence of monoclinic phase and residual stresses caused by the laser treatment modifies the transformation kinetics, so that an overall enhancement of LTD has been observed.

A subsequent thermal treatment at 1200°C during 1 hour anneals the compromised microstructure and enhances LTD resistance. The transformation is delayed thanks to a long incubation period, which is a result of *m → t* phasereversion and texturization of the *t*-phase aas well as the existence of a microcrack network that obstructs autocatalytic tranformation. The delay in *t → m* transformation makes the annealed-laser patterned material even more resistant to LTD than not treated 3Y-TZP.

In order to ensure the long-term integrity of laser patterned 3Y-TZP an annealing treatment at 1200°C during 1 is therefore recommended.

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