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Original Article

Low temperature degradation of laser patterned 3Y-TZP: Enhancement of resistance after thermal treatment

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ABSTRACT

The aim of this study is to characterize the resistance to low temperature degradation (LTD) of the surface of dental-grade zirconia (3Y-TZP) patterned with a Nd:YAG laser (532 nm harmonic and pulse duration of 10 ns) employing an interference setup.

Laser patterning decreases the resistance to LTD of 3Y-TZP because of the presence of monoclinic phase and residual stresses, induced by the thermal shock during laser-material interaction. A thermal treatment (1 h at 1200 °C) anneals the affected microstructure and increase the resistance to LTD of laser patterned 3Y-TZP. Transformation delay may be attributed to monoclinic phase reversion, texture in the tetragonal phase and the existence of a net of shallow microcracks on the surface, accommodating autocatalytic transformation.

1. Introduction

Tetragonal Zirconia Polycrystal stabilized with 3 mol% Y_2O_3 (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 [5–7]. 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 [8]. All these are highly desirable characteristics for biomedical applications [7].

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 [9] and [10].

Laser pulse melts locally the substrate and capillary forces generated thanks to temperature difference on the surface cause material flow and pattern formation [11]. Due to the shortness of the laser pulse and the low thermal conductivity of 3Y-TZP [12], 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 $t \rightarrow m$ phase transformation, texturization of *t*-phase and residual stresses and strains. Furthermore, the highly energetic laser irradiation activates color

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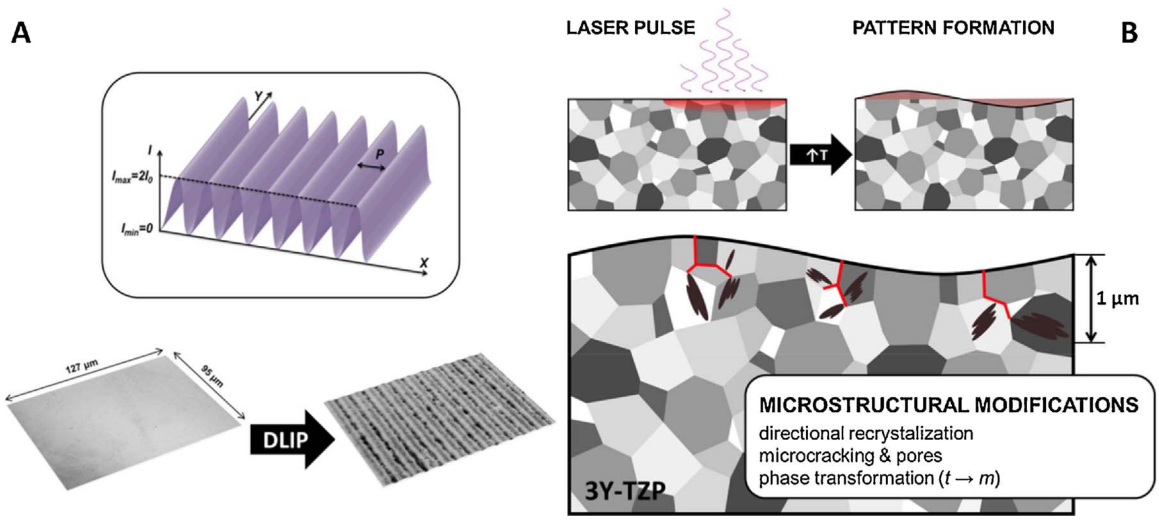

Fig. 1. Schematic representation of DLIP technique. (A) 3Y-TZP surface before (left) and after (right) laser patterning; laser intensity distribution on the treated surface is represented in the inset. (B) Pattern formation mechanism and laser-induced modifications in the microstructure of 3Y-TZP.

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 [13].

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 [14]. 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 [15,16].

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 [17]. 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 [18,19], sandblasting [19] and air-borne particle abrasion [20] are able to increase the resistance to LTD of 3Y-TZP while soft polishing [21,22] and acid etching [23] 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 [20] and rough polishing [21]. On the contrary, it has been demonstrated that tensile residual stresses reduce LTD resistance of 3Y-TZP [21,22,24].

Laser pattering induces several microstructural modifications that may affect the LTD resistance [11]. These features are mainly shallow microcraking, grains elongation, surface texture, $t \rightarrow m$ transformation and possibly residual stresses, which have been proven as possible causes of modification in LTD resistance of zirconia materials [17,25].

At date, there has been no report on the LTD resistance of laser patterned 3Y-TZP. 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.

2. Materials and methods

2.1. Material processing

Commercially available powder of Tetragonal Polycrystalline Zirconia stabilized with 3% molar Y_2O_3 (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 2 mm 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/cm^3 (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 h, 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).

2.2. Laser patterning

A Q-switched Nd:YAG laser (Spectra Physics Quanta-Ray PRO210) with a fundamental wavelength of 1064 nm was employed in the DLIP setup. The output wavelength of 532 nm obtained by second harmonic generation was 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/cm^2. 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, as schematized in Fig. 1. It can be described by:

$$I(x, y) = I_o\left[cos\left(\frac{4\pi x}{\lambda}\sin\alpha\right) + 1\right] \quad (1)$$