EFFECT OF Er,Cr:YSGG AND DIODE LASER TREATMENT ON SURFACE PROPERTIES OF 3Y-TZP FOR DENTAL APPLICATIONS

Masters Thesis
Presented in partial fulfillment of the requirements for the Degree of Master of Science in the Graduate School of The Ohio State University

By

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ABSTRACT

Purpose: The purpose of this study was to investigate the effect of Er,Cr:YSGG, diode laser and a combination of diluted hydrofluoric acid and diode laser on the flexural strength, surface topography and crystalline phase of 3Y-TZP. Methods: Partially stabilized zirconia powder (TZ-3YE, Tosoh® USA Inc.) was compressed in a 25mm diameter silicone mold at 300 MPa using a cold isostatic press for 10 minutes. The cylindrical blanks were sintered at 1500°C for 2 hours at a heating rate of 5°C/min and furnace-cooled. A total of 120 samples (1.8 mm thick) were randomly assigned into four different groups (n=30 per group). Extreme clinically relevant conditions were applied with Er,Cr:YGSS, and diode laser to the samples for a total of 2 minutes. A third group had a surface graphite coating applied and a solution of diluted hydrofluoric acid prior to diode laser treatment. The root mean squared surface roughness (R_{rms}) was measured on atomic force micrographs before and after the various laser treatments. Scanning Electron Microscopy (SEM) was done in order to confirm change in roughness for the etched and diode laser group. The biaxial flexural strength was tested using a ball-on-ring-of-balls fixture on a Universal Testing Machine. Crystalline phases were analyzed by x-ray diffraction (XRD). Statistically significant differences between groups were assessed by ANOVA and Tukey’s test (p≤0.05). The biaxial flexural strength data was analyzed using Weibull statistics. Results: In the pilot study, microcracking was observed only in experimental groups treated with a surface graphite coating. This was confirmed by
an optical micrograph and SEM. X-ray diffraction revealed no phase transformation for the experimental groups. No surface alteration was observed for groups treated with Er, Cr:YSGG or diode laser. Concurrently, marked surface roughening was observed after diode laser treatment combined with diluted HF application. There was no statistical difference between Er, Cr:YSGG groups and Diode Laser groups before or after laser treatment \((1.57\pm0.22\text{nm} \leq R_{\text{rms}} \leq 1.87\pm0.35\text{nm})\). A significant difference \((p < 0.001)\) was measured for the diode/HF group before \((1.89\pm0.19\text{nm})\) and after laser treatment \((15.10\pm1.85\text{nm})\). SEM confirmed a change in surface topography and evidence of roughness for diode/HF group. The crystalline phase analysis by means of x-ray diffraction (XRD) revealed only tetragonal phase after laser treatment for all tested groups. The Er, Cr:YSGG group exhibited the highest mean flexural strength \((1245.5\pm148.0 \text{MPa})\), followed by the diode laser group \((1173.5\pm166.6 \text{MPa})\) and the control group \((1113.9\pm119.9 \text{MPa})\). There was no statistically significant difference between Er, Cr:YSGG laser, diode laser and control groups \((p>0.05)\). The group treated with a combination of diluted HF and diode laser exhibited significantly lower mean biaxial flexural strength \((799.7\pm320.8 \text{MPa})\) than the remaining three groups \((p<0.001)\). The control group exhibited the highest Weibull modulus \((m=12.53)\), followed by the Er, Cr:YSGG group \((m=10.21)\), the diode laser group \((m=7.93)\) and the diode/HF group \((m=2.60)\).

**Conclusion:** Under extreme clinically applicable conditions, the use of Er,Cr:YSGG and Diode Lasers caused no significant difference in flexural strength, roughness values and crystalline phase compared to the control group. Diode/HF treatment would be precluded for any clinical application due to low Weibull modulus and possibility of high flaw population.
DEDICATION

I would like to dedicate this research project to my family, friends and mentors
for their support during my residency at The Ohio State University.
ACKNOWLEDGMENTS

I would like to express my gratitude to Dr. Isabelle Denry for her tremendous dedication and time spent on this research project. Her teaching and helping skills were always excellent.

I would also like to express my gratitude to my advisor Dr. Julie Holloway and Dr. Purnima Kumar for their intellectual support on this project.

I would also like to thank Dr. Meade Van Putten for giving us the opportunity to use his Biolase.
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CHAPTER 1

INTRODUCTION

In our modern society, esthetic dentistry has become one of the major fields of interest. New advances in dental ceramics have led to the application of yttrium-stabilized tetragonal zirconia (3Y-TZP) as an alternative for fixed dental restorations.\(^1\) Zirconia has several important characteristics that make the material suitable for dental applications: biocompatibility, good mechanical properties, better esthetic properties than metal, and high fracture toughness.\(^2,3\) With new technologies in milling and direct machining, zirconia has increased in popularity.\(^4\)

In dental applications, zirconia can be utilized in multiple applications. Sub-frames for single crowns and fixed partial dentures have become a substitute for a conventional metal substructure, thereby enhancing esthetics.\(^5,6\) Zirconia is also an option in the fabrication of dental implant abutments, helping to avoid the transmission of a metallic hue through the gingival tissues. More recently the introduction of zirconia implants, endoposts and orthodontic brackets have been incorporated in clinical applications.\(^4\) In addition, zirconia is very well tolerated by human tissues, exhibits low bacterial adhesion in the oral cavity and has low thermal conductivity.\(^7\)

Zirconia is a polymorphic material that exists in three different crystallographic forms, giving the material excellent physical and mechanical properties.\(^8\) These forms are: monoclinic, tetragonal and cubic.\(^9\) The monoclinic form is stable at room
temperature, stimulation by heat and energy can transform it into the tetragonal form.\textsuperscript{10} The tetragonal form is stable at temperatures between 1170ºC and 2370ºC.\textsuperscript{11} The cubic form exists up to the melting point at 2680ºC.\textsuperscript{12} The transformation of the tetragonal form of zirconia into the monoclinic form is reversible upon heating and cooling. This transformation occurs around 950ºC and is accompanied by volumetric expansion of 4.5\% as temperature increases and volumetric contraction as temperature decreases.\textsuperscript{8} Also during cooling, a smaller expansion occurs when the cubic form transforms into tetragonal form of 2.13\%.\textsuperscript{9}

Volumetric expansion caused by the transformation of the crystallographic forms of pure ZrO\textsubscript{2} will induce high stresses during cooling from high temperatures. This stresses cause cracking, leading to a catastrophic failure upon cooling.\textsuperscript{11} Cracking upon cooling can be avoided by incorporating different oxides into the zirconia (doping). Alloying ZrO\textsubscript{2} with oxides such as magnesium oxide (MgO), cerium oxide (CeO\textsubscript{2}), calcium oxide (CaO), or yttrium oxide (Y\textsubscript{2}O\textsubscript{3}) will help to stabilize the tetragonal form at room temperature to prevent cracking.\textsuperscript{10,13,14}

Some biomedical zirconia is partially stabilized with 3 mol\% yttrium oxide (3Y-TZP) to help achieve the desired physical and mechanical properties. The stability of the tetragonal phase depends on the grain size, yttria content and stresses upon cooling.\textsuperscript{10} Tetragonal zirconia can be fully stabilized with 8mol\% yttria, however concentrations above or below 3mol\% yttria have been shown to decrease the strength of the ceramic.\textsuperscript{15} A stable tetragonal form helps control the stresses incorporated during the tetragonal to monoclinic phase transformation, creating a material with higher toughness, arresting crack propagation and making it suitable for dental
In 1975, Garvie was the first to describe this process known as 
*transformation toughening*, a unique property where transformation between different 
crystallographic forms when stress is applied “self-heals” cracks. In addition 
microcrack toughening, crack deflection and contact shielding also help toughen 
zirconia based ceramics.

Multiple research studies have shown that surface treatments on 3Y-TZP can trigger a 
tetragonal to monoclinic stress-induced phase transformation. 3Y-TZP when 
subjected to external stresses, such as sandblasting or grinding, create an increase in 
volume placing the surface in compression and thereby increasing flexural strength 
and fracture toughness. This is limited by the size and depth of the flaw in the 
surface of Y-TZP however and deep flaws may act as stress concentrators. 
Surface treatments tend to accelerate surface degradation, areas with residual scratches and 
defects may also promote an additional t-m phase transformation. In addition, if 
the material is further subjected to a heat treatment, this may have a counteracting 
effect, causing a reverse m-t transformation and leading to a degradation in 
strength.

It has been documented in the literature for more than 20 years that 3Y-TZP can be 
affected by an aging phenomenon known as low temperature degradation (LTD). 
First reported by Kobayashi, LTD is a slow t-m transformation that occurs in the 
surface grains, in a humid environment at low temperatures (150-400C). LTD usually 
originates at the surface of polycrystalline zirconia and later progresses towards the 
bulk of the material, causing an increase in volume, stresses to surrounding grains and 
inducing microcracking, grain pullout and surface roughening that lead to strength
Water penetration exacerbates the process of surface degradation and the transformation from grain to grain. Any detrimental factors that may affect the stability of tetragonal zirconia will exacerbate the susceptibility to LTD. This would include: grain size, amount of stabilizer and presence of residual stresses. This aging phenomenon has been known to cause phase transformation and roughening of the material, leading to wear and fractures, as shown in 1997 by the US Food and Drug Administration (FDA) after failures of zirconia femoral heads for hip prostheses were reported. (http:www.fda.gov/cdrh/steamst.html)

The presence of a cubic phase in zirconia has been shown to have detrimental effects on the longevity of 3Y-TZP. When subjected to temperatures above 1550°C, it can achieve a dual microstructure, including cubic and tetragonal grains. This may lead to an enrichment of yttria in the cubic grains, decreasing the stability of neighboring tetragonal grains. Cubic grains will act as nucleation sites for further t-m transformation, accelerating the ageing process. This transformation will also affect the strength of the material.

The use of zirconia in implant dentistry has been reported in the literature for implant abutments, substructures for crowns and fixed partial dentures and more recently zirconia implants. It has been reported that zirconia implants while in intimate contact to bone, in an undisturbed wound healing period can achieve successful osseointegration. Peri-implant tissues have shown to react successfully to zirconia implant surfaces, achieving healthy soft tissues. This biocompatibility and strength make zirconia a possible option for dental implant material. One of the complications encountered in implant dentistry is local infection of the peri-implant tissues due to
poor oral hygiene. Contamination by oral microorganisms may lead to inflamed, swollen and bleeding tissues around the implant surface. Various techniques to treat tissues surrounding implants have been advocated, dental lasers being one of the most effective methods due to its haemostatic effects, bactericidal effects and decontamination of the implant surface.\textsuperscript{32}

Dental lasers provide an alternative to conventional surgical procedures, offering the possibility of working both on hard and soft tissues. The most common lasers used in dentistry are: the neodymium-yttrium aluminum garnet laser (Nd-YAG), the erbium-yttrium aluminum garnet laser (Er-YAG), CO\textsubscript{2} laser and diode lasers.\textsuperscript{33} Some of the indications of dental lasers include: peri-implantitis, implant uncovery, gingivectomy, frenectomy, soft tissue incisions, crown lengthening, sulcular debridement, tooth preparations (enamel, dentin), etc.\textsuperscript{34} Contraindications for laser therapy are present in patients who are allergic to topical or local anesthetics, or have heart disease, bleeding disorders or an immunologic deficiency. The advantage of dental laser treatment include: reduced amount of bacteria, good hemostasis, reduced trauma and pain and time management. Main disadvantage of lasers is the limited possibility of side cutting and shaping action.\textsuperscript{34}

Clinically, dental lasers utilize a focal point, which refers to the point where the beam is reduced to a minimum. The final target of the laser is called the irradiated spot size and is where the greatest amount of energy is emitted. The smaller the diameter of the beam (closest space between fiber tip and spot size) represents a higher power density. The rate at which energy is generated by a laser is called laser power, expressed as joules or watts. The term total energy represents the total energy utilized
during a procedure and is also expressed as joules. The basic laser components include a pumping mechanism that is responsible for providing the initial energy so that stimulated emission can occur within the active medium and an optical resonator collimates the photons and the laser light is produced. There are different emission and delivery modes in which lasers can be used: continuous wave emission and free running pulse. All types of emission will produce a thermal effect on the target and temperature must be controlled to avoid adverse reactions in tissue.\textsuperscript{35}

The use of laser therapy for the treatment of peri-implantitis around titanium dental implants has been reported and favorable results have been noted after 3 and 6 months of healing.\textsuperscript{36} With the recent introduction of zirconia implants, several studies have evaluated the surface of 3Y-TZP after laser treatment, simulating a clinical setting.\textsuperscript{31} SEM analysis has shown that Er:YAG and diode lasers cause no visible surface alteration as compared to untreated surfaces. Undesirable effects were noted on zirconia when the CO\textsubscript{2} laser was applied, severe melting and cracking was observed. No alteration of mechanical or physical properties has been reported however.\textsuperscript{31}

One of the clinical problems encountered when using zirconia restorations that are cemented to natural teeth is that the cement cannot bond to the surface of the zirconia. Multiple surface treatments of high strength ceramics have been done with the objective of achieving a rougher surface that enhances a better mechanical bond. Treating the surface of zirconia with lasers has shown to be an effective way to achieve a higher bond strength.\textsuperscript{37} Laser treatment with Nd:YAG has shown better results than conventional sandblasting with aluminum oxide and the Rocatec system when using resin-based materials.\textsuperscript{38} It is important to control the laser settings (power,
pulse) in order to prevent damage of the zirconia. Using Er:YAG power settings above 200mj have shown to produce severe cracking when applied in the presence of a graphite coating.\textsuperscript{37} In addition, enhancing the wettability of zirconia based ceramics has also been tested. After Nd:YAG laser treatment, it was shown that an increase in roughness influenced the wettability characteristics, having beneficial changes in the way biological fluid interacts in the bone-implant interface.\textsuperscript{39}

The aim of this study was to evaluate the effect of different clinically relevant settings of the Er,Cr:YGSS laser and Diode laser on flexural strength, crystallographic form and surface topography of 3Y-TZP.

It was hypothesized that Er,Cr:YGSS and Diode laser irradiation would affect flexural strength, crystallographic form or surface topography of 3Y-TZP under simulated clinical settings. The null hypothesis was that there would be no difference in flexural strength, crystallographic form, or surface topography between groups for Er,Cr:YGSS and Diode laser under clinically applicable conditions.
CHAPTER 2

MATERIALS AND METHODS

2.0 Specimen Preparation

Partially stabilized zirconia powder (TZ-3YE, Tosoh® USA Inc.) was compressed in a 25 mm diameter silicone mold at 300 MPa using a cold isostatic press (Flow Autoclave Systems, Inc.) for 10 minutes. The chemical analysis of the powder is given in table 2.1; as provided by the manufacturer. The cylindrical blanks were pre-sintered at 850°C, sectioned into discs (1.8 mm thick) using a low speed wet diamond saw (Isomet™ Low Speed Saw). A total of 120 samples were randomly assigned into four different groups (n=30 per group). All samples were then sintered for 2 hours at a heating rate of 16°C/min and furnace-cooled. All specimens had an adhesive paper template in order to control the spot size during laser irradiation.

<table>
<thead>
<tr>
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<th>Specification</th>
<th>Result of Analysis</th>
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<tr>
<td>Y2O3 %:</td>
<td>4.95 ~ 5.35</td>
<td>5.28</td>
</tr>
<tr>
<td>Al2O3 %:</td>
<td>0.15 ~ 0.35</td>
<td>0.249</td>
</tr>
<tr>
<td>SiO2 %:</td>
<td>Max. 0.02</td>
<td>0.004</td>
</tr>
<tr>
<td>Fe2O3 %:</td>
<td>Max 0.01</td>
<td>Max 0.002</td>
</tr>
<tr>
<td>Na2O %:</td>
<td>Max 0.04</td>
<td>0.024</td>
</tr>
<tr>
<td>Ig-loss %:</td>
<td>Max 1.2</td>
<td>0.76</td>
</tr>
<tr>
<td>Specific Surface Area m²/g:</td>
<td>13 ~ 19</td>
<td>15.1</td>
</tr>
<tr>
<td>Crystallite Size Å:</td>
<td>Not specified</td>
<td>260</td>
</tr>
</tbody>
</table>

Table 2.1. Chemical Analysis of Tosoh Zirconia Powder as provided by the manufacturer. Lot No.Z306234P
2.1 Pilot Study

In order to assess the response of 3Y-TZP to laser surface irradiation, a pilot study was conducted, with various experimental settings. This settings are summarized in Table 3.1.

2.2 Treatments

The various groups consisted of a control group, two laser treatment groups with clinically relevant settings and one laser group with experimental settings, most likely to induce surface alterations. The first laser treatment group consisted of samples irradiated with Er,Cr:YSGG, Waterlase MD Turbo (BioLase Technology, Inc) with a fiber-optic delivery system. A 1,000 µm diameter fiber tip was used with a power setting of 4.5 watts and a pulse frequency of 15 pps. The water setting was 95% and total exposure time to the laser was 2 minutes. A distance of approximately 1mm was kept between the laser tip and the specimen surface. The second laser treatment group consisted of samples irradiated with Diode laser, KaVo GENTLEray 980 Classic (KaVo Dental Corporation) with a laser fiber diameter of 300 µm. The power selected was 6 watts, in a continuous mode for a total time of 2 minutes, at a distance of approximately 1mm from the specimen surface. The experimental group consisted of samples irradiated with Diode laser, KaVo GENTLEray 980 Classic (KaVo Dental Corporation). The same parameters for group 2 were utilized. In addition, the samples were coated with graphite pencil to achieve better laser absorption and a solution of hydrofluoric acid (HF) was applied prior to laser irradiation. The last group received no surface treatment or irradiation and served as control.
2.3 Surface characterization

One specimen per group was polished (Struers RotoPol-15) to a 0.5 µm finish using a series of abrasives ending with diamond pastes. Each sample was ultrasonically cleaned in ethanol prior to atomic force microscopy (AFM) examination in contact mode (di-CP-II scanning probe microscope, Veeco Instruments Inc.). Specimens were indented with a microhardness tester in order to enable the identification of the same location before and after laser treatment. In addition, the surface of each specimen was characterized before and after laser irradiation. Roughness measurements (R\textsubscript{rms}) were performed on AFM images (25 x 25µm) \((n=6)\) before and after treatment.

2.4 Crystalline Phases

The crystalline phases were analyzed by x-ray diffraction (XRD) on bulk specimens before and after treatment. Scans were performed in the two-theta range 27-32 degrees at a scanning rate of 0.2 degrees per minute (Miniflex II diffractometer, Rigaku Corp.; \(\lambda\text{CuK}\alpha =1. 5406\text{Å}\)). The x-ray diffraction was done in order to identify any tetragonal to monoclinic phase transformation in the zirconia disks after laser treatment.
2.5 Biaxial Flexural Strength

Specimens (n=30 per group) were tested in biaxial flexure mode with a ball on ring-of-balls fixture at a crosshead speed of 0.5 mm/min using a Universal Testing machine (Instron Corp.). The maximum radial and tangential stresses for the specimens are equal and were calculated from the following equation:

\[
\sigma_m = \frac{3P(1+\nu)}{4\pi t^2} \left[ 1 + 2\ln\left(\frac{a}{b}\right) + \frac{(1-\nu)(1+\nu)}{2} \left(1 - \frac{b}{a}^2\right) \right] \left(\frac{a^2}{R^2}\right)
\]

Where: 
- \( P \) = load
- \( b \) = radius of uniform loading at center
- \( t \) = disk thickness
- \( R \) = disc radius
- \( a \) = radius of support circle
- \( \nu \) = Poisson’s ratio

2.6 Statistical Analysis

The data collected from the test groups were analyzed by ANOVA followed by Tukey’s test. Any analyses generating a \( p \)-value of <0.05 were considered statistically significant. The reliability of the 3Y-TZP was analyzed using the Weibull distribution function. In the Weibull modulus, \( m \) is the slope of the \( \ln(\ln(1/1-P_t)) \) vs. \( \ln(\text{strength}) \) plots.
CHAPTER 3

RESULTS

3.1 Pilot Study

In order to explore the effect of laser treatment on the surface of 3Y-TZP, a pilot study on polished specimens \( n=3 \) per group was conducted. The various conditions tested for both Er,Cr:YSGG and diode laser groups, including time of exposure, power setting, pulse rate, amount of water, and type of surface coating are reported in tables 3.1 and 3.2, respectively. In the case of the diode laser groups, the surface was kept moist by repeatedly adding drops of distilled water. Some of the groups were coated with graphite to promote laser radiation absorption. A 1mm-diameter fiber tip was used for both Er,Cr:YSGG and diode laser treatments. The surface topography was assessed by optical microscopy in differential interference contrast. Results of the microscopic assessment are presented Tables 3.1 and 3.2. A representative optical micrograph with surface microcracking is presented in Figure 3.1. Scanning Electron Microscopy (SEM) was performed for group F (4.5W, 15 pps, 2 minutes) to investigate the extensive microcracking noted by optical microscopy. Micrographs showing the surface damage are displayed in Figure 3.2 (A and B). Zirconia grains are clearly distinct, showing evidence of thermal etching. Dendritic formations of elongated grains show further evidence of localized high temperatures (Figure 3.2A). Figure 3.2B reveals large polygonal grains characteristic of cubic zirconia, with intergranular cracking.
X-ray diffraction (XRD) on bulk specimens revealed only tetragonal phase for all treatment groups.

Based on the results of this pilot study and in order to reproduce the most extreme clinically relevant conditions, one set of parameters was selected for each Er, Cr:YSGG laser and diode laser. Coating with graphite was eliminated for both groups. A third treatment group targeted at producing an etched surface was added. This group combined graphite coating, diluted hydrofluoric acid (HF) application and diode laser treatment.

**TABLE 3.1.** Laser parameters used to treat polished 3Y-TZP surface with Er,Cr:YSGG Laser.

<table>
<thead>
<tr>
<th>Group (n=3)</th>
<th>Power (W)</th>
<th>Pulse rate (pulse per second)</th>
<th>Time (Min)</th>
<th>Water (%)</th>
<th>Coating (Graphite)</th>
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<td>A</td>
<td>2.25</td>
<td>50</td>
<td>4</td>
<td>90</td>
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<td>No detectable alteration</td>
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<tr>
<td>B</td>
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<td>5</td>
<td>90</td>
<td>No</td>
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<td>C</td>
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<td>3</td>
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<td>No</td>
<td>No detectable alteration</td>
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<td>D</td>
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**TABLE 3.2.** Laser parameters used to treat polished 3Y-TZP surface with diode laser.

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<th>Group (n=3)</th>
<th>Power (W)</th>
<th>Total Time (sec.)</th>
<th>Water</th>
<th>Coating (Graphite)</th>
<th>Polished Surface</th>
<th>Microscopic assessment</th>
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Figure 3.1. Representative optical micrograph showing surface microcracking after Er,Cr:YSGG laser treatment of pilot group E.
Figure 3.2. Scanning Electron Micrographs of zirconia surface after Er, Cr:YSGG laser treatment of pilot group F. (A): Evidence of thermal etching and cracking, elongated grains with dendritic organization could indicate partial surface melting. (B): large polygonal grains are typical of cubic zirconia, which could also indicate that very high temperatures were reached locally.
3.2 Surface characterization – Roughness Analysis

Representative atomic force micrographs of polished specimens for each group are displayed in Figure 3.3 (A through F). Surface porosity helped in identifying the same location before and after laser treatment. No surface alteration was observed for groups treated with Er, Cr:YSGG (Figures 3.3A and B) or diode laser (Figure 3.3C and D). However, marked surface roughening was observed after diode laser treatment combined with diluted HF application (Figures 3.3E and F).

The mean square roughness ($R_{rms}$) results after various laser treatments for tested groups are displayed in Figure 3.4. There was no statistical difference between Er, Cr:YSGG group and Diode Laser group before and after laser treatment ($1.57\pm0.22\text{nm} \leq R_{rms} \leq 1.87\pm0.35\text{nm}$). A significant difference ($p < 0.001$) was measured for the diode/HF group before ($1.89\pm0.19\text{nm}$) and after laser treatment ($15.10\pm1.85\text{nm}$). Surface roughening after treatment with combined diluted HF application and diode laser can be clearly seen on Figure 3.5.
Figure 3.3. Atomic Force Micrographs of polished specimens before and after laser treatment. Er, Cr:YSGG group: 4.5W-15PPS-2 min: (A) Before, (B) After. Diode laser group: 6W-2Min: (C) Before, (D) After. Etched diode laser group: 6W-2Min: (E) Before, (F) After. Arrow indicates same location before and after treatment.
Figure 3.4 Mean surface roughness (Rrms) of tested groups before and after laser treatment. No significant difference noted between Er, Cr:YSGG and Diode laser groups. Significant amount of roughness observed on Diode laser and etching group after laser treatment. Horizontal line indicates no significant difference (p>0.05).
Figure 3.5. Scanning Electron Micrographs of 3Y-TZP surface: polished specimen (A) and after diluted HF application combined with diode laser treatment (B).
3.3 Crystalline Phases Analysis

The crystalline phases of various test groups were examined before and after laser treatment by means of x-ray diffraction (XRD). X-ray diffraction patterns are displayed in Figure 3.6. Scans were performed in the 27-32 two theta range in order to detect any t-m phase transformation of zirconia after laser treatment. Only tetragonal phase was identified after laser treatment for all tested groups.
Figure 3.6. X-ray diffraction patterns of polished specimens for each group after laser treatment.
3.4 Biaxial Flexural Strength and Weibull Modulus

The results for the mean biaxial flexural strength are graphically displayed in Figure 3.7. The Er, Cr:YSGG group exhibited the highest mean flexural strength (1245.5±148.0 MPa), followed by the diode laser group (1173.5±166.6 MPa) and the control group (1113.9±119.9 MPa). There was no statistically significant difference between Er, Cr:YSGG laser, diode laser and control groups (p>0.05). The group treated with a combination of diluted HF and diode laser exhibited significantly lower mean biaxial flexural strength (799.7±320.8 MPa) than the remaining three groups (p<0.001).

The results of the Weibull statistical analysis are represented in Figures 3.8. The control group exhibited the highest Weibull modulus (m=12.53), followed by the Er, Cr:YSGG group (m=10.21), the diode laser group (m=7.93) and the diode/HF group (m=2.60).
Figure 3.7: Mean biaxial flexural strength of various test groups. Horizontal line indicates no significant difference ($p>0.05$)
Figure 3.8. Weibull plots for treatment groups after laser treatment (A) Er, Cr:YSGG: 4.5W-15PPS-2min. (B) Diode laser: 6W-2min. (C) Diode laser and etching: 6W-2min. (D) Control
CHAPTER 4

DISCUSSION

Pilot Study

The pilot study was conducted on polished specimens in order to gain a basic understanding of the effect of laser treatment on the surface of 3Y-TZP. Various clinically relevant laser settings were explored, as well as some experimental settings representing more extreme conditions. A graphite surface coating was applied to the polished 3Y-TZP specimens prior to laser treatment in order to optimize laser energy absorption by the ceramic.\textsuperscript{37,38} As reported by Cavalcanti \textit{et al.}\textsuperscript{37} surface deterioration may occur after laser application with high power settings and graphite surface coatings. In the present pilot study microcracking was detected on specimens treated with both Er,Cr:YSGG and diode lasers, with the combination of water irrigation and graphite coating. Similar surface cracking has been previously reported by Spohr \textit{et al.}\textsuperscript{38} and interpreted as micro-explosions due to energy discharge, damaging the graphite coated surface of 3Y-TZP.

After a first inspection by optical microscopy showing evidence of microcracking, scanning electronic microscopy (SEM) was performed for one group after Er,Cr:YSGG laser treatment. As shown in Figure 3.2, SEM confirmed the presence of microcracking and evidence of thermal etching. Elongated grains with dendritic organization bordering crater-like areas could further indicate that partial
surface melting occurred. Large polygonal grains, typical of cubic zirconia were identified at the center of these craters, this could also indicate that very high temperatures were reached locally. The intergranular microcracking observed is likely due to the thermal shock associated with high temperatures, followed by extremely rapid cooling after switch off of the laser beam.

The melting temperature of zirconia has been reported by Subbarao et al. to be around 2716°C. The formation of cubic zirconia has been shown to be detrimental to both aging resistance and stability of 3Y-TZP by causing a depletion of yttrium in the surrounding tetragonal grains, which act as nucleation sites for a spontaneous tetragonal to monoclinic phase transformation. Aging occurs by a slow t-m phase transformation of grains in contact with water or body fluid, leading to surface roughening, grain pull out and micro-cracking. This was linked with a series of fractures of femoral heads in 2001. The presence of cubic grains in laser-irradiated 3Y-TZP, in addition to intergranular microcracking is therefore likely to be further detrimental to the performance of the ceramic.

X-ray diffraction however showed no presence of monoclinic phase, only the tetragonal phase was identified after laser treatment. This indicates that the parameters used in the pilot study did not trigger a t-m phase transformation and no appreciable amount of cubic phase was formed to be detected by XRD. Interestingly, microcracking after either Er,Cr:YSGG or diode laser treatment was observed only in the presence of graphite surface coating. Conversely, it was noted that laser irradiation had no detectable effects on uncoated surfaces. Since no coating is used clinically, our results seem to indicate that under relevant clinical conditions Er,Cr:YSGG and diode
laser radiation treatments do not induce surface alterations or phase transformations in 3Y-TZP ceramics.

Surface characterization – Roughness Analysis

Atomic Force Microscopy examinations on polished specimens before and after laser treatment in the same location, revealed no surface alterations and no significant roughening for both treatment groups corresponding to clinically relevant conditions (Figures 3A - D). These results are in good agreement with a previously published study by Stubinger et al. showing no surface alterations after treatment of Y-TZP with Er: YAG laser at different power settings for 10 seconds.

On the contrary, the experimental group combining graphite coating, diluted HF application and diode laser irradiation showed evidence of significant surface roughening (Figure 3E and F). Surface roughening was also evident after SEM observations on a polished area, compared to an irradiated area (Figure 3.5A and B). Surface roughness data analysis confirmed these findings and revealed significant roughening after HF/Diode laser irradiations, with no statistical significant difference in $R_{\text{rms}}$ observed after treatment with either laser under the highest settings of clinically relevant conditions. This indicates that under these conditions, the surface of 3Y-TZP is left unaltered by laser irradiation.

Previous investigations have been documented using dental lasers for surface roughening of zirconia. Hao et al. reported using Nd: YAG laser to increase the surface roughness of a zirconia-based bioceramic (MgO-PSZ) in order to promote better bone-implant interface. Surface melting and resolidification into a different
microstructure following laser treatment was found to be the major phenomena influencing the wettability characteristics. Other authors have advocated surface treatments with lasers in order to promote micromechanical retention and achieve better bonding properties of adhesive cements to zirconia and other high strength ceramics. Da Silveira *et al.*\(^4^3\) reported higher bond strength values after Nd: YAG laser treatment (2W, 20 pps, 2 min) on In-Ceram Alumina compared to sandblasting (Al\(_2\)O\(_3\)) and sandblasting with a silica coating. (Rocatec Plus). Spohr *et al.*\(^3^8\) also reported higher bond strength values after laser surface treatment of In-Ceram Zirconia with Nd: YAG laser (2W, 20 pps, 2 min), compared to sandblasting (Al\(_2\)O\(_3\)) or sandblasting with silica powder. (Rocatec Plus) Calvacanti *et al.*\(^3^7\) reported laser surface treatments with Er: YAG at multiple power settings (2W,4W,6W, 10 pps, 10 seconds) on 3Y-TZP (Cercon\(^8\)) and Procera Zirconia. Melting, cracking and increased surface roughness were noted when irradiating at 4W and 6W power settings.

*Crystalline Phase Analysis*

X-ray diffraction analysis of specimens after various laser treatments confirmed the presence of only tetragonal phase (figure 3.6). No \(t-m\) phase transformation was detected for the specimens after any of the laser treatments. The presence of monoclinic phase at the surface of 3Y-TZP after aging is easily detected by AFM.\(^4^4\) It is associated with surface roughening and formation of facets, typical of self-accommodating martensitic variants.\(^4^5\) No faceting or signs of monoclinic phase formation was observed after laser radiation using clinically relevant conditions. The group treated with a combination of Diode laser irradiation and diluted HF application exhibited roughening but no evidence of faceting was observed. This confirms the XRD findings, indicating no phase transformation. However, it should be noted that
the \textit{t-m} phase transformation is reversible and that localized high temperatures may have been sufficient to cause the reverse transformation.\textsuperscript{3,45}

\textit{Biaxial Flexural Strength and Weibull Modulus}

The results of the present study revealed that under clinically relevant conditions no statistically significant difference in flexural strength and Weibull modulus were noted between laser treatment groups and the control group. The results obtained for the control group (1245.5±148.0 MPa ; \textit{m}=12.53) are in agreement with previous studies on 3Y-TZP, by Tinschert \textit{et al}., who dynamically evaluated (four point bend test) the flexural strength of 3Y-TZP and reported values of 913±50.3 MPa and \textit{m}=18.4 for the Weibull modulus. Kosmac \textit{et al}.,\textsuperscript{11} reported values of 1021±89.5 MPa and \textit{m} = 10.7 for the flexural strength and Weibull modulus of 3Y-TZP after grinding and sandblasting the surface. However, it should be noted that the sintering temperature and duration was 1530°C for 2 h in one study\textsuperscript{46} and either 1500 °C/ 2 hours or 1550°C/ 4 hours in the other study \textsuperscript{11}while 3Y-TZP in the present study was sintered at 1500°C for 2 hours. It is well established that sintering temperatures influence grain size in 3Y-TZP, higher sintering corresponding to larger grain size.\textsuperscript{8,45} Sintering conditions may therefore explain the slight differences in flexural strength and Weibull modulus among studies. Larger grain sizes are associated with a greater ability to transform into monoclinic phase, and higher strength and reliability. Clearly, the roughening and surface alterations observed with the HF/Diode laser group were detrimental to the flexural strength and reliability of 3Y-TZP. The absence of transformation also indicates that no compressive surface stresses were present after laser treatment, unlike what is usually observed after grinding or sandblasting.\textsuperscript{11,24}
Bonding adhesive dental cements to 3Y-TZP has been under research for several years, the minimal glassy phase present in 3Y-TZP makes the material resist conventional etching methods.\textsuperscript{47,48} Etching with HF cannot be as efficient as in silicate-based materials, perhaps the combination of laser energy and HF successfully opened the Zr-O-Zr bonds and led to surface degradation and etching. As reported by Fang et al.\textsuperscript{49}, in a study of corrosion and erosion of ceramic materials, the interaction of partially stabilized zirconia and 1.5\%HF + 5\%HCl led to the formation of pores and internal corrosion layer, associated with a degeneration of the mechanical properties of the ceramic surface. This confirms that treatment with a combination of graphite coating, diluted HF and diode laser to create micromechanical retentions in zirconia dental restorations is not practical, mainly due to the extremely low reliability of the ceramic after treatment.
The stated null hypothesis for this study was that Er,Cr:YSGG and Diode laser irradiation would not affect flexural strength, crystallographic form or surface topography of 3Y-TZP under simulated clinical settings. This hypothesis was accepted. Within the limitations of this study, we concluded the following for 3Y-TZP:

- Microcracking and surface alterations were observed after laser irradiation only in the presence of a surface graphite coating.
- Only tetragonal phase was detected by x-ray diffraction after the various laser treatments, the absence of phase transformation also indicates that no compressive surface stresses were present after laser treatment, unlike what is usually observed after grinding or sandblasting.
- The combination of graphite coating, diluted HF application and diode laser irradiation created significant surface roughening of 3Y-TZP. This was associated with a significant decrease in mean flexural strength and a low Weibull modulus. This type of treatment cannot therefore be recommended for creating micromechanical retentions in 3Y-TZP.

Further research on laser irradiation of 3Y-TZP in combination with diluted acidic solutions is needed to optimize experimental conditions and create roughening without being detrimental to the mechanical properties of the material. Monitoring of
the temperature with a thermocouple during laser irradiation might help characterize the extent of thermal shock sustained by the specimens during laser irradiation and devise a method to avoid rapid cooling and prevent surface microcracking.
BIBLIOGRAPHY

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