Influence of titanium oxide additions with CO2 laser treatment on the microstructural properties of glazes layer-dental zirconia ceramics

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Abstract: This paper presents the effect of CO2 laser on the glazes layer-dental zirconia ceramics after adding TiO2 nanoparticles to the glazes and study the its improvement. The specimens has been prepared by using CAD/CAM dental machine and sintered at 1530°C. Then the surface was glazed by VITA Glaze with (5% and 10%) of nano-TiO2 additions. The glaze layer were irradiated by continuous CO2 laser of 15Watts as indicated power. It was found that the main phases of the ceramic substrate are tetragonal zirconia with a percentage of alumina in the corundum phase. The glazing of the ceramic substrate led to a change in the X-ray diffraction pattern by the emergence of new phases, thus changing the crystallite size and percentage of lattice strain. The change in grain size measured by AFM technique, ranging from 88.46 nm to 62.18 in addition to changing surface roughness due to the emergence of centers of nuclei and grain growth. Moreover, the addition of TiO2 and laser irradiation changed the residual stresses on the surface, and this was reflected in the increasing hardness values from 575 kg/mm2 to 1215 kg/mm2 after added 5% TiO2 with laser treatment. Generally, addition of 5% TiO2 is better than 10% in terms the structure of the glaze layer surface and hardness, as the additions of 10% need a higher glazing temperature.

Keywords: CAD/CAM; Dental ceramics; CO2 laser; Zirconia; Glazing; Residual stress, Grain size.

1. Introduction
The Stone Age and the Bronze Age were named according to the materials which dominated these historical periods. And therefore Modern era, facing an increasing variety of ceramic materials for industrial or biomedical use, therefore this marked the era of ceramics. Ceramic materials used for medical and dental purposes are called bio-ceramics. Over the years that have passed, Zirconia technology has been encouraged. The rapid development of metal-free dental minerals, which provided a high proportion of Dynamic compatibility, improved aesthetic teeth and increased strength [1]. The addition of “Stabilizing” oxides to pure zirconia allows to generate multiphase materials known as Partially Stabilized Zirconia (PSZ) whose microstructure at room temperature generally consists of cubic zirconia as the major phase, with monoclinic and tetragonal zirconia precipitates as the minor phase [2]. Various oxides, such as yttrium oxide (Y2O3), calcium oxide (CaO) or magnesium oxide (MgO), can be added to zirconia for stabilization, allowing for a quadrilateral shape at room temperature after flocculation [3]. In the early stages of the development, several solid solutions (ZrO2-MgO, ZrO2-CaO, ZrO2-Y2O3) were tested for biomedical applications. But in the following years the research efforts appeared to be more focused on zirconia-yttria ceramics, characterized by fine grained microstructures known as Tetragonal Zirconia Polycrystalline (TZP) [4]. In order to produce glass ceramics, we use controlled crystallization method. We apply heat on the glass material, thus crystals of the structure get nucleated, and they become larger and embedded in the glass matrix [5]. In fact, surface compression layer was found to occur on a wide range of ceramic materials following different treatment processes that acts to strengthen ceramic
material. It can be achieved by thermal tempering, machining and polishing and the application of a glazing layer with a lower coefficient of thermal expansion than the adjacent ceramic material. The CO₂ laser is well suited for the treatment of glazes because its emission wavelength is almost totally absorbed by glass. It was suggested that laser treatment of glass-ceramic surfaces inhibits the formation of microcracks, leading to greater mechanical resistance of the glazes [6]. Therefore, the aim of this study was to evaluate the surface hardness, surface morphology and structure of zirconia dental surface glazing layer. The originality in the subject is to convert part of the amorphous glaze layer into crystallized glass ceramic by adding Nano titanium oxide and laser treatment for better specification.

2. Material and methods

2.1 Specimens preparation

The used Zircon material is from (Easy co) company - Origin of high purity (99.9%) Zircon. The specimens were cut to small cylinders by CAD/CAM dental machine with diameter (0.5 cm) and height (0.5 cm). The specimens were sintered at temperature 1530°C for 120 min as hold time. Glazing process of the surface uses mixture of the following; VITA AKZENT Plus Glaze LT (Low Temperature) of weight (0.060 g) with 3 drops of (VITA AKZENT PLUS, POWDER FLUID) and with two different percentages of TiO₂ (5% and 10%) nanoparticles (< 26 nm), purity ≥ 99.8% supplied by Cheng Du Micxy Chemical Co Ltd – China was added to glaze mixture to produces two different glazing layers. A special low fusing glaze material is now available for ceramics with low firing temperatures. After the completion of glazing process on specimens surfaces, the specimens was dried and firing up to 800°C.

2.2 Irradiation parameters

The experimental procedure of laser engraving is done using a CNC CO₂ laser machine with 10.6 µm wavelength, the beam spot size was used in treatment is 145 µm and output power range from 1-70Watt. Because of the high potential temperature of irradiated porcelain with this wavelength and safety of ceramics, the value of energy output power used is 15Watt, with Overlapping space 0.01 mm. The irradiation was done offline After 10 mm, the size of the beam spot is aimed at the entire specimen surface with speed 500 mm/min and time 4.14 min. The laser hand piece was keep perpendicular to the irradiated surfaces.

2.3 X-ray diffraction

The technique give us information about the measurement phase contrast, crystal size, the crystallization degree and composition material. X-ray diffraction (Shimadzu 6000-XRD) scan range is (20-80 deg.). The mode of scan is a continual scan, scan velocity is (10 deg. /min), and XRD device has X-ray tube Cu( Filter ) (1.5406 Å) , This examination helps us to provide the data necessary to identify the crystal structure of output and phase information. The crystallite size of the structure is estimated by using Scherer's formula:

\[ D_c = \frac{K\lambda}{\beta \cos \theta} \]  \hspace{1cm} (1)

Where K≈0.94 and \( \lambda \) is the wave length of X-Ray used, which is Cu Kα radiation (\( \lambda=1.54 \) Å) and \( \beta \) is the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane. The lattice strain (\( \epsilon \)) was calculated using the formula [7, 8, 9].

\[ \epsilon = \frac{\beta}{4 \tan \theta} \]  \hspace{1cm} (2)

2.4 Atomic Force Microscopy

The Atomic Force Microscopy device (AFM) type SPM-AA 3000 Angstrom (USA) is used in surface science laboratories to obtain grain size and distribution, as well the images with atomic resolutions of 10⁻¹⁰ m or one tenth of nanometer. This type of microscopy can be effectively
applied in the field of specimen to study the surface characteristics of a specimen. The instrument is based on the principle that when a tip, integrated to the end of a spring cantilever, is brought within the interatomic separation between the tip and sample, interatomic potentials are developed between the atoms of the tip and the atoms of the surface.

2.5 Hardness test
Before you perform a hardness test, the surfaces of all specimens were meticulously inspected by a magnifying glass to exclude Samples with no surface defect. The micro hardness was measured by Vickers micro hardness apparatus. for all specimens after surface roughness measurement to ensure that the specimens have the same hardness =330.7 HV. The measurements were made with load of 30 kg for 15 second as a hold time. Three measurements were taken at the center of laser spot and averaged to one value.

3. Results and Discussion
‘Figure 1’ shows the results of crystallite size calculated from X-ray diffraction data. We note from the figure that the crystallite size was 38.08 nm in the case of glaze with laser treatment of the zirconia surface without any addition. That value decreased to 21.34 nm when 5% of nano TiO$_2$ powder was added and the change caused by TiO$_2$ in terms of the appearance of other crystalline phases and decreased surface transparency turned white.

![Figure 1. Crystallite size of specimens: (control: TZP with glazes and with laser treatment).](image)

The decrease in crystalline size is due to the increase in the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane from 0.23 to 0.4 in degrees when adding 5% TiO$_2$ compared to control specimen, as shown in ‘Figure 2’. M. Vashista & S. Paul [12] found that there is a close relationship between the FWHM and the amount of residual stresses between the glazes coating layer and the surface of the ceramic substrate, where increasing the FWHM means increasing the residual stresses. In contrast, it was observed that laser treatment did not significantly affect the crystallite size and FWHM, therefore expect that the laser will not affect the residual stresses between glaze coating layer and ceramics.
The increase in TiO$_2$ percentage up to 10% in the glaze mixture was led to a clear change in crystallite size and increased up to 46.56 nm. This can be attributed to the increased crystalline phases due to increased TiO$_2$ interaction with alumina on the ceramic surface. The doubling of the TiO$_2$ percentage has reduced the FWHM to 0.19 in degrees, which means that the residual stresses will decrease. The removal of the residual stresses significantly may be detrimental to the success of the glazing process, in which a certain amount of residual stresses, especially the compressive stresses should be present between glaze layer and ceramic substrate. This undesirable decline of the residual stresses in the glazing of the ceramic surfaces has been processed and improved by laser treatment. This was observed by increasing the FWHM to 0.23 in degrees with decreasing crystallite size up to 36.7 nm.

In the case of a stress-free material, the inter planner spacing $d$, for a particular reflection (hkl), is constant from one crystallite to another, when it is deformed elastically, the lattice spacing of the crystallites change from their stress free values, and cause a shift in the Bragg angle. The strain calculated from this shift is termed the lattice strain. The lattice strain will depend upon the orientation of the reflecting group of the crystallites with respect to the direction of stress [13].

Percentage of lattice strain behavior is similar to FWHM behavior and the effect of laser treatment is evident on the strain values as shown in ‘Figure 3’.

**Figure 2.** Variation the full width at half maximum (FWHM) with TiO$_2$ addition and laser treatment.

**Figure 3.** Variation the lattice strain with TiO2 addition and laser treatment.
The average of grain size was determined using the Atomic force microscopy (AFM) device as well as the grain size distribution. Figure 4(a) shows the statistical distribution of grain size to the (TZP-Glazes) control specimen, the grain size ranged between 60 and 120.

![Figure 4. Grain size distribution for: (a) control specimen (TZP + glazes with laser), (b) TPZ+glazes+5% TiO2, (c) TPZ+glazes+5% TiO2 with laser, (d) TPZ+glazes+10% TiO2, (e) TPZ+glazes+10% TiO2 with laser.](image)

The statistical distribution diagram of glazes without addition of TiO$_2$ is more skewed to the right and the average grain size of this specimen is 74.26 nm as shown in ‘Figure 5’. The addition 5% of Nano TiO$_2$ for specimen (TZP-Glazes+5% TiO$_2$) led to a change in the grain size distribution of the glaze layer and led to decreasing the amount of the Nano grains. The effect of the addition seems clear in the distribution of granular sizes to extend from 50 nm to greater than 140 nm and the shape of statistical distribution is like to bimodal and symmetrical due to the wide range of granular sizes, as shown in ‘Figure 4’(b). The average of grain size increased up to 88 due to the emergence of crystallized phases of TiO$_2$ reaction with glazing mixture components as shown in ‘Figure 5’[14].
After the treatment by laser of the specimen (TZP-Glazes+5% TiO₂ with laser), there is a clear change in the grain distribution of the glaze surface. The statistical distribution is narrow to a specific range within nanoscale, which is the range from 65 nm to 100 nm as shown in ‘Figure 4’(c). While the average of grain size was decreased to 76.4 nm due to the formation of nuclei formed between the glazes and TiO₂ components with alumina separated on the surface of the ceramic substrate as shown in ‘Figure 5’. The statistical distribution of grain size was repeated by adding 10% of TiO₂, and this distribution was corresponded to the bimodal and symmetrical with in max Nano size granular range less than 100 nm, as shown in ‘Figure 4’(d). The symmetry distribution means more homogeneity in grain size and also obtaining uniform surface in granular distribution, and inhibits the continued growth of granular of glazes mixture. The average grain size was at its lowest value of 62.18 nm, which is due to increased crystallization due to the increase in the amount of TiO₂, which is an important factor in the nucleation and glass-ceramic formation. The laser effect on the 10% TiO₂ enhanced glaze was clear, and the grain size distribution of the specimen in this case is called negatively or left skewed as shown in ‘Figure 4’(e). So that the extent of the distribution of grain sizes is wider to range from 50 nm to 100 nm and the average of grain size increased up to 77.47 nm, due to the effect of the laser on the structure of the glaze layer through the fusion of crystalline nuclei together.

The topography images of glazed specimens taken by using AFM were illustrated in the ‘Figure 6’, the measurement range for all specimens is (2×2 µm). This figure shows 3D topographies profiles under different TiO₂ additives, where the max high (peak-peak) of the grain size was increased with 5% TiO₂ compared to the TiO₂-free coating layer. The value has become 45.32 nm for glazes layer without TiO₂ and decreased to 8.85 nm when 5% TiO₂ was added due to the emergence of crystallization nuclei. The laser effect was evident in removing the high peaks of the grains to reach the value of 2.61 nm. The height of the peaks does not change much when added 10%TiO₂ to glaze mixture and reach to 2.39 nm. The maximum value of the peak-peak of the grain size was obtained when the 10% TiO₂ surface was treated with laser to reach 58.26 nm. This means that there was a large variation in the grain size distribution due to the grain growth caused by the laser treatment.
Figure 6. 3D AFM scan data for: (a) control specimen (TZP + glazes with laser), (b) TPZ+glazes+5% TiO₂, (c) TPZ+glazes+5% TiO₂ with laser, (d) TPZ+ glazes +10% TiO₂, (e) TPZ+glazes+10% TiO₂ with laser.

The roughness was clearly depend on the TiO₂ additions and laser treatment as shown in ‘Figure 8’ The interpretation of the variation in the roughness values corresponds to the change in grain size peak with grain size average and statistical distribution.

Figure 7. Variation of roughness average for different specimens.

Hardness is one of the important mechanical properties of the material surface. It is a measure of the surface toughness of the scratch and wear resistance. The increase in hardness as shown in ‘Figure 8’ is due to increased crystalline phases for glazes added 5% TiO₂ and irradiated by laser, but the hardness dropped after adding 10% of TiO₂ and resumed rising after laser treatment. Increasing of hardness not necessarily to increase the toughness of glazed surface, because the toughness is heavily depends on the grain sizes and distribution. In glazed surfaces, increased hardness can be estimated as an increase in residual surface stresses arising from reaction between the glaze components and ceramic substrate. This is useful if the remaining stresses are in a compressive state and this is due to the difference between the coefficient of thermal expansion of the ceramic substrate and glaze layer [15].

Figure 8. Variation of Hardness for different specimens.

‘Figure 9’ represents the x-ray diffraction pattern for all specimens sintered at 1530°C and glazed with different percentages of frit glass supported with nano titanium dioxide powder. Scheme TZP shows the main structures of the substrate ceramic material without glazing, and it is clear that the components are tetragonal zirconia (t-ZrO₂) and alumina (α-Al₂O₃), which represent the components of toughed zirconia. Alumina increases the toughness when added to zirconia at limited percentage. [10] We also notice that the percentage of cubic phase is low and
the monoclinic phase is absent. After glazing without any addition of TiO\textsubscript{2} and with laser surface treatment, we observe the appearance of amorphous phases between the crystalline phases represented by the peaks of the TZP as in the scheme (TZP-Glazes). These amorphous phases led to atrophy of the α-alumina phase (corundum) [11]. Adding 5\% of TiO\textsubscript{2} to the glazes and without laser treatment, we notice a slight change in the components of the glass layer as in the scheme (TZP-Glazes+5\% TiO\textsubscript{2}), and thus the little (5\%) ratio of the rutile enhanced the appearance of the ceramic glass. While after the treatment of the surface by laser, this process led to the emergence of crystalline phases clearly as in the scheme (TZP-Glazes+5\% TiO\textsubscript{2} with laser), and this indicates the increase in the proportion of glass-ceramic composite.

Figure 9. X-ray diffraction patterns of specimens.
The increase of the TiO$_2$ to 10% without laser treatment led to the emergence of the rutile phase with the increased appearance of crystalline phases in the glass mixture, or the transformation of part of the amorphous glass compounds into crystalline phases, as shown in scheme (TZP-Glazes+10% TiO$_2$). Thus, new characteristics may emerge that may help to improve the properties associated with synthetics such as mechanical properties. After laser treatment, all crystalline phases have become clear, and new phases can be introduced if the surface is treated with higher temperatures. This is evident from scheme (TZP-Glazes+10% TiO$_2$ with laser).

4. Conclusions
The addition of titanium oxide is an important factor in the appearance of crystallized and nucleating agent of ceramic phases due to the interaction with the components of glaze mixture and with alumina in the zirconia components type TZP. Surface treatment by CO$_2$ laser, enhanced the appearance of crystalline phases and the appearance of overlay of glass-ceramic. In addition to the control of grain size, especially in the large additions of titanium oxide (10% TiO$_2$), where the laser increases the grain growth of the glaze layer and thus grain size average was increases. One of the most important roles played by laser irradiation is to control the residual stresses. If their values are high due to grain growth or the difference in thermal expansion coefficients, the laser reduces these stresses. If the residual stresses are low, laser irradiation works to increase them so that the glaze layer remains in permanent compressive stress, which is the most important factor in the success of the glazing process. CO$_2$ laser reduces roughness on the surface of 5% TiO$_2$ specimen, while it cannot do by 15 W when doubling the amount of TiO$_2$ to 10% due to the centers of glass-ceramic nuclei increases and that need higher laser energies or longer irradiation times, and because the glazing coted layer needs high hardnees, so the optimum conditions to achieve this is by adding 5% nano TiO$_2$ ceramics and the power of laser irradiation is 15 Watt.

References
[1] Vagkopoulou, T., Koutayas, S. O., Koidis, P. and Strub, J. R. (2009). European Journal of Esthetic Dentistry, 4(2).
[2] Mahalaxmi Sekar, V Sujatha, Renjith Babu and Ajit George Mohan; Article, ISSUE 1, January 2014.
[3] Thamaraiselvi, T. and Rajeswari, S. (2004). Carbon, 24(31), 172.
[4] Minh, N.Q., Badwal, S.P.S., Bannister, M.J. and Hannink, R.H.J., 1993. Technomic, Lancaster, pp.652-687.
[5] Rezvani, M., Marghussian, V. K. and Eftekhari Yekta, B. (2011). International Journal of Applied Ceramic Technology, 8(1), 152-162.
[6] Abdalliah, R.M., Hammouda, I.M., Mohammed, M.K., Abouelatta, O.B. and El Fallal, A.A.,
[7] Rajesh Kumar, B. and Hymavathi, B. (2017). Journal of Asian Ceramic Societies, 5(2), 94-103.
[8] Aly, K. A., Khalil, N. M., Algamal, Y. and Saleem, Q. M. (2016). Journal of Alloys and Compounds, 676, 606-612.
[9] Aly, K. A., Khalil, N. M., Algamal, Y. and Saleem, Q. M. (2017). Materials Chemistry and Physics, 193, 182-188.
[10] Maji, A. and Choubey, G. (2018). Materials Today: Proceedings, 5(2), 7457-7465.
[11] Yamamoto, L. T., Rodrigues, V. A., Dornelles, L. S., Bottino, M. A., Valandro, L. F. and Melo, R. M. D. (2016). Brazilian dental journal, 27(5), 543-547.
[12] Vashista, M. and Paul, S. (2012). Philosophical Magazine, 92(33), 4194-4204.
[13] Balasingh, C. and Singh, A. K. (2000). Metals materials and Processes, 12(2 amp;), 269-280.
[14] Chavoutier, M., Caurant, D., Majérus, O., Boulesteix, R., Loiseau, P., Jousseaume, C. and Lecomte, E. (2014). *Journal of Non-crystalline solids*, 384, 15-24.

[15] Wang, Y., Darut, G., Luo, X. T., Poirier, T., Stella, J., Liao, H. and Planche, M. P. (2017). *Ceramics International*, 43(5), 4606-4611.