The surface denaturation analysis of lithium disilicate glass ceramics milled by ultraviolet picosecond laser

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Abstract. Dental glass ceramic has good optical properties and biological compatibility. This material has been widely used in the field of the porcelain restoration. Because the shape of the missing tooth varies from patient to patient, dental restoration need to be personalized. Traditional CAD/CAM milling cutter method has problems of high wear cost, low processing efficiency, general processing accuracy. In this study, a 30W ultraviolet picosecond laser was used to mill lithium disilicate glass ceramics. The transparent recoagulation layer and cracks were formed in the condition of some special laser parameters. X-ray diffraction (XRD) material composition test showed that the main composition of the transparent recoagulation layer was not changed. The surface denaturation of different laser cutting parameters were analyzed. The experimental results showed that whether the transparent recoagulation layer generated is the comprehensive result of the laser parameters which contains output power, repetition frequency and scanning speed of galvanometer. The reasons of the transparent recoagulation layer and cracks produced by laser were discussed. By optimizing the laser parameters, the formation of transparent recoagulation layer and cracks can be avoid. The test laid a good experimental foundation for the ultrafast laser milling dental glass ceramics equipment.

1. Introduction

In the development of dental materials science, ceramic materials are favored by people because of their good bio-compatibility, safety, durability and aesthetic properties similar to natural teeth [1,2,3]. Since Land first made low-strength feldspar porcelain into all-ceramic crowns for clinical application in 1903[4], mechanical properties and colors of dental all-ceramic crowns have been greatly developed after more than 100 years of scientific research. In the past decades, dental ceramics have developed rapidly[5]. One of the dental glass ceramics commonly used in dental restoration is lithium disilicate glass ceramics, which called IPS e. max CAD glass ceramics. Lithium silicate (2SiO2-Li2O) dental ceramics was first introduced into the market as a hot pressed core material in 1988 and was named IPS Empress 2 (Ivoclar Vivadent, Lichtenstein)[6]. IPS Empress 2 is classified as glass ceramics, a
ceramic classification with granular glass, which contains about 70% of crystal lithium disilicate filler [7,8]. The pressure casting process used in its production enables the material to have fewer defects and more uniform crystal distribution [9]. Ivoclar Vivadent company has reformulated and refined the production process of IPS Empress 2 and improved a new ceramic production line. The new ceramic formulation was named and published as IPS e. max Press in 2005 [10]. With the emergence of digital dentistry and the progress of computer-aided design and computer-aided manufacturing methods, a lithium disilicate glass-ceramic named IPS e.max CAD was introduced by Ivoclar Vivadent company in 2006 [11]. Because its appearance color is blue, we call it "blue porcelain". After the milling process is completed, the material is further glazed by heat treatment to form the final lithium disilicate restoration.

At present, the main processing technology for the dental glass ceramics is CAD/CAM diamond cutting tool. Its main principle is to control the needle turning path of detachable diamond cutter on CAD/CAM cutting equipment through numerical control program [12, 13]. However, dental ceramics are recognized as hard and brittle materials. Due to the high hardness and low fracture toughness of these materials, the traditional diamond cutting method has serious disadvantages of tool wear and high needle consumption, which increases the processing cost of the dental glass ceramics. At the same time, there are some problems such as low machining efficiency, long machining time and general machining accuracy.

As a non-contact processing tool, laser shows its powerful advantages in many aspects such as tool wear, environmental protection, noise level, processing speed, machining dimension and machining accuracy. Ultraviolet laser directly destroys the molecular bonds on the surface of the material in the process of processing and the thermal influence zone is small. It belongs to "cold" processing and is widely used in fine processing [15]. At present, scholars have carried out a series of studies on laser in dental restoration system. Miku kazama-koide [16] et al verified the possibility and effectiveness of processing this kind of dental ceramics with the nanosecond Nd: YVO4 laser. Daniel Sola et al. [17] used the Nd:YAG laser system with a wavelength of 1064nm at 11W and Nd:YVO4 laser system with a wavelength of 532nm at 7.2w to process and milling Ceran Suprema glass ceramics produced by Schott, and explored the influence of laser defocusing amount and material hardness on material removal rate.

In this study, during the milling process of dental glass ceramics with 30W ultraviolet picosecond laser system, it was found that when the average output power of the laser was higher and the scanning speed of the galvanometer was lower, the recoagulated layer formed on the processed surface and cracks occurred in the ceramic block. The composition of the recoagulated layer was further measured, and the causes of the heavy solidified layer were analyzed, as well as how to avoid the problems.

2. Material and method

2.1. Experimental material

The lithium disilicate glass-based ceramics used in the experiment were the IPS e.max CAD porcelain block produced by Ivoclar Vivadent company. As stated by the company, the main chemical components are SiO$_2$ (57-80%) and additional components are Li$_2$O (11-19%), K$_2$O (0-13%), P$_2$O$_5$ (0-11%), ZrO$_2$ (0-8%) and ZnO (0-8%) [9]. Its main physical properties are shown in table 1 [18].
Table 1. The Main Physical Properties of the Ips E.Max Cad before Thermocycling and After Thermocycling

| Physical properties of IPS e.Max CAD | Flexural Strength (MPa) | Vickers hardness (VHN) | Fracture toughness (MPa•m^{1/2}) |
|-------------------------------------|-------------------------|------------------------|----------------------------------|
| Before thermocycling                | After thermocycling     | Before thermocycling   | After thermocycling              | Before thermocycling | After thermocycling |
| Mean value±SD                       | 112.4 ± 3.2             | 112.1 ± 2.3            | 6.4 ± 0.1                        | 6.3 ± 0.1            | 2.34 ± 0.04        | 2.33 ± 0.03        |

2.2. Experimental method

By changing the average output power and scanning speed of 30W ultraviolet picosecond laser (IceFyre serious, spectre-physics), different laser parameters were used for laser milling IPS e.max CAD dental glass ceramics in an area of 5x5mm². The ceramic blocks with laser recoagulation layer on the surface were cleaned with anhydrous ethanol. In this experiment, in order to characterize the phase composition after laser ablation, the diamond wire and agate bowl mill (MSK-SFM-8) were used to obtain the ablation powder. X-ray diffractometer (XRD) (Malvern PANalytical Empyrean, Netherlands) was conducted with copper target tube pressure of 30KV/15mA and with scanning angel (2 theta) ranging from 10° ~ 90° at an angular sweeping rate of 0.02°. Then, the scanning structure was analyzed by X'pert Highscore Plus(v1.0d) software, the surface composition and crystallinity of the material were determined by ICCD powder diffraction card. The crystallinity of recoagulation layer was observed by polarizing microscope (CX43, OLYPUS).designations.

3. Results And Discussion

3.1. Material surface composition analysis

Surface recoagulation layer and cracks produced by 30W picosecond laser system was shown in Fig1. XRD was used for phase analysis and phase content calculation, the XRD spectra of the recoagulated layer on the surface of dental glass ceramics after laser milling and without laser milling were shown in figure 2. The spectrum peaks of the recoagulated layer were consistent with the lithium disilicate crystal, and all the higher main peaks in the spectrum were lithium silicate phase. Compared with test material surface without laser radiation, the intensity of test material radiated with 30W 355nm picosecond laser system was higher and he degree of surface crystallization after laser irradiation is higher.

![Fig 1. Surface recoagulation layer and cracks produced by 30W picosecond laser system](image)
3.2. Microstructure analysis

In order to further observe the microstructure of the recoagulation layer of IPS e. max CAD dental glass ceramic surface after the action of 30W picosecond laser on the surface of IPS e. max CAD dental glass ceramic under specific laser parameters, the grinded ceramic material powder was observed with an orthogonal polarized light microscope and the experimental results were shown in figure 2. The crystal material in the blue line was the dental glass material with no action of 30W picosecond laser. The crystal material in the red line was the recoagulation layer formed by 30W picosecond laser system and the material becomes transparent after laser ablation. Although the material composition did not change, the crystal structure and crystallinity changed. Through experiments, Wang bin et al verified that lithium disilicate glass-based ceramics can produce crystal structures with different crystallinity at a specific temperature. Temperature changing affect the nucleation and crystallization process of lithium disilicate glass ceramic crystals and change the crystallinity and microstructure of the ceramics, so that the ceramics present different physical and optical properties [19, 20].

3.3. The conditions of producing recoagulation layer and cracks

Ceramic materials contain ionic bond and covalent bond structure, high bond energy, strong bonding force between atoms, low surface free energy, small atom spacing, compact accumulation, no free electron movement. These characteristics give ceramic materials such distinctive characteristics as high melting point, high hardness, high stiffness, high chemical stability, high insulation and perfect...
adiabatic performance, low thermal conductivity, small coefficient of thermal expansion, small coefficient of friction and no ductility [18].

The interaction between UV picosecond laser and dental lithium disilicate glass ceramics directly destroys the ionic and covalent bonds of ceramic materials. Since its pulse width is only on the picosecond scale, the peak power density can reach $10^{13}$ W/cm$^2$. This energy generated heat and break ionic and covalent bonds. When the energy density of the single pulse was higher than the bond energy that destroys the ionic bond and covalent bond of the ceramic material, the excess energy accumulated in the material and converted into heat. In addition, if the scanning speed of the galvanometer was low and the number of laser pulses per unit distance was high, the heat accumulation in the fixed area increased. The relationship between the parameters of ultraviolet picosecond laser and the IPS e. max CAD glass ceramic surface denaturation was shown in table 2.

### Table 2. The relationship between ultraviolet picosecond laser parameters and IPS e.max CAD glass ceramics surface denaturation

| Laser output power/W | Scanning speed/(mm/s) | 200 | 500 | 1000 | 1500 | 2000 |
|----------------------|------------------------|-----|-----|------|------|------|
| 5                    |                        |     |     |      |      |      |
| 10                   |                        |     |     |      |      |      |
| 15                   |                        |     |     |      |      |      |
| 20                   |                        |     |     |      |      |      |
| 25                   |                        |     |     |      |      |      |
| 30                   |                        |     |     |      |      |      |

- Represents ultraviolet picosecond laser didn’t form recoagulation layer on dental glass ceramic surface.
- Represents recoagulation layer was formed on the surface of dental glass and ceramic by ultraviolet picosecond laser, but no crack was generated.
- Represents that the ultraviolet picosecond laser formed recoagulation layer on the surface of dental glass ceramics and generated cracks.

As can be seen from table 2, when the average laser output power is 5W and 10W, no recoagulated layer generated on the surface of dental glass ceramics. When the average laser output power was 15W and scanning speed was less than 500mm/s, the re-coagulated layer was generated on the surface of the dental glass ceramic, but no cracks. When the scanning speed was higher than 1000mm/s, the surface denaturation of dental glass ceramics was occurred, and the re-condensation layer didn’t form on the surface of dental glass ceramics. In the condition of the average output power of the laser was 20W, different processing effects was produced by controlling the scanning speed of the galvanometer. When the scanning speed was lower than 200 mm/s, the regulation layer on ceramic material surface and crack was produced. When scanning speed was 500 mm and 1000 mm/s, the regulation layer on ceramic material surface was produced without cracks. When the scanning speed was 1500 mm and 2000 mm/s, surface processing was in good condition without regulation layer and cracks. In the condition of output power is 25W, the situation was similar to that when the average output power was 20W. In the condition of average output power was 30W, cracks and re-solidified layers appeared on the surface of ceramic materials, and the processing condition should be avoid.

### 4. Conclusion

In the process of laser milling the dental lithium disilicate glass ceramics, whether the ceramic surface produces a transparent re-coagulated layer and cracks are related to the average output power of the laser system and scanning speed of the galvanometer.
The components of the transparent re-coagulated layer remain unchanged. Under the condition of higher output power of laser system and lower scanning speed of galvanometer, heat will be generated on the process surface. Then the crystallinity of glass ceramics was changed, which must be avoided.

When using laser to milling lithium disilicate glass ceramics, the average output power of the laser should be controlled no more than 20W, and the corresponding scanning speed of the galvanometer should be matched.

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