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Effects of Irradiation with a CO_2 Laser on Surface Structure and Bonding of a Zirconia Ceramic to Dental Resin Cement

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Studies have suggested that irradiation with a CO_2 laser may improve the shear bond strength between resin cement and zirconia. One hundred and ten specimens of zirconia randomly divided into four groups, of which we respectively treated the first three with air abrasion, irradiation with a CO_2 laser, and irradiation with a CO_2 laser followed by air abrasion, with the fourth group serving as an untreated control. Resin cement create a column 2 mm thick and 3.6 mm in diameter on each ceramic specimen. The shear bond strength between the resin and ceramic was determined at a crosshead speed of 0.5 mm/min. The bond strength between the resin and laser-treated ceramic varied with the laser power setting at which the ceramic was treated. The strength was greatest at a power setting of 8W, with a value of 6.7 MPa. Combined treatment of the zirconia ceramic with CO_2 laser irradiation and air abrasion produced a threefold greater strength of the resin-to-ceramic bond over that with the zirconia control and a 20% greater strength between the resin and the ceramic treated with air abrasion. The CO_2 laser irradiation of zirconia ceramic can significantly increase the adhesive strength of its bonding to a dental resin cement. DOI:10.2961/jlmn.2011.02.0014
Key words: luting cement, shear bond strength, ceramics

1. Introduction

A number of ceramic systems composed of partly stabilized zirconium oxide (ZrO_2; zirconia) have recently been introduced into dentistry for use in fixed-implant-supported prostheses on the basis of their chemical stability and high biocompatibility with gingival tissue or bone [1-3]. Ceramics composed of yttria-stabilized tetragonal zirconium dioxide have particularly shown significantly better mechanical properties than the feldspathic porcelains historically used in dental prostheses, in terms of bending strength, tensile strength, and Young's modulus. Indeed, these partially stabilized zirconia ceramics exhibit higher degrees of strength and toughness than feldspathic porcelains [1]. These properties of partly stabilized zirconia ceramics have brought them into wide use in fixed partial dentures and dental implant superstructures, which require superior mechanical properties for withstanding occlusal and mechanical loading. However, the clinical success of zirconia prostheses requires that they have a reliable bonding strength in order to resist fracture and provide greater longevity than porcelain-based prostheses [4].

Both mechanical and chemical retention are needed for the strong bonding of a dental resin cement to zirconia. To achieve this, various techniques have been suggested for the surface treatment of zirconia before bonding, including air abrasion, coating with tribochemical silica, the use of adhesive agents containing a phosphate monomer, silane coupling, and the use of metal-adhesive primers [5-10]. In this context, it has been shown that bonding of high strength and durability could be achieved on air-abraded surface with the use of 10-methacryloyloxydecyl dihydrogen phosphate (MDP)-containing primers or composite resins[8,10]. Contrastingly, a coping material made of zirconia ceramic, because of its mechanical properties, could not be sufficiently roughened by airborne particle abrasion or coating with tribochemical silica to permit bonding, and neither did it react sufficiently with a primer or silane coupling agent to provide effective bonding [11-14].

Carbon dioxide (CO_2), Nd:YAG, and Er:YAG lasers are generally used as instruments for both intraoral soft tissue surgery and hard tissue applications [15-17]. These lasers have also been used to process dental materials, especially for fusion to metal surfaces or for adhesion to tooth substrates as in porcelain crowns [17]. Irradiation with a CO_2 laser is an optimal treatment for porcelain materials because it emits radiation at a wavelength that is almost totally absorbed by porcelain. Moreover, a focused CO_2 laser beam induces heat in a porcelain surface that typically produces conchoidal tears in the surface [17], which permit the mechanical retention of a composite resin by the porcelain. These findings suggest that CO_2 laser irradiation of the surface of an object made of zirconia ceramic may also change its structure in a way that improves the strength of bonding of resin cements to this surface [18].

Accordingly, we examined whether irradiation with a CO_2 laser of the surface of a zirconia ceramic would affect the strength of adhesion of a dental resin cement to the surface of the ceramic.

2. Experimental set-up

For the purpose of our study, we randomly divided 110 specimens of a ceramic material composed of partly yttria-stabilized tetragonal zirconium dioxide, with a mass composition of 87.0 to 95.0% ZrO_2, 4.0 to 6.0% Y_2O_3, 1.0% to 5.0% HfO_2, and 0.0 to 1.0% Al_2O_3 (IPS e.max ZirCAD, Ivoclar Vivadent, Schaan, Principality of Liechtenstein) with each specimen measuring 13 × 7 mm (3 mm thick) into four groups. The surface of each zirconia ceramic specimen was then polished with a silicon carbide-coated abrasive paper (#320; Struers A/S, Rodovre, Denmark) under water irrigation. The first two of these groups were to be treated with air abrasion (the number of specimens for each group (N) = 10) or CO_2 laser irradiation ($N = 80$), and the third was to serve as an untreated group of specimens ($N = 20$). And the specimens for CO_2 laser irradiation were subdivided into eight groups, each of which was to be treated either at a specific CO_2 laser power setting or for a different period of time. The untreated specimens of zirconia ceramic were subdivided into two groups, which were to be treated with the application of a ceramic primer (control) or left untreated (−ceramic primer).

Table 1. Surface treatment of each group

Surface Treatment	primer	CO_2	AA	Number
-Ceramic primer	−	−	−	10
Control	+	−	−	10
AA	+	−	+	10
6W−CO_2-ir	+	6W,60sec	−	10
7W−CO_2-ir	+	7W,60sec	−	10
8W−CO_2-ir	+	8W,60sec	−	10
9W−CO_2-ir	+	9W,60sec	−	10
10W−CO_2-ir	+	10W,60sec	−	10
8W−CO_2 +AA	+	8W,60sec	+	10
45s	+	8W,45s	−	10
90s	+	8W,90s	−	10

CO_2-ir = CO_2 laser irradiation; AA = air abrasion.

Air abrasion of the surfaces of the first group of zirconia ceramic specimens was accomplished with 50-μm particles of aluminum oxide (Al_2O_3; Perlablast® micro; Bego, Bremen, Germany) propelled from a grit blaster (emission pressure: 0.4 MPa, nozzle diameter: 1 mm) whose nozzle was positioned 5 mm from the surface of the zirconia ceramic.

The CO_2 laser irradiation of the second group of zirconia ceramic specimens was done by a Nanolaser GL-II (GC Corporation, Tokyo, Japan). The power density of this apparatus was 10^4~10^5 W/cm^2, and wave length was 10.6 μm. The CO_2 laser was irradiated with normal mode of oscillation pattern and continuous mode of irradiation condition for 60 seconds with the tip of the laser positioned 5 mm from the surface of the zirconia ceramic. The size exposed to the laser beam was 3.6 mm in diameter with a static laser beam. The CO_2 laser-irradiated specimens in each of the five subgroups mentioned earlier were treated at laser power settings of 6W, 7W, 8W, 9W, or 10W, respectively. The surfaces of all of the zirconia ceramic specimens were then observed under a scanning electron microscope (SEM; DS-720; Topcon Corp., Tokyo, Japan).

After each surface treatment, the zirconia ceramic specimens were cleaned ultrasonically in 96% isopropanol for 3 minutes before application of the dental resin cement. A primer (ceramic primer, GC Corporation, Tokyo, Japan) with a composition of liquid A (ethanol and silane coupling agent) and liquid B (methacrylate, ethanol, urethane dimethacrylate and organic acid) was first applied in a thin layer (approximately 3-5μm) to the cleaned surface of each zirconia ceramic test specimen with a disposable paintbrush, and the resin cement consisted of fluoroalminosilicate glass, urethane dimethacrylate, methacrylate, silica powder, catalyst and pigment (Linkmax; GC Corporation) was then poured into a matrix over each ceramic specimen to create a column 2 mm thick and 3.6 mm in diameter. At 20 minutes after pouring, the matrix was carefully removed and the zirconia ceramic specimen with the resin bonded to it was stored in distilled water at 37°C for 24 hours. The shear-strength values of the bonds between the adhesive resin cement and the different zirconia ceramic specimens were determined on a universal testing machine (Autograph DCSC-2000; Shimadzu, Kyoto) at a crosshead speed of 0.5 mm/min. Data obtained for the shear strength of the bonds in each of the four groups of zirconia ceramic specimens were compared statistically through one-way analysis of variance (ANOVA) and the Student–Newman–Keuls test, with a 5% limit of error (the provability of incorrectly rejecting the null hypothesis (P) < 0.05). These statistical analysis was achieved by SigmaStat® 3.1 (Systat Software, Inc., CA, USA).

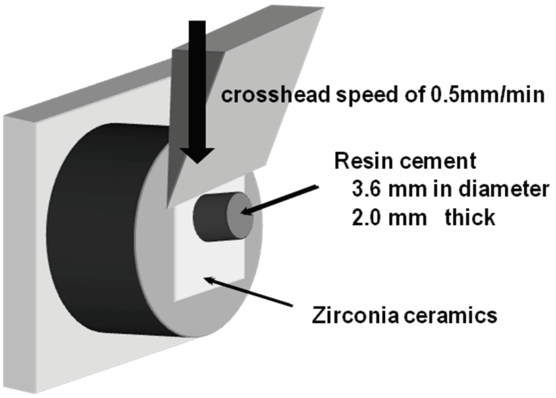

Fig 1. Schematic view of shear bond strength measurement.

After testing of the shear strengths of the bonds between the dental resin and the surfaces of the zirconia ceramic specimens, the fractured interfaces of the ceramic

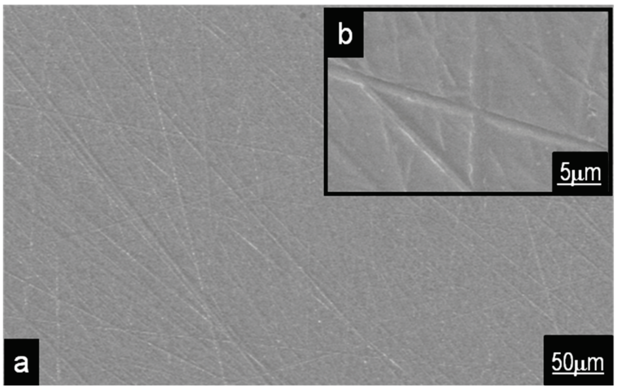

Fig 2. (A) SEM image of surface of control specimen of zirconia ceramic (magnification: 200x). (B) Detailed view of surface (magnification: 3000x).

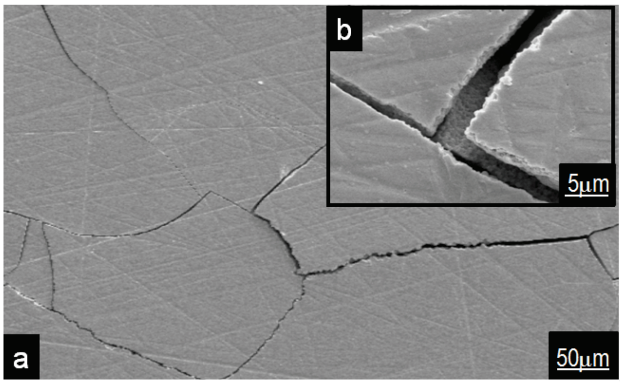

Fig 4. (A) SEM image of surface of zirconia ceramic specimen treated with CO_2 laser irradiation (magnification: 200x). (B) Detailed view of surface (magnification: 3000x).

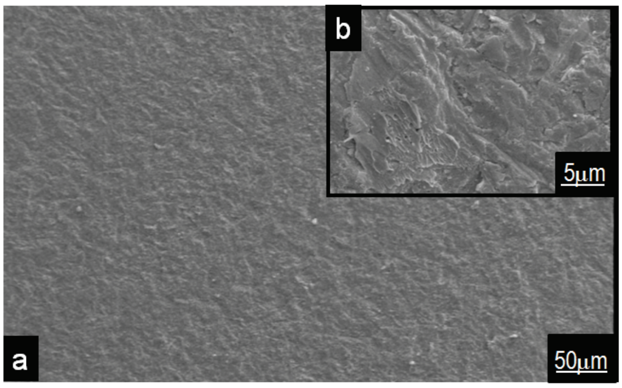

Fig 3. (A) SEM image of surface of zirconia ceramic specimen treated with air abrasion (magnification: 200x). (B) Detailed view of surface (magnification: 3000x).

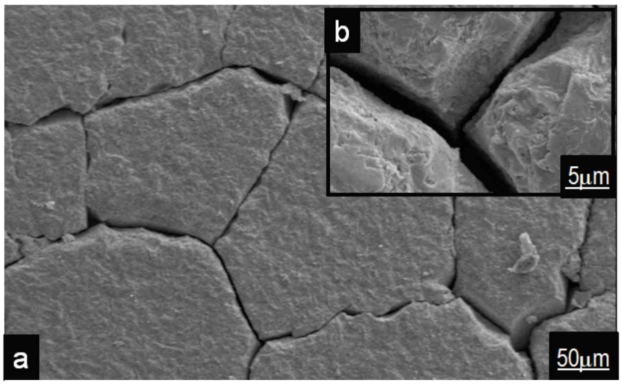

Fig 5. (A)SEM image of surface of zirconia ceramic specimen treated with air abrasion after CO_2 laser irradiation (magnification: 200x). (B) Detailed view of surface (magnification: 3000x).

specimens at the sites of the bonds were examined under a light microscope, with the type of failure caused by shear fracture classified as adhesive, cohesive, or mixed-mode failure. The fractured surfaces were then also observed with the SEM described earlier. SEM images were transferred to image analyzed software (SigmaScan® Pro 5.0. Systat Software, Inc.) and measured the length.

3. Results

Zirconia ceramic surface showed a scratched surface pattern from polishing with the silicon carbide abrasive paper used on all of the specimens (Fig. 2) and air abrasion produced a rough and superficial layer on the surface of the zirconia ceramic specimens (Fig. 3). The CO_2 laser-irradiated specimens of zirconia ceramic had many grooves in their irradiated surfaces, with each groove reaching about 100 µm in depth, and induced a slight delamination of the solidified layer from the substrate (Fig. 4). The air abrasion of zirconia ceramic specimens that had first been subjected to CO_2 laser irradiation removed the edges of the grooves created by the laser in the surface of the ceramic (Fig. 5).

The mean shear strength of the bonds between the air abrasion-treated zirconia ceramic surfaces and the resin cement was significantly higher, at 5.39 ± 0.64 MPa (Table 2), than that of the bonds between the surfaces of the control specimens of ceramic, at 2.21±0.53 MPa ($P < 0.05$). Irradiation of the zirconia ceramic with the CO_2 laser produced resin-to-ceramic bonds of high strength, with the bond strength depending on the power setting of the laser. The mean shear bond strength of bonds with the CO_2 laser upturned to 8W and downturned over 8W. The mean shear strength of these bonds reached its peak at a laser setting of 8W, with a value 6.68 ±1.69 MPa, which did not differ significantly from the mean shear strength of the bonds between the resin and the surfaces of the air-abraded ceramic specimens. However, the number of specimens showing mixed-mode fracture was greater in the CO_2 laser-irradiated than in the air-abraded group. The combination of laser irradiation and air abrasion resulted in a threefold increase in the strength of resin bonding to the zirconia ceramic surface (7.49 ± 3.08 MPa) over that of the untreated zirconia controls (2.21 ± 0.53 MPa), and a 20% increase in bonding strength over the strength of resin bonding to the surfaces of the zirconia specimens treated with air abrasion (5.39 ± 0.64 MPa), although the significant difference was not detected between the CO_2 laser-irradiated group or air abrasive group ($P > 0.05$). The resin bonds to all of the specimens treated with air abrasion or the combination of air abrasion and CO_2 laser irradiation showed mixed-mode fracture (Fig. 6).

With regard to the type of bond failure produced by shear stress on the bonds between the resin and zirconia ceramic (Fig. 6), the bonds on all 10 of the control specimens of

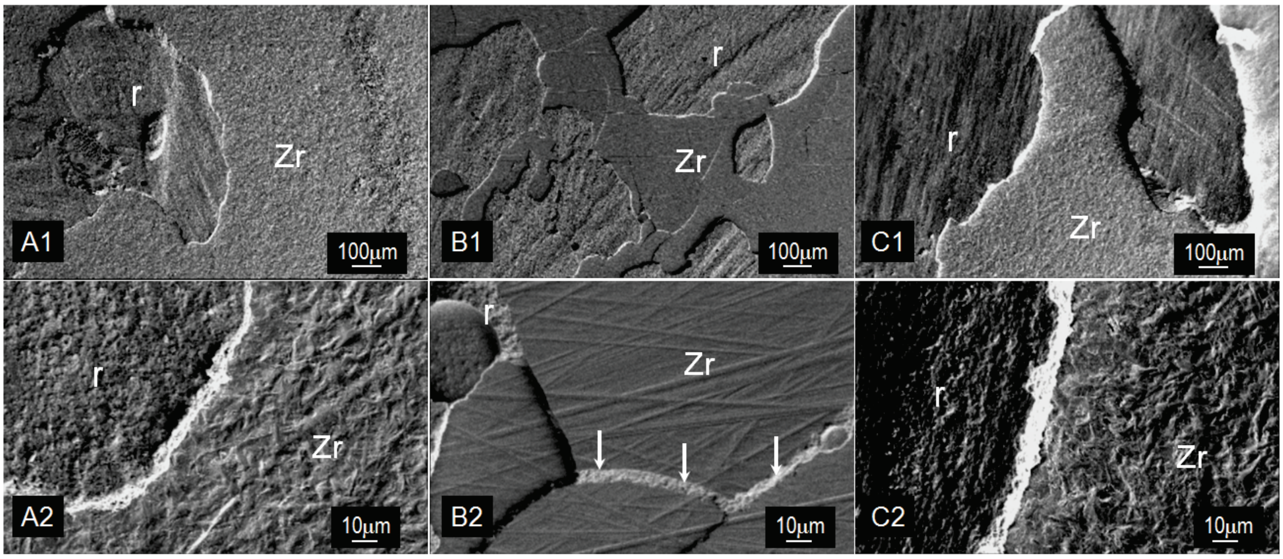

Fig 6. SEM image of surfaces of zirconia ceramic specimens treated with different modalities after shear testing of bonds between the surfaces of the specimens and adhesive dental resin. (A) Air abrasion. (B) CO$_2$ laser irradiation. (C) Air abrasion after CO$_2$ laser irradiation. (1) Magnification: 80x. (2) Magnification: 800x. r = Resin cement. Arrow = Resin cement in groove produced by CO$_2$ laser irradiation in surface of zirconia ceramic.

Table 2. Shear strength values of bonds between resin cement and zirconia ceramic surfaces conditioned with different methods

Surface Treatment	Shear Strength Mean (SD)*
-Ceramic primer	1.78 (0.56) a
Control	2.21 (0.53) b
AA	5.39 (0.64) c
6W－CO$_2$-ir	4.95 (1.54) c
7W－CO$_2$-ir	5.03 (1.30) c
8W－CO$_2$-ir	6.68 (1.69) c
9W－CO$_2$-ir	6.46 (1.23) c
10W－CO$_2$-ir	6.06 (1.26) c
8W－CO$_2$＋AA	7.49 (3.08) c

Mean values designated with the same letters (a, b, c) were not significantly different from one another (*P*>0.05). *N = 10.
Key: –ceramic primer = control specimen without ceramic primer; CO$_2$-ir = CO$_2$ laser irradiation; AA = air abrasion.

Table 3. Shear strength values of bonds between resin cement and zirconia ceramic treated with CO$_2$ laser irradiation at 8W for differing periods

Surface Treatment	Shear Strength Mean (SD)*
45s	*4.94 (1.24)
60s	6.68 (1.69)
90s	*5.75 (1.41)

*Mean values that did not differ significantly from one another (*P*>0.05). **N* = 10.

zirconia ceramic and on all 10 of the ceramic specimens treated with the ceramic primer showed adhesive failure. Among the sets of 10 specimens each that were treated with laser irradiation for 60 seconds, the frequency of adhesive failure of the bonds between the resin and ceramic decreased and the frequency of mixed-mode failure increased with each of the increasing laser power settings from 6W to 10W. The bonds on all 10 ceramic specimens treated with CO$_2$ laser irradiation at 8W followed by air abrasion showed mixed-mode failure, while the bonds on 7 of the 10 specimens in each of the two groups treated respectively with 45 seconds of CO$_2$ laser irradiation at 8W or with 90 seconds of laser irradiation at 8W, followed in each case by air abrasion, showed adhesive failure, with the remaining 3 specimens in each group showing mixed-mode failure. In the three groups of 10 zirconia ceramic specimens each that were subjected to CO$_2$ laser irradiation at 8W for periods of 45 seconds, 60 seconds, and 90 seconds, the respective shear strengths of the bonds between the resin and zirconia ceramic were 4.94 ± 1.24 MPa, 6.68 ± 1.69 MPa, and 5.75 ± 1.41 MPa (Table 3).

4. Discussion

In our study, air abrasion of zirconia ceramic specimens produced a roughened surface layer on the ceramic, indicating that this treatment could be a first-line measure in achieving a high bond strength between zirconia and dental resin cement used in this study. The air abrasion had the capacity to remove loose and contaminated material from the surface of the zirconia ceramic and permit its mechanical interlocking with an adhesive dental resin. Moreover, the air abrasion removed the weak edges of the grooves created by the laser in the surface of the zirconia. The absorption of CO$_2$ laser irradiation by the zirconia ceramic would induce heating of its surface. The focused beam of laser irradiation directed at the surfaces of the zirconia ceramic specimens in our study produced grooves in these surfaces, as shown in electronography (Fig. 4). These grooves would be formed by thermo-shock effect [19,20], which can lead to cracks on the zirconia surface by shrinkage with a solidification of the melting substrate during cooling down. This grooves also provided effective mechanical retention of the resin, as shown in electronography (Fig. 6), in which resin is seen in these grooves. Although the grooves or cracks on the zirconia surface would delaminated the solidified layer from the substrate, any exfoliation of layer from substrate did not detected after the shear bond test. The failure mode of all specimens were adhesive failure between resin cement or cohesive failure in resin cement not in zirconia. Therefore, these cracks would affect on the increased mechanical retention. Although examination of the zirconia ceramic specimens with an SEM showed different surface textures in the specimens treated with air abrasion and CO_2 laser irradiation, the microscopic anchoring structures provided by both treatments augur well for a high bond strength between the ceramic and an adhesive resin.

In general, the greater the surface area of any material for the adhesion of another material, the greater will be the strength of the adhesion. And by producing grooves in the surface of the zirconia ceramic that markedly increased its surface area, the CO_2 laser irradiation used in our study was able to increase the strength of bonding between the ceramic and the resin used in the study to the same extent as did air abrasion of the ceramic surface, although the laser irradiation did not increase the surface area over that achieved with air abrasion.

The grinding of a zirconia framework surface in feldspathic ceramic crown generates the two counteracting effects of introducing surface flaws and creating a thin superficial layer of compressive stresses in the ceramic [21]. The magnitude of the compressive stresses is enhanced by the tetragonal-to-monoclinic phase transformation of the zirconia surface produced by air abrasion or grinding [22]. Any increase in the strength of adhesive bonding to the transformed surface would be related to the volume of transformed zirconia and the depth of the surface layer subjected to these compressive stresses. Apparently, air abrasion also effected a tetragonal-to-monoclinic phase transformation in the surface of the zirconia ceramic used in our study, thereby also increasing the strength of its bonding of the adhesive resin used in the study.

The application of air abrasion following CO_2 laser irradiation effectively removed the weakened surface layer and the edges of the laser-generated grooves in the zirconia ceramic used in our study, yielding higher shear strengths of the resin-to-ceramic bonds than in any of the other treatment groups of ceramic in the study. In the SEM images of the ceramic surfaces subjected to such combined treatment, the surface area of the adhesive resin cement applied to the zirconia ceramic was greater than that with either air abrasion or CO_2 laser irradiation of the ceramic. All of the ceramic specimens treated with CO_2 laser irradiation followed by air abrasion in our study showed mixed-mode failure. Each prosthesis is needed to function in union with abutment. The adhesive failure on the prosthesis surface could cause a fracture of prosthesis especially in all ceramic crowns. These findings suggested that treatment with CO_2 laser irradiation followed by air abrasion would be particularly effective for the bonding of a dental resin to abutment teeth made of zirconia ceramic in a dental prosthesis. The setting of CO_2 laser should be recommen ded 8W for 60 seconds in continuous-pulse of normal mode with the apparatus used in this study. However, the approximately 100-μm-deep grooves produced in the surface of the zirconia ceramic by CO_2 laser irradiation observed in our study might result in damage to such prosthesis. The 100-μm-deep groove in zirconia ceramic may cause weighty subject of fracture of prosthesis, because the thickness of zirconia framework is from about 0.3 mm to 1mm. The zirconia framework treated CO_2 laser irradiation should secondly treated with air abrasion to remove the weak edges of the grooves created by the laser in the surface of the zirconia.

5. Conclusion

Within the limitations of the study reported here, the irradiation of a zirconia ceramic with a CO_2 laser can increase the adhesive strength of a resin cement in bonding to the ceramic, although the effect of the grooves produced by CO_2 laser irradiation remains to be clarified.

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