The effects of laser etching on shear bond strength at the titanium ceramic interface

Jin-Tae Kim, DDS,* and Sung-Am Cho, DDS, PhDb
College of Dentistry, Kyung-Pook National University, Daegu, South Korea

Statement of problem. The use of titanium has increased for metal ceramic restorations, as well as for use in titanium implants, with developments in CAD/CAM technology. Some surface treatments of titanium have been introduced to enhance the titanium bond strength to low-fusing porcelains, however, a more reliable, easily used dental laboratory method has not been established.

Purpose. The purpose of this study was to compare the effect of laser etching as a titanium surface treatment with 3 other surface treatments (maching, airborne-particle abrasion, and acid etching), evaluating their ability to enhance the bond strength between a titanium substrate and porcelain.

Material and methods. A total of 64 specimen rods of commercially pure titanium (ASTM grade 2, 20 mm in length and 5.7 mm in diameter) were divided into 4 experimental groups (n=16) to receive different surface treatments: machining with no treatment (MS), airborne-particle abraded with alumina particles (250 μm) (APAS), acid etched with 10% HCl (AES), and laser etched (LES) using a neodymium-doped yttrium aluminum garnet laser (Nd:Y_AL5O12, or Nd/YAG). Low-fusing porcelain (Tricera) was applied (4-mm thickness) to the treated titanium surfaces and fired. Shear bond strength testing was performed in a universal testing machine. All of the data were compared using 1-way ANOVA and the post hoc multiple range Tukey test (p<0.05). Measurement of roughness (Ra value) and SEM analysis were also performed for 1 specimen of each group before and after the shear bond strength test to evaluate the nature of the fracture surface.

Results. Shear bond strength values for the APAS group (22.22 (4.04) MPa) and the LES group (21.22 (3.41) MPa) were significantly greater (p<0.05) than for the MS group (13.76 (3.16) MPa) and the AES group (14.98 (3.36) MPa). The SEM image after debonding of MS and AES showed porcelain retained on the surface. However, there was no difference in appearance between the APAS and AES before and after debonding.

Conclusions. Laser etching of titanium surfaces using an Nd/YAG laser was effective in improving bond strength with low-fusing porcelain, as compared to the acid-etching method. However, there was no significant difference between laser etching and airborne-particle-abrasion surface treatment. (J Prosthodont 2009;10:101-106)

Clinical implications. Laser etching as a titanium surface treatment to enhance the bond strength of a titanium substrate to porcelain could be an alternative to airborne-particle abrasion, demonstrating a higher bond strength than that demonstrated by the acid-etching method.

In recent years, titanium has become a material of great interest in restorative dentistry due to its superiority in certain properties, such as biocompatibility and corrosion resistance.2,3 titanium is used not only for dental implants, but also for metal ceramic restorations.4 Although the high temperature required for casting titanium is a challenge for its use in metal ceramic restorations, CAD/CAM technology has made this application increasingly feasible.5 Titanium has an excessively thin oxide layer at the temperature necessary for firing conventional dental porcelain (over 800°C).4 The laser etching method causes the lateral expansion of titanium (8.4 x 10^-6/°C) which is compared to that for conventional noble metal ceramic alloys (13.6 x 10^-6/°C).6-8 results in a mismatch of

*Clinical Instructor, Department of Prosthodontics; private practice, Daegu, South Korea.
**Professor, Department of Prosthodontics.
The thermal expansion coefficients of titanium and porcelain, and causes bond failure of titanium to ceramic. Thus, low-fusing ceramic materials have been developed to minimize the difference in thermal expansion between titanium and porcelain, as well as to minimize high-temperature oxidation.11,12 However, a limitation of low-fusing porcelain is its lower bond strength compared to traditional medium-fusing porcelain.13 Therefore, it would be helpful to obtain greater bond strengths for low-fusing porcelain. Acid etching and airborne-particle abrasion were reported to increase the bond strength with titanium by removing the excess oxide,14,15 yet there has been controversy regarding acid-etching and airborne-particle-abrasion methods.16-18 Reyes et al.14 stated that airborne-particle abrasion, machining, and acid-etching surface treatment methods.

**MATERIAL AND METHODS**

Titanium bars (ASTM F67-00; Ti-Titanium Industries, Inc, Rockaway, NJ) were sectioned with a lathe (Comput- erized Optimal Control Auto Lathe Type SA-12 S/N 0010; Star Micronics Co, Ltd, Shizuoka, Japan) into 64 specimens, 20 mm in length and 5.7 mm in diameter. All specimens were machined from long metal rods to the same specified dimensions. The 64 titanium specimens were divided into 4 experimental groups (n=16) to receive different surface treatments. No specimens were subjected to acid-etched surface (AES) treatment of the titanium substrate to enhance the bond strength with low-fusing porcelain. Acid etching and airborne-particle abrasion were performed to increase the bond strength with the ceramic substrate to porcelain. The research hypothesis was that laser-etching the titanium surface would enhance the titanium-porcelain bond strength when compared with airborne-particle abrasion, machining, and acid-etching surface treatment methods.

To evaluate the bond strength of the interface between the metal and ceramic, the shear bond test, which has been described by other investigators, was performed.21–23 The device containing the ceramic specimen was placed in a universal testing machine (Model 4202; Instron Corp, Norwood, Mass) at a crosshead speed of 0.5 mm/min. The load was applied at a distance of 0.5 mm from the metal-porcelain interface using a crosshead speed of 0.5 mm/min.24 The highest mean bond strength value was obtained in the airborne-particle-abraded groups (APAS) followed by the laser-etched groups (LES), acid-etched groups (AES), and control group (Means of shear bond strength values (MPa) for 4 experimental groups and Tukey analysis (A). Table I). There was a significant difference in shear bond strength with respect to surface treatment (F=22.749, df=3, 56, P<0.05). The highest mean bond strength value (SD) was found in the APAS group (22.22 (4.04) MPa), followed by the LES group, the AES group, and then the MS group (21.22 (3.41) MPa, 14.98 (3.26) MPa, and 13.76 (3.16) MPa, respectively). The results of the Tukey multiple range tests showed that there were no significant differences in bond strength between the APAS group and the LES group, or between the AES group and MS group. However, there were differences in bond strength between the APAS group and MS group.

The majority of the specimens in the 4 groups showed adhesive fracture at the titanium-ceramic interface with small amounts of porcelain on the metal surface. The Ra value of the airborne-particle-abraded groups (APAS) demonstrated higher Ra (2.60 μm) than the other groups: laser-etched surface (LES), 0.68 μm; acid-etched surface (AES), 0.28 μm; and machined surface (MS), 0.21 μm. The photomicrographs of the surface morphology are shown in Table I.
to airborne-particle abrading or other surface pretreatment techniques for enhancing the bond strength of dental materials to metal surfaces. However, the use of lasers in dental material processing has been limited. The purpose of this study was to compare the effect of laser etching as a titanium surface treatment with 3 other conventional surface modifications (machining, airborne-particle abrasion, and acid etching) introduced for enhancing the bond strength of the titanium substrate to porcelain. The research hypothesis was that laser etching the titanium surface would enhance the titanium-porcelain bond strength when compared with airborne-particle abrasion, machining, and acid-etching surface treatment methods.

**MATERIAL AND METHODS**

Titanium bars (ASTM F67-00; Titania Industries, Inc, Rockaway, NJ) were sectioned with a lathe (Computomatic Quickmill; Computerized Machining, Inc, Vacaville, CA) to 0.2 mm (SA-12 S/N 0010; Star Micronics Co, Ltd, Shizuoka, Japan) into 64 specimens, 20 mm in length and 5.7 mm in diameter. All specimens were machined from long metal rods to the same specified dimensions. The 64 titanium specimens were divided into 4 experimental groups (n = 16) to receive different surface treatments. No specific surface treatment was performed for the machined surface group (MS), which served as the control group.

The airborne-particle-Abraded surface (APAS) specimens were abraded with alumina particles (250 μm) with a dental airborne-particle-abrasion unit (Micro-Blaster; Daedong Industrial Co, Ltd, Daegu, Korea). The air pressure was set at 2 bar, and the distance between the nozzle tip and the specimen surface was maintained at 15 mm, during the airborne-particle abrasion, for 20 seconds (10 scans in 20 seconds, at the rate of 1 scan every 2 seconds). The acid-etch surface (AES) specimens were subjected to chemical surface treatment by submerging the specimens in a 10%-by-weight aqueous solution of HCl (DC Chemical Co, Ltd, Seoul, Korea) in a heat-resistant glass container and boiling for 30 minutes, taking care to avoid contact between specimens.

The laser-etched surface (LES) specimens were treated using a Nd:YAG laser (Jenoptik Laser Optik Systeme GmbH, Jena, Germany). The titanium surfaces of the specimens were irradiated by the linear movement of a glass fiber of the Nd:YAG laser at a power setting of 7 W, representing energy and frequency levels of 120 μJ with 50-Hz frequency. After the surfaces were treated, a spring-loaded specimen from the laser unit was measured to determine Ra values with a surface roughness measuring instrument (Strato 710; Mitutoyo, Kawasaki, Japan), and then microscopic analysis was performed with a scanning electron microscope (SEM) (JSM-6700F; JEOL, Tokyo, Japan).

After the application of the respective surface treatment, all specimens were subjected to cleaning with water steam spray and ultrasonic cleaning using distilled water for 10 minutes at 80°C, and then rinsed in distilled water. The excess water was removed by air at room temperature, and all specimens were air dried. Low-fusing porcelain (Triceram, Esprident GmbH, Ispringen, Germany) was used in this investigation. Specimens for the bond test were held firmly during the shear bond test (Fig. 1). The device containing the metal ceramic specimen was placed in a universal testing machine (Model 4202; Instron Corp, Norwood, Mass) with a 500-g load cell. A perpendicular load was applied at a distance of 0.5 mm from the metal-porcelain interface using a crosshead speed of 0.5 mm/min.

The bond strength was measured with a universal testing machine (M/S-Instron, Canton, Mass) with the measurement of the load required to separate the specimens. The load was applied until fracture of the metal-porcelain interface occurred, and the maximum load at fracture was expressed in megapascals (MPa). After fracture, SEM observation was once more performed to evaluate the nature of the fractured surfaces. Three photomicrographs with x2000 magnification were made of different regions of the treated surface and the fractured surface of each specimen. All of the data for shear bond strength were subjected to 1-way analysis of variance (ANOVA) to determine whether significant differences existed between the groups. This was then followed by the post hoc multiple range Tukey test (α = .05).

**RESULTS**

The majority of the specimens in the 4 groups showed adhesive fracture at the titanium-ceramic interface with small amounts of porcelain on the metal surface. The Ra value of the airborne-particle-abraded groups (APAS) demonstrated higher Ra (2.60 μm) values than the other groups: airborne-particle-abraded surface (APAS), 0.28 μm; AES, 0.21 μm; MS, 0.16 μm. The highest mean bond strength value (SD) was found in the APAS group (22.22 ± 4.04 MPa), followed by the AES group, the LES group, and then the MS group (21.22 ± 3.41 MPa, 14.98 ± 3.26 MPa, and 13.76 ± 3.16 MPa, respectively). The results of the Tukey multiple range tests showed that there were no significant differences in bond strength between the APAS and the LES group, or between the AES group and MS group. However, there were differences in bond strength values between the APAS and the AES group and the MS and AES group.

**TABLE I.** Means of shear bond strength values (MPa) for 4 experimental groups and Tukey analysis

<table>
<thead>
<tr>
<th>Group</th>
<th>Mean (SD) in MPa</th>
<th>Tukey Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>13.76 (3.16)</td>
<td>A</td>
</tr>
<tr>
<td>AES</td>
<td>14.98 (3.26)</td>
<td>A</td>
</tr>
<tr>
<td>LES</td>
<td>21.22 (3.41)</td>
<td>B</td>
</tr>
<tr>
<td>APAS</td>
<td>22.22 (4.04)</td>
<td>B</td>
</tr>
</tbody>
</table>

The photomicrographs of the fractured surfaces of each group are shown in Fig. 2. The AES group showed a more complete fracture, whereas the LES group showed an incomplete fracture. The APAS group showed a more complete fracture than the AES group, but the MS group showed an incomplete fracture. The AES group had more complete fracture than the MS group. The photomicrographs of the fractured specimens are shown in Fig. 3. The AES group showed more complete fracture than the MS group.

**CONCLUSIONS**

1. Laser etching was an effective method for improving bond strength with low-fusing porcelain in comparison with airborne-particle abrasion. However, Husaeni et al. indicated that airborne-particle abraded specimens showed greater bond strength than acid-etched specimens. The possibility of surface contamination with alumina particles, which could weaken the mechanical bonding between porcelain and titanium, has also been reported. If acid etching and airborne-particle abrasion were reported to increase the bond strength with titanium by removing the excess oxide, yet there has been controversy regarding acid-etching and airborne-particle-abrasion methods. Reyes et al. stated that airborne-particle-abrasion was an effective method for improving the bond strength of dental materials to metal surfaces. However, many of these advances have during the last decade have resulted in the increased use of lasers in dentistry. Many of these advances have been directed at the use of lasers in dental materials to metal surfaces. However, the use of lasers in dental material processing has been limited. The purpose of this study was to compare the effect of laser etching as a titanium surface treatment with 3 other conventional surface modifications (machining, airborne-particle abrasion, and acid etching) introduced for enhancing the bond strength of the titanium substrate to porcelain. The research hypothesis was that laser etching the titanium surface would enhance the titanium-porcelain bond strength when compared with airborne-particle abrasion, machining, and acid-etching surface treatment methods.
treated surfaces of each group are shown in Figure 2. The surface of the AES group appeared rough compared to that of MS group. The SEM image of the laser-etched surface appeared to be relatively smooth as compared with the images of other groups. The photomicrographs of the metal surface after debonding are presented in Figure 3. All of the experimental groups exhibited small amounts of porcelain retained on the surface. This observation indicated that the mode of bond failure was primarily adhesive between the porcelain and titanium.

DISCUSSION

The study results indicated that part of the research hypothesis could be accepted. Laser etching enhanced the titanium bond strength more than machining and acid etching, but not more than airborne-particle abrading. Although no statistical analysis was performed for surface roughness, the Ra of the LES was lower than that of the APAS. As demonstrated in Figure 2, the surface pattern of the laser-treated specimen appears smooth (Ra = 0.68 μm) rather than rough, compared with the airborne-particle-abrasion groups (Ra = 2.60 μm), indicating that the APAS showed an irregular or hollowed appearance compared to the morphology of the LES specimen. With a low Ra value, the LES showed similar strength as compared to the APAS. Gaggl et al.24 reported that laser processing is an effective method for producing an appropriate surface roughness without any contamination. HCl produced some roughness (Ra = 0.28 μm) in the AES group, compared to the control group MS (Ra = 0.21 μm), but not more than airborne-particle abrasion, which may produce excessive roughness (Ra = 2.60 μm). Acid etching did not have a significant effect on the titanium-ceramic bond, compared with machining. Although the surface texture was discernibly changed after chemical etching, as seen in the photomicrographs (Fig. 2), the surface after the fracture test was not distinguishable from that of the group shown in Figure 3. For the AES group, the heating process in HCl for 30 minutes could potentially produce a thick oxide layer, which could result in a weak bond.11

The minimum debonding/crack-initiation strength for the porcelain-metal combination set by ISO standard 9693 is 25 Mpa.13 However, the ISO-recommended 3-point bending test method could make it difficult to interpret the bond strength measurement because of uneven stress distribution at the interface between ceramic and metal, compared to the shear bond strength measurement method.22,23 The sole purpose of the circular-planar interface shear test used in the current study was to evaluate shear bond strength; thus, the clinically recommended porcelain thickness of 1.5 mm would not be practical.22 The reason that a thicker porcelain layer of 4 mm was used, rather than the recommended thickness of 3.5 mm, is that the diameter of the specimen in this study (5.7 mm) was wider than that used in the Chong et al.23 study (4 mm) (Fig. 1). A limitation of the present study was that only a single brand of low-fusing porcelain was tested; the findings related to this product cannot be extrapolated to similar materials.14 With a low Ra value, the LES showed similar strength as compared to the APAS. The relationship between roughness and bond strength requires further study.

CONCLUSIONS

Within the limitations of this study, the following conclusions were drawn:

1. The laser-etching surface treatment showed a significant difference in improving bond strength to a low-fusing porcelain as compared to acid-etching and machining surface treatment methods (P < .05).

2. The laser-etched surfaces demonstrated no significant difference in bond strength compared to airborne-particle-abrasion surfaces (P > .05).

REFERENCES

treated surfaces of each group are shown in Figure 2. The surface of the AES group appeared rough compared to that of MS group. The SEM image of the laser-etched surface appeared to be relatively smooth as compared to that of MS group. The SEM image of the AES group appeared rough compared to that of the MS group shown in Figure 2. The surface of the treated surfaces of each group are airborne-particle abraded.

DISCUSSION

The study results indicated that part of the research hypothesis could be accepted. Laser etching enhanced the titanium bond strength more than machining and acid etching, but not more than airborne-particle abrading. Although no statistical analysis was performed for surface roughness, the Ra of the LES was lower than that of the APAS. As demonstrated in Figure 2, the surface pattern of the laser-treated specimen appears smooth (Ra=0.68 μm) rather than rough, compared with the airborne-particle-abrasion groups (Ra=2.60 μm), indicating that the APAS showed an irregular or hollowed appearance compared to the morphology of the LES specimen. With a low Ra value, the LES showed similar strength as compared to the APAS. Gaggl et al24 reported that laser processing is a new method of treating implant surfaces to produce a high degree of purity with adequate surface roughness, in comparison with other surface treatments. Cho and Jung 25 also demonstrated that laser etching is an effective method for producing surface roughness without any contamination.

HCl produced some roughness (Ra=0.28 μm) in the AES group, compared to the control group MS (Ra=0.21 μm), but not more than airborne-particle abrasion, which may produce excessive roughness (Ra=2.60 μm). Acid etching did not have a significant effect on the titanium-ceramic bond, compared with machining. Although the surface texture was discernibly changed after chemical etching, as seen in the photomicrographs (Fig. 2), the surface after the fracture test was not distinguishable from that of the machined group (Fig. 3). For the AES group, the heating process in HCl for 30 minutes could potentially form a thick oxide layer, which could result in a weak bond.13

The minimum debonding/crack-initiation strength for the porcelain-metal combination set by ISO standard 9693 is 25 Mpa.13 However, the ISO-recommended 3-point bending test method could make it difficult to interpret the bond strength measurement because of uneven stress distribution at the interface between ceramic and metal, compared to the shear bond strength measuring method.22,23 The sole purpose of the circular-planar interface shear test used in the current study was to evaluate shear bond strength; thus, the clinically recommended porcelain thickness of 1.5 mm would not be practical.23 The reason that a thicker porcelain layer of 4 mm was used, rather than the recommended thickness of 3.5 mm, is that the diameter of the specimen in this study (5.7 mm) was wider than that used in the Chong et al22 study (4 mm) (Fig. 1). A limitation of the present study was that only a single brand of low-fusing porcelain was tested; the findings related to this product can not be extrapolated to similar materials.14 With a low Ra value, the LES showed similar strength as compared to the APAS. The relationship between roughness and bond strength requires further study.

REFERENCES

As a service to our subscribers, copies of back issues of The Journal of Prosthetic Dentistry for the preceding 5 years are maintained and are available for purchase from Elsevier Inc until inventory is depleted. Please write to Elsevier Inc Subscription Customer Service, 6277 Sea Harbor Dr, Orlando, FL 32887, or call 800-654-2452 or 407-345-4000 for information on availability of particular issues and prices.


10. Kim, Assistant Professor of Adult Restorative Dentistry, University of Nebraska Medical Center, Omaha, NE, 68198-1 Samduck 2Ga, Jung-Gu, 700-412 Daegu, SOUTH KOREA. E-mail: sacho@knu.ac.kr

11. Present at the 37th Annual Meeting of the American Association for Dental Research, Dallas, Tex, April 2008.


22. Amara Abreu, DDS, MSD,a Maria A. Loza, DMD, MS,b Augusto Elias, DMD, MSD,c Siuli Mukhopadhyay, PhD,d Stephen Looney, PhD,e and Frederick A. Rueggeberg, DMD, MSf Medical School of Georgia, Augusta, Ga; School of Dental Therapy, Medical Sciences Campus, University of Puerto Rico, San Juan, Puerto Rico; Indian Institute of Technology, Mumbai, India

Statement of problem. The ability of a resin cement to bond to a restorative alloy is critical for maximal crown retention to nonideal preparations. Treatment surface and metal type may have an important role in optimizing resin-to-metal strength.

Purpose. The purpose of this study was to examine the effect of surface pretreatment on the tensile strength of base and noble metals bonded using a conventional resin cement.

Material and methods. Cylindrical plastic rods (9.5 mm in diameter), cast in base (Reexistium NBF) or noble metal (IPS eSIGN 53), were divided into rods 10 mm in length (n=10-12). Specimens were heated in a porcelain furnace to create an oxide layer. Test specimens were further subjected to airborne abrasion (250 μm AO, Al2O3 particles) alone or with the application of a metal primer (Alloy Primer). Similarly treated rod ends were joined using resin cement (RelYARC), thermocycled (x500, 5°C–55°C) and stored (24 hours, 37°C) before debonding using a universal testing machine. Debond stress and failure site were recorded. Rank-based ANOVA for unbalanced designs was used to test for significant interaction (p<.05). Each type of treatment was compared separately for each metal (Bonferroni-adjusted significance level of .0083, overall error rate for comparisons, .05). The 2 metals were compared separately for each of the 3 treatments using an adjusted significance level of .017, maintaining an overall error rate of .05. A multinomial logit model was used to describe the effect of metal type and surface pretreatment on failure site location (α=0.05).

Results. Interaction between metal type and surface pretreatment was significant for stress values (p<.019). Metal type did not significantly affect tensile bond strength for any of the compared surface pretreatments. Metal primer significantly improved tensile bond strength for each metal type. Most failures tended to occur as either adhesive or mixed in nature.

Conclusions. Metal primer application significantly enhanced tensile bond strength to base and noble metal. No significant differences in tensile stress were found between alloys. Differences in failure site incidence were found to be related to metal type and surface pretreatment (J Prostheth Dent 2009;101:107-118).