Effect of hydrofluoric acid concentration and etching duration on select surface roughness parameters for zirconia

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An increasing number of metal ceramic restorations are being replaced with ceramic systems. The opaque metal coping reflects light, which produces an artificial appearance of the restoration. Metal blocks out 100% of light; thus, it does not pass through to the gingival tissue. Zirconia has excellent esthetic properties, is semi-translucent, and is light in color. Light transmission is approximately 48%, and the refractive index is 2.3.\(^1,\(^2\)

Zirconia restorations have excellent mechanical properties compared with other ceramic systems used in dentistry.\(^3,\(^4\)\) However, the hardness of yttria-stabilized zirconia (3Y-TZP) causes problems with surface enhancement and makes it difficult to ensure appropriate preparation for bonding between the luting cement and the prosthetic restoration. The homogenous, densely packed structure of zirconia crystals and the absence of a glass matrix make etching and silanization impossible. For this reason, bond strength is lower than for glass ceramic restorations.\(^4,\(^5\)\) The minimum tensile bond strength acceptable in clinical conditions ranges between 10 and 13 MPa.\(^6\) A strong, durable resin-to-ceramic bond is established through the formation of chemical bonds and by micromechanical interlocking.\(^7,\(^9\)\)

Several surface roughening and coating methods have been used to optimize the surface of zirconia and to improve its bond strength with resin-based cements. However, they were not effective in significantly increasing the zirconia-resin bond strength.\(^10\) Aside from mechanical retention, to date, the only effective method for ensuring chemical bonding to zirconia surfaces is one that requires the use of a modified bisphenol A glycidyl

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**ABSTRACT**

**Statement of problem.** The surface of zirconia is resistant to chemical treatment. Roughening the surface of densely sintered zirconia still poses a challenge in dentistry.

**Purpose.** The purpose of the study was to examine the effects of hydrofluoric acid on the quality of surface roughening of zirconia.

**Material and methods.** One hundred cylindrical disks made from zirconia (Ceramill Z; Amann Girrbach AG) were divided into 4 groups. Three groups (n=30) were distinguished on the basis of hydrofluoric acid (HF) concentration: 40% HF, 9.5% HF, and 5% HF. The groups were then further divided into 3 groups of 10 specimens, each based on etch time (1, 5, or 15 minutes). The control group (n=10) consisted of specimens polished with SiC abrasive paper. The surface was examined with scanning electron microscopy, and the roughness was measured with a profilometer and confocal laser scanning microscope. The mean arithmetic profile deviation (Ra mean) and mean maximum height of profile (Rz mean) results for the etched surfaces in relationship to the baseline surfaces were compared with the Student t test for averaged data (α=.05).

**Results.** When etched with 40% HF concentration, the Ra mean and Rz mean results were statistically higher (P<.01) for the etched surfaces than for the baseline surfaces. When etched with 9.5% HF concentration, the higher Ra mean and Rz mean results were only statistically significant (P<.01) after 15 minutes. Etching with 5% HF concentration showed no significant differences (P> .05).

**Conclusions.** Etching with a 5% HF solution should not be recommended as a method for roughening zirconia surfaces. (J Prosthet Dent 2015;113:596-602)
Clinical Implications
Applying 5% hydrofluoric acid to zirconia restorations does not ensure an acceptable degree of surface roughness.

methacrylate resin luting agent (Panavia 21; Kuraray). This agent contains the adhesive phosphate monomer and self-etching universal resin cement (RelayX Unicem; 3M ESPE) and provides a stable bond that resists hydrolysis during different artificial aging procedures. Unfortunately, this stable bond is not sufficient to ensure retention of adhesive zirconia restorations, thereby resulting in debonding under function. In vitro aging is used to study bond stability under controlled laboratory conditions.

The methods used to increase micromechanical retention such as airborne-particle abrasion with Al2O3 causes insignificant surface modification but also induces an unfavorable transformation of the material from a tetragonal to monoclinic phase. This results in the buildup of surface compression, subsurface tension, and residual flaws. The disturbed phase stability increases susceptibility to degradation, which can lead to aging of the surface with grains breaking off, formation of microcracks, and reduced material fatigue strength. In addition, neither airborne-particle abrasion nor grinding with abrasive paper or diamond rotary instruments, despite being technically simple to perform, significantly increased the bond strength between ZrO2 and luting cements.

Traditional silanes used in silica ceramics are not an effective means of conditioning a polar zirconia surface, which is characterized by hydroxyl ions bound both chemically and mechanically to water. The absence of a silica layer prevents both a reaction between the methoxy silane groups and bonding with the ZrO2 surface.

The CoJet and Rocatec systems (3M ESPE) consist of a tribochemical silica coat, which forms as a result of airborne-particle abrasion, where the abrasive material contains the appropriate silica compounds in addition to aluminum oxide. This results in the emergence of a surface ceramic layer and micromechanical retention. Taken together, this improves the bonding action with the luting cement.

One innovative surface roughening technique is selective infiltration etching (SIE). SIE is based on the principle of heat-induced infiltration, which can lead to the rearrangement of zirconia crystals and also result in the formation of intergrain nanoporosities, where low-viscosity resinous materials can flow and interlock after polymerization.

Casucci et al devised an experimental method for ZrO2 surface roughening. They used an acid with methanol, 37% HCl, and ferric chloride at a temperature of 100°C. This process increased the mean arithmetic profile deviation (Ramean) roughness parameter. Nevertheless, there was an effect of weakness over time, which may be due to the low concentration of silica on the insufficiently abraded hard surface of ZrO2. The surface of zirconia, which is resistant to chemical and mechanical factors, is a suitable surface for experimental studies on its enhancement by increasing the etching time and concentration of HF.

MATERIAL AND METHODS
A total of 100 cylindrical specimens of 3Y-TZP (Ceramill Zi; Amann Girrbach AG) were sintered in a furnace (Ceramill Therm; Amann Girrbach AG) by using a universal program (8°C per minute from 200°C to 1450°C, 2 hours at a fixed temperature of 1450°C, and the correct cooling time). The sintering process lasted approximately 10 hours. Material shrinkage amounted to approximately 21%. After sintering, the specimens had a diameter of 9 mm and height of 5 mm. Ninety of the specimens were divided into 3 groups (n=30) on the basis of acid concentration and were further divided into 3 groups of 10 specimens, each based on etch time. Specimens were etched with hydrofluoric acid (HF) in concentrations of 40%, 9.5%, and 5% for 1, 5, or 15 minutes. Table 1 shows the characteristics of the acid and its commercial origin. A concentration of 40% acid was prepared for experimental purposes in a laboratory. The surface of the specimens had been polished successively with 220, 400, 600, and 800 grit size abrasive paper with a Metasine grinding machine with water cooling. The specimens were then washed in an ultrasonic cleaner (Quantrex 90 WT; L&R Manufacturing Inc) in ethanol for 10 minutes and air dried. A control group (n=10) consisted of specimens polished with SiC abrasive paper.

Acid was applied to each of the 10 specimens for 1, 5, or 15 minutes and then rinsed off with acetone in an ultrasonic cleaner. The specimens were then neutralized in a powder consisting of calcium carbonate and sodium carbonate (CaCO3 and Na2CO3) for 5 minutes, rinsed once more for 20 seconds in distilled water, and air dried.

The specimens were examined with a Hitachi S300N scanning electronic microscope (SEM). Depending on the type of registered signal emitted by the specimen (after being stimulated by electron beams), 2 types of images were registered in SE secondary electrons (surface...
topography) and retrospectively in backscattered BSE electrons (so-called material contrast).

Profilometric tests were made with a Nikon MA200 confocal laser scanning microscope (CLSM) with an image resolution of 512×512 pixels. The surfaces of the specimens were scanned with an argon laser at a wavelength of $\lambda=488$ nm. Measurements were made with a microscope at $\times500$ magnification. The measured section was 275 μm in length. Three images (at 3 different sites) were obtained from each specimen. These images were registered with EZ-C1 software. The data obtained with microscopy were analyzed with software (Mountains Map Premium 6; Digital Surf). A mean roughness profile was achieved from each image, and the parameters were determined for $R_{a\text{mean}}$ and mean maximum height of profile ($R_{z\text{mean}}$). The mean value was then calculated for each of these parameters.

Three 275×275 μm images were scanned for each tested specimen. Roughness profiles were determined for each area with MMP software, that is, 512 profiles each in the north-south and east-west direction. Each individual profile was used to establish roughness parameters. To determine the final roughness parameters for the tested surfaces, the arithmetic mean was established for values from all 1024 profiles for 3 scanning fields. These results were analyzed by using the PQ Stat v1.4.2.324 statistical package. The $R_{a\text{mean}}$ and $R_{z\text{mean}}$ results for the etched surfaces in relationship to the baseline surfaces were compared with the Student $t$ test for averaged data. A test probability of $P<.05$ was regarded as significant, while a test probability of $P<.01$ was considered to be statistically significant.

RESULTS

Examinations made with an SEM in an image of SE secondary electrons and dispersed BSE electrons are presented in Figures 1, 2. The images revealed slight differences in the surface topography of the tested specimens after etching with HF at concentrations of 5%, 9.5%, and 40% each specimen had been etched for 1, 5, and 15 minutes. The differences are expressed on a nanometric scale.

Microscopic images obtained with CLSM are presented in Figures 3, 4. Slight differences were observed in the surface topography of the etched surfaces compared with the baseline specimens. The data are expressed on a nanometric scale.

The results of the numerical values of roughness parameters and their standard deviations are presented in Tables 2-4. Figures 5, 6 feature the percentage changes in the increase in the values of roughness parameters, $R_{a\text{mean}}$ and $R_{z\text{mean}}$, depending on the etching time.

The images presented here show that the tested surfaces were poorly enhanced. An increase in acid concentration and etching duration resulted in slightly greater surface enhancement, although the size, which is
expressed in nanometers, is most likely not sufficient to ensure an effective bond between the luting cement and abutment teeth.

Statistically significant differences ($t=-6.71$, $P<.001$) were observed in the $R_a$ results between the baseline surface and the surface etched with 40% HF concentration after 1 minute, with higher results observed for the etched surface. Statistically significant differences ($t=-5.66$, $P<.001$) were also observed in the $R_a$ results between the baseline surface and the surface etched with 40% HF concentration after 5 minutes, with higher results observed for the etched surface. Statistically significant differences ($t=-8.48$, $P<.001$) were observed in the $R_a$ results between the baseline surface and the surface etched with 40% HF concentration after 15 minutes, with higher results observed for the etched surface.

Figure 4. CLSM images of surfaces of specimens after HF etching with 5%, 9.5%, and 40% HF concentrations after 1 minute, 5 minutes, and 15 minutes at ×500 magnification.

Table 2. Mean arithmetic roughness parameters $R_a$ and $R_z$ for baseline specimens and specimens etched with 40% HF concentration

<table>
<thead>
<tr>
<th>Etching Time</th>
<th>Baseline Surface</th>
<th>Surface Treated</th>
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<tbody>
<tr>
<td></td>
<td>$R_a$ (µm)</td>
<td>$R_z$ (µm)</td>
</tr>
<tr>
<td>1 min</td>
<td>0.002</td>
<td>0.000</td>
</tr>
<tr>
<td>5 min</td>
<td>0.003</td>
<td>0.000</td>
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<td>15 min</td>
<td>0.001</td>
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$R_a$ mean arithmetic profile deviation; $R_z$ mean maximum height of profile; HF, hydrofluoric acid.

Table 3. Mean arithmetic roughness parameters $R_a$ and $R_z$ for baseline specimens and specimens etched with 9.5% HF concentration

<table>
<thead>
<tr>
<th>Etching Time</th>
<th>Baseline Surface</th>
<th>Surface Treated</th>
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<tbody>
<tr>
<td></td>
<td>$R_a$ (µm)</td>
<td>$R_z$ (µm)</td>
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<tr>
<td>1 min</td>
<td>0.002</td>
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<td>5 min</td>
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<tr>
<td>15 min</td>
<td>0.002</td>
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$R_a$ mean arithmetic profile deviation; $R_z$ mean maximum height of profile; HF, hydrofluoric acid.

Table 4. Mean arithmetic roughness parameters $R_a$ and $R_z$ for baseline specimens and surfaces etched with 5% HF concentration

<table>
<thead>
<tr>
<th>Etching Time</th>
<th>Baseline Surface</th>
<th>Surface Treated</th>
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<tr>
<td></td>
<td>$R_a$ (µm)</td>
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<tr>
<td>1 min</td>
<td>0.002</td>
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<td>5 min</td>
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<tr>
<td>15 min</td>
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$R_a$ mean arithmetic profile deviation; $R_z$ mean maximum height of profile; HF, hydrofluoric acid.
Statistically significant differences \((t=-9.69, P<.001)\) were observed in the \(R_\text{zmean}\) results between the baseline surface and the surface etched with 40% HF concentration after 1 minute, with higher results observed for the etched surface. Statistically significant differences \((t=-3.97, P=.003)\) were also observed in the \(R_\text{zmean}\) results between the baseline surface and the surface etched with 40% HF concentration after 5 minutes, with the higher results noted for the etched surface. Statistically significant differences \((t=-18.20, P<.001)\) were also observed in the \(R_\text{zmean}\) results between the baseline surface and the surface etched with 40% HF concentration after 15 minutes, with higher results noted for the etched surface. In summary, etching with 40% HF concentration produced significantly higher \((P<.01)\) \(R_\text{a}\) and \(R_\text{z}\) results for the etched surfaces in relationship to the baseline surfaces.

No significant \((t=0, P=1.000)\) differences were observed in the \(R_\text{a}\) results between the baseline surface and the surface etched with 9.5% HF concentration after 1 minute. No significant differences \((t=0, P=1.000)\) were observed in the \(R_\text{z}\) results between the baseline surface and the surface etched with 5% HF concentration after 15 minutes. However, after 15 minutes, significant \((t=-2.24, P<.038)\) differences were observed in the mean \(R_\text{a}\) results between the baseline surface and the surface etched with 9.5% HF concentration, with higher results observed for the etched surface.

Significant differences \((t=-2.24, P=.038)\) were observed in the \(R_\text{z}\) results between the baseline surface and the surface etched with 9% HF concentration after 1 minute, with higher results observed for the etched surface. No significant differences \((t=-1.11, P=.278)\) were found in the \(R_\text{z}\) results between the baseline surface and the surface etched with 9.5% HF concentration after 5 minutes. Statistically significant differences \((t=-3.51, P=.003)\) were observed in the \(R_\text{z}\) results between the baseline surface and the surface etched with 9.5% HF concentration after 15 minutes. There were still no significant differences \((t=-1.58, P=.149)\) in the \(R_\text{a}\) results between the baseline surface and the surface etched with 9.5% HF concentration after 5 minutes. No significant differences \((t=0, P=1.000)\) in the \(R_\text{z}\) results were observed when the surfaces were etched with 5% HF concentration after 15 minutes. Taken together, the results show that etching with 40% HF concentration produced significantly higher \((P<.01)\) \(R_\text{a}\) and \(R_\text{z}\) results for the etched surfaces in relationship to the baseline surfaces.

When etching was done with a 40% HF concentration, the mean increase in parameters \(\Delta R_\text{a}\) and \(\Delta R_\text{z}\) achieved significantly higher \((P<.01)\) values over time. Nevertheless, despite the increase in roughness, these parameters still remained at the level of several to a dozen nanometers and may have resulted in less bonding with
the luting cement. However, at HF 9.5% and HF 5%, these changes were slight or nonexistent.

**DISCUSSION**

To ensure high retention, prevention of microleakage, and increased fracture/fatigue resistance, bonding techniques for zirconia-based systems must be improved. Strong resin bonding relies on micromechanical interlocking and adhesive chemical bonding to the ceramic surface and requires surface activation for chemical adhesion. In some instances, high-strength ceramic restorations do not require adhesive bonding to a tooth structure and can be placed using conventional cements, which rely on micromechanical retention alone. However, resin bonding is desirable when the prepared tooth structure is unusually short or tapered. Adhesion is dependent on the type of luting cement used and its bonding capacity between a suitably prepared ceramic surface and the enamel and dentin.

Many studies have focused on the problem of selecting the appropriate cement to achieve the optimal retention of crowns and partial fixed dental prosthesis. Another factor of importance for strong and long-term bonding is appropriate surface treatment. A rough and irregular surface of 3Y-TZP creates microretentive depressions for the bonding systems. Thus, not only is the bonding surface greater, but the wetting and surface energy are also greater. Airborne-particle abrasion has been used in an attempt to enhance the surface area available for bonding; although an improvement in the average surface roughness has been recorded on a micrometer scale, the treatment appeared to be inadequate to establish reliable ceramic/cement bonds.

Alternative technologies are advocated to change these high-strength ceramic cores into more retentive substrates. SIE has recently been proposed because it has achieved promising results in terms of bond strength values at the zirconia-resin cement interfaces. The use of SIE improved nanomechanical retention of zirconia by increasing the surface area available for bonding.

Casucci et al have shown that a hot chemical etching solution produces a surface roughness that is significantly greater than when SIE is used. This technique could possibly enhance the mechanical retention of ZrO2 and increase the Ra, roughness parameter of the 3Y-TZP surface from 26 nm after 10 minutes to 103 nm after 60 minutes. In the same studies, etching with 9.5% HF also achieved a parameter value of Ra, 5 nm after 90 seconds.

In the studies presented here, the value of the Ra, parameter after etching with 9.5% HF was 0.002 after 60 seconds, and the same result was achieved after 5 minutes and 0.003 after 15 minutes. However, etching with a 5% HF solution achieved Ra, parameter values of 0.002 after 60 seconds, 0.001 after 5 minutes, and 0.002 after 15 minutes.

The majority of authors have reported that the application of a 9.5% or 5% HF concentration to a zirconia surface does not cause any morphologic changes in its structure and does not increase surface roughness and that the roughness is less compared with conventional ceramics. We obtained similar conclusions for our study.

Significantly higher (P<.01) Ra, and Rz, results on the etched surfaces compared with the baseline surfaces were achieved with 40% HF concentration, and the mean increase in parameters  and (t) achieved statistically significant (P<.01) values over time. The data obtained in this study were detectable on a nanometric scale, which indicates that the quality of surface enhancement may be insufficient to improve bond strength with luting cements. Etching zirconia with HF has limited effectiveness because of the dense crystal network and the small amount of glass matrix and is not recommended as a treatment method for this material.

**CONCLUSIONS**

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

1. An increase in etching time has a positive effect on the quality of the treated zirconia surface, although it is also dependent on the concentration of acids used for etching.
2. Etching with a 5% HF solution is not recommended as a method for roughening zirconia surfaces.

**REFERENCES**


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Noteworthy Abstracts of the Current Literature

Evidence and the practice of prosthodontics: 20 years after EBD introduction

Carr AB
J Prosthodont 2015;24:12-16

Prosthodontics has a rich history related to the principles embedded in evidence-based health care. This paper reviews the evidence-based prosthodontics activity over the past 3 decades. It also discusses the impact of health care reform on evidence-based medicine as it relates to broader context of care outcomes. Finally, the value associated with an Evidence Stewardship emphasis in prosthodontics is presented. This emphasis suggests that combining evidence from clinical trials with evidence from clinical practice environments best equips clinicians for the management of patients in the future. Adoption of a strategic Evidence Stewardship direction is an extended commitment to change that recognizes health care reform aims and seeks to be an accountable provider group in the broader health care arena. The vision to form a representative network of prosthodontic practitioners that augments a commitment to Cochrane "clinical trial" data demonstrates a responsibility to professional transparency about who we are, adds value for patients and oral health care providers, impacts teachers and students in dental education, and provides a measure of care accountability unique in dentistry.

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