ORIGINAL ARTICLE

Effect of liner and porcelain application on zirconia surface structure and composition

Tariq F Alghazzawi[1,2] and Gregg M Janowski[2]

The purpose of this study was to determine if there is an effect of liner and porcelain application (layering and pressing techniques) on the surface of yttria-stabilized tetragonal zirconia polycrystals (Y-TZP), which were exposed to permutations of liner, layered porcelain, and pressed porcelain. Scanning electron microscope (SEM)/energy dispersive spectroscope (EDS) was used to identify changes in composition and microstructure after removing liner and porcelain with hydrofluoric acid. Simulated aging was also conducted to determine the effect of liner and porcelain on low-temperature degradation. The control group had a typical equiaxed grain structure, referred to as unaffected. When covered with liner or porcelain, some areas changed in structure and composition and were termed affected. The frequency of affected structure decreased when liner was covered with either layered porcelain or pressed porcelain. There were statistical differences ($P < 0.05$) in the composition between affected and unaffected for zirconium (layered porcelain with liner: affected $= 60\%$ (0.8%) (m/m), unaffected $= 69\%$ (4%), layered porcelain without liner: affected $= 59\%$ (3%), unaffected $= 65\%$ (3%)) and oxygen (layered porcelain with liner: affected $= 35\%$ (2%), unaffected $= 26\%$ (4%), layered porcelain without liner: affected $= 35\%$ (3%), unaffected $= 30\%$ (2%)). However, there were statistical differences ($P < 0.05$) in the composition for zirconium and oxygen of the aged layered porcelain without liner only. The liner should not be used before porcelain application, especially when using the layering technique for zirconia restorations. Furthermore, pressing should be considered the technique of choice over layering.

INTRODUCTION

Zirconia exists with tetragonal, monoclinic, rhombohedral, and cubic crystal structures, depending upon stress, temperature, oxide additions, and pressure. Many mechanical and physical properties depend upon crystal structure, including the coefficient of thermal expansion (CTE). The tetragonal phase has a CTE of 10.8×10^{-6} per °C whereas the monoclinic phase has a CTE of 7.5×10^{-6} per °C.[1] When the CTE (8.6×10^{-6} to 9.6×10^{-6} per °C) of veneering porcelain is 1×10^{-6} to 2×10^{-6} per °C below the zirconia, a durable bond between zirconia and veneering porcelain is promoted.[2–3]

The tetragonal phase is desirable on the basis of toughness and thermal expansion and is achieved in yttria-stabilized tetragonal zirconia (Y-TZP) by the addition of $\sim 3\%$ (n/n) Y_2O_3. Routine dental laboratory procedures used to fabricate zirconia frameworks such as grinding, sandblasting, and polishing before porcelain veneering may induce the tetragonal to monoclinic transformation.[4–9] The monoclinic phase is not suitable for veneering because of its lower CTE compared with the porcelain.[1] Furthermore, the tetragonal to monoclinic transformation is accompanied by volumetric expansion, which may result in grain pull-out and weakening of the zirconia/veneer bond (initial failure).[10]

A post-fabrication heat treatment (regeneration firing) above 1 000 °C (mimicking firing of porcelain) is routinely applied to reverse the tetragonal to monoclinic transformation.[11] However, evidence shows that not all of the monoclinic phase transforms.[11]

Core-veneered zirconia restorations may suffer from chipping (cohesive) and delamination (adhesive) failures of the veneer[12] with delamination failures being more frequent than chipping.[13] The underlying mechanism for the failures is not known but could be a result of interdiffusion and reactions at interface.[14–16] The veneering porcelain may dissolve the stabilizing dopant (yttria) and (1) induce a phase transformation of the zirconia or (2) disturb the grain boundaries, either of which could translate into chipping at the surface. Furthermore, failure could be caused (or made more likely) by the presence of residual stress (CTE mismatch, excessive thickness of the veneer porcelain, uneven thickness of the veneer porcelain, large core-veneer thickness ratio) and tetragonal to monoclinic transformation.[17]

A large number of other factors have been reported to affect the failure of veneering porcelain on zirconia. Processing and material parameters that have been cited include thermal history including cooling rate,[18] unfavorable thermal expansion mismatch,[19–20] number

[1]Department of Prosthetic Dental Sciences, College of Dentistry, Taibah University, Madina, Kingdom of Saudi Arabia and [2]Department of Materials Science and Engineering, School of Engineering, The University of Alabama at Birmingham, Birmingham, USA
Correspondence: Dr TF Alghazzawi, Department of Prosthetic Dental Sciences, College of Dentistry, Taibah University, PO Box 51209, Madina 11543, Riyadh, Kingdom of Saudi Arabia
E-mail: drtariq05@gmail.com

of veneering porcelain firings,[21] thermal conductivity associated with the thermal diffusivity of zirconia,[22] and firing protocol. Geometric reasons that have been mentioned are core/veneering porcelain thickness ratio,[23–25] thickness of the porcelain,[18] and framework design.[26] Finally, failure of the veneer porcelain can be affected by structural reasons including reduced flexural strength of the porcelain due to internal flaws,[23,27–28] sandblasting,[3,5–7] the application of liner,[6,7,9,16,20,29] application of modifier,[30] fabrication technique for the veneer porcelain,[23,27–28,31] silica coating,[32] sandblasting followed by heat treatment,[8] color of zirconia core,[33] and wettability of zirconia.[34]

The objectives of this study were to determine (1) if there is an effect of liner application on the surface of Y-TZP zirconia using layering and pressing techniques; and (2) if porcelain application technique affects the surface topography of zirconia. The hypotheses were: (1) the liner decreases the interdiffusion at zirconia–porcelain interface; and (2) there will be no difference in the veneering technique for the interdiffusion process. These effects of these variables on the zirconia/porcelain interface were previously studied using X-ray diffraction.[17]

MATERIAL AND METHODS
Specimen preparation and surface treatments
Thirteen tetragonal zirconia blanks (CTE $= 10.8 \times 10^{-6}$ per °C, Argen Corporation, San Diego, CA, USA; composition of ZrO_2 90.95%, Y_2O_3 4.5%-6.0%, $HfO_2 \leqslant 5\%$, $Al_2O_3 \leqslant 0.5\%$; 4 mm thick, 10 mm long, and 10 mm wide) were machined using a DWX-50 dental mill (Roland DGA, Irvine, CA, USA) in presintered form. These blanks were sintered according to the manufacturer instructions (1st ramp up $= 4$ °C · min^{-1}, temperature 1 525 °C, hold 120 min; 1st ramp down $= 7$ °C·min^{-1}, temperature 1 000 °C; 2nd ramp down $=$ natural, temperature $=$ room temperature) to simulate core fabrication before application of porcelain. The final samples after milling and sintering were not polished or glazed and designated as Mil-Sin group (control group). Then this group was exposed to various combinations of surface treatments and then distributed into 13 groups (three samples were used for each group) as shown in Figure 1. Groups were selected in order to determine the effects of individual and combinations of processing steps. Variables included (1) hydrofluoric acid (HF) treatment, (2) application of liner, (3) application of porcelain by manual layering, (4) application of porcelain by pressing, and (5) artificial aging to induce low-temperature degradation. The surface treatment with HF alone (HF group) was used

to determine the effect of HF on the microstructure of zirconia surface when this acid is used for dissolving the liner, layered and pressed porcelain followed by exposing the surface of zirconia samples.

Hydrofluoric acid surface treatments
All surface treatments including liner and porcelain applications were performed on the top surface which was not inscribed, whereas the (+) symbol was inscribed on the bottom surface using a sharp knife to differentiate the top and bottom surfaces after removal of the liner and porcelain. As the porcelain on the top surface of the samples was of a darker color (Vitapan classical shade D4), this layer was readily delineated and removed by application of the HF acid. This procedure exposed the top surface of the zirconia chemically and did not subject it to mechanical cutting with a diamond stone that would induce tetragonal to monoclinic transformation. Assuming that the HF acid application for removal of the porcelain would cause minimal or no effect on the top surface of the samples going to be investigated by scanning electron microscope (SEM), the data from the aging process should provide reliable and accurate analysis. All the samples (except Groups Mill-Sin and Ag) were immersed in fresh HF acid (Stripit, Keystone Industries, Winder, GA, USA) and contained in mini-rubber bowl (Pulpdent Corporation, Watertown, MA, USA) for 45 min per the manufacturer's recommendation for complete removal of porcelain and liner from core. The concentration of the hydrofluoric acid was not declared by the manufacturer.

For the layering of the porcelain, the veneering and firing were performed according to ISO 9693:1999 with the aid of a silicone fixture to achieve standardized thickness of the layered porcelain. Thickness was measured using a caliper with accuracy ± 0.001 mm (L.S. Starrett Company, Athol, MA, USA). The zirconia liner (CTE $= 9.1 \times 10^{-6}$ per °C, shade Base Stain; Kuraray Noritake Dental, Tokyo, Japan) was applied to form a thickness of 0.1 mm. The porcelain application (CTE $= 6.8 \times 10^{-6}$ per °C, Cerabien ZR; Kuraray Noritake Dental, Tokyo, Japan) was implemented with a wash-dentin-firing technique for the initial wetting of zirconia samples. This technique involved the firing of a very thin layer of veneering porcelain (dry-out time $= 7–10$ min, low temperature $= 600$ °C, start vacuum $= 600$ °C, heat rate $= 45$ °C·min^{-1}, vacuum level $= 96$ kPa, release vacuum $= 930$ kPa, hold time in the air $= 1$ min, high temperature $= 930$ °C, and cool time $= 4$ min) with a thickness of 0.5 mm in a furnace chamber.
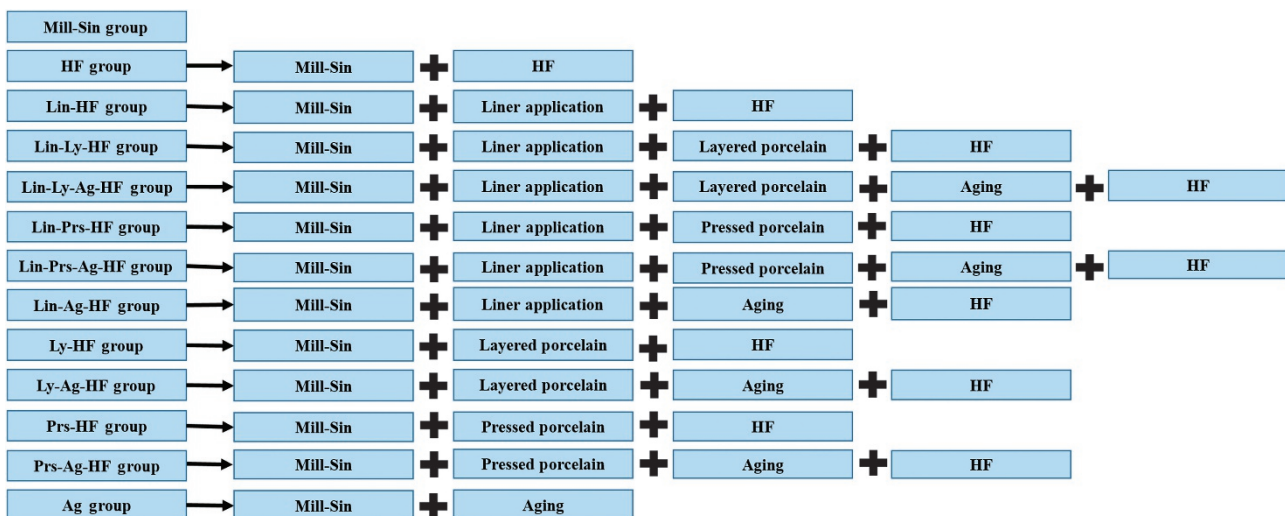

Figure 1 Distribution of samples into 13 groups which allowed each variable to be considered in combination with each other variable. Each group was given different surface treatments except Mill-Sin group.

Subsequently, the building up and firing of the dental porcelain was completed, followed by finishing and polishing. The total thickness of the liner and dentin porcelain was adjusted to 2 mm.

For the pressing of porcelain, the liner was applied using the same method as layering of porcelain. However, an inlay wax (rapid dipping wax; AST, Huntsville, AL, USA) was added onto the zirconia samples. The samples with wax were sprued, invested and pressed with porcelain (CTE = 10.5×10^{-6} per °C, e.max Zirpress; Ivoclar Vivadent, Amherst, NY, USA) according to manufacturer instructions. The total thickness of the liner and dentin porcelain was adjusted to 2 mm.

Aging process
The samples were placed inside different alumina crucibles and then inserted into an autoclave unit to be exposed directly to a steam to simulate aging of zirconia samples. The procedure was processed with a temperature of 134 °C at pressure of 0.2 MPa as recommended by International Standard ISO 13356.[35] The aging cycles ran for a total of 50 h.

Scanning electron microscope
After the treatments specified in Figure 1 were complete, the samples were ultrasonically cleaned in acetone for 20–30 min and then thermally etched at a temperature of 1 500 °C for 30 min. Thermal etching of zirconia results in topographical contrast due to differential material removal which is a result of localized composition and bonding differences. Scanning electron micrographs of these specimens were obtained using high-vacuum mode on a Quanta SEM with an accelerating voltage of 30 kV after gold palladium sputter coating. Quantitative microstructural measurements were not made, and only qualitative descriptions will be presented. Energy dispersive spectroscopy (EDS) was conducted at ten different points for each sample to determine if there is any difference in the element composition (aluminum, calcium, fluorine, potassium, magnesium, sodium, oxygen, silicon, titanium, yttrium, zinc, zirconium) between different groups and between liner, layered, and pressed porcelain.

Statistical analysis
The sample size was based on past publications.[36] The data analysis for the amount of each element in different groups used a one-factor analysis of variance (ANOVA) model. When the ANOVA was significant, the Bonferroni *post hoc* test was used to determine which groups were significantly different. Additionally, the *t*-test was used to determine the difference in the element composition of the same sample. Statistical significance was set at $P = 0.05$.

RESULTS
Composition differences among liner, layered porcelain, and pressed porcelain
The elemental analysis of the porcelains is presented in Figure 2. There was a statistical difference ($P < 0.05$) in the composition between layered and pressed porcelain for silicon and oxygen only. The layered porcelain had composition (*m/m*) of silicon 33% ± 4%, and oxygen 45% ± 3% (*m/m*) whereas the pressed porcelain had less composition of silicon = 27% ± 7%, and oxygen = 40% ± 4%. There was a statistical difference in the composition between liner, layered and pressed porcelain in which the liner had more Al (10% ± 2%), K (8% ± 3%), Na (9% ± 1%) elements than layered porcelain (Al = 6% ± 3%, K = 5% ± 2%, Na = 8% ± 1%), and pressed porcelain (Al = 7% ± 2%, K = 5% ± 1%, Na = 6% ± 2%). There was no Zn, F, and Ti elements in layered and liner porcelain. There was no Mg observed in pressed porcelain.
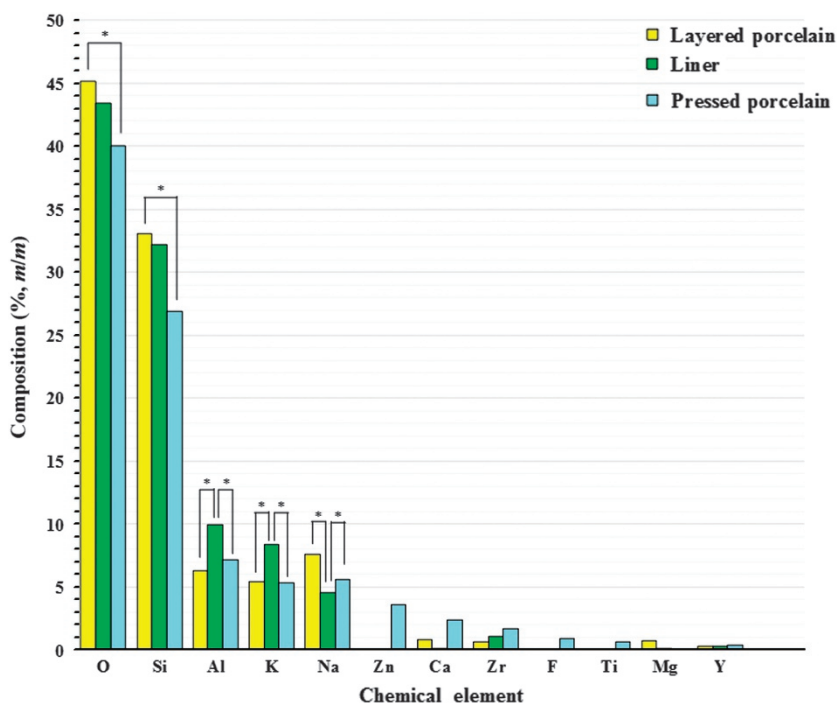
Figure 2 The composition for layered, liner, and pressed porcelain as determined by EDS in weight percent. There was a statistical difference ($P < 0.05$) in the composition between layered and pressed porcelain. The layered porcelain had more Si, and O than pressed porcelain. There was statistical difference in the composition between liner and layered, pressed porcelain in which the liner had more Al, K, and Na than layered and pressed porcelain. There was no Zn, F, and Ti elements in liner and layered porcelain. There was no Mg element in pressed porcelain. Al, aluminum; Ca, calcium; EDS, energy dispersive spectroscopy; F, fluorine; K, potassium; Mg, magnesium; Na, sodium; O, oxygen; Si, silicon; Ti, titanium; Y, yttrium; Zn, zinc; Zr, zirconium.

Composition difference between groups (Zr, O, and Y)

The elemental analysis of the zirconia samples is illustrated in Figure 3. After HF immersion as shown in Figure 3 compared with Figure 2, all the groups had Zr, Y, and O only which were the same elements (with different compositions due to different surface treatments as shown in Figure 3) of Group Mill-Sin which was not covered by either liner or porcelain. Furthermore, very small amounts of Zr and Y elements were contained in the liner and porcelain, as shown in Figure 2. Thus, the zirconia base must be the source of Zr and Y elements in any reaction layer, and this indicates that this HF treatment completely removed liner and porcelain. The composition of each sample group was measured using EDS to determine if the application and removal of liner and each porcelain type altered the surface composition. These measurements were made at a sufficiently low magnification to present an "average" without resolving differences at the grain size scale.

There was a statistical difference ($P < 0.05$) in the composition between Group Mill-Sin ($72\% \pm 7\%$) and Group Ly-HF ($62\% \pm 4\%$), Group HF ($71\% \pm 3\%$) and Group Ly-HF ($62\% \pm 4\%$), Group Lin-Ly-HF ($65\% \pm 6\%$) and Group Ag ($72\% \pm 3\%$), Group Lin-Prs-HF ($70\% \pm 4\%$) and Group Ly-HF ($62\% \pm 4\%$), Group Lin-Ly-HF ($65\% \pm 6\%$) and Group Ag ($72\% \pm 3\%$), Group Ly-HF ($62\% \pm 4\%$), and Group Ag ($72\% \pm 3\%$).

There was a statistical difference ($P < 0.05$) in the composition between Group HF ($24\% \pm 3\%$) and Group Ly-HF ($32\% \pm 4\%$), Group Lin-Ly-HF ($30\% \pm 6\%$) and Group Ag ($23\% \pm 3\%$), Group Ly-HF ($32\% \pm 4\%$) and Group Ag ($23\% \pm 3\%$).

There was a statistical difference ($P < 0.05$) in the composition between Group Lin-HF ($5\% \pm 0.5\%$) and Group Lin-Ag-HF ($4\% \pm 0.4\%$), Group Lin-HF ($5\% \pm 0.5\%$) and Group Prs-Ag-HF ($4\% \pm 0.7\%$), Group Lin-Ag-HF ($4\% \pm 0.4\%$) and Group Ly-HF ($6\% \pm 0.6\%$), Group Lin-Ag-HF ($4\% \pm 0.4\%$) and Group Ly-Ag-HF ($6\% \pm 0.9\%$), Group Ly-HF ($6\% \pm 0.6\%$) and Group Lin-Prs-Ag-HF ($4\% \pm 0.4\%$), Group Ly-HF ($6\% \pm 0.6\%$) and Group Prs-Ag-HF ($4\% \pm 0.7\%$), Group Ly-Ag-HF ($6\% \pm 0.9\%$) and Group Prs-Ag-HF ($4\% \pm 0.7\%$).

On the basis of these results, the application of liner and veneering porcelain resulted in composition changes of the dental zirconia.

## Effect of HF, liner, and porcelain on microstructure (no aging)

The surface topography of each of the unaged specimen groups is shown in Figure 4. The control group (Group Mill-Sin) had a typical grain shape with the range in sizes that is necessary for a high-density ceramic material. This structure will be referred to as "unaffected zirconia." When these irregular grains were etched with hydrofluoric acid (Group HF), there was no change in the size, shape, or contrast compared with the Group Mill-Sin. However, when Group Mill-Sin was covered with liner (Group Lin-HF), there were two distinct microstructural features. Grains similar to Group Mill-Sin were observed, and some areas appeared to be unetched with flat, polished tops. This result suggests that a reaction between the liner and zirconia affected the thermal etching process. This structure will be referred to as "affected zirconia." When the liner (Group Lin-HF) was covered with porcelain using layering (Group Lin-Ly-HF) or pressing (Group Lin-Prs-HF), the frequency of affected zirconia decreased. There was no difference in frequency of affected zirconia due to the two veneering techniques (Groups Lin-Ly-HF and Lin-Prs-HF). Furthermore, when the porcelain (without liner) was fired on the Group Mill-Sin using different veneering techniques (layering: Group Ly-HF, pressing: Group Prs-HF), there was only a small amount of affected zirconia. Thus, the liner application had the largest effect of the structure of the dental zirconia.

Effect of aging on microstructure

The surface topography of each of the specimen groups is shown in Figure 5. Simulated aging has an effect on the unaffected zirconia grains, independent of liner and veneering porcelain. When Group
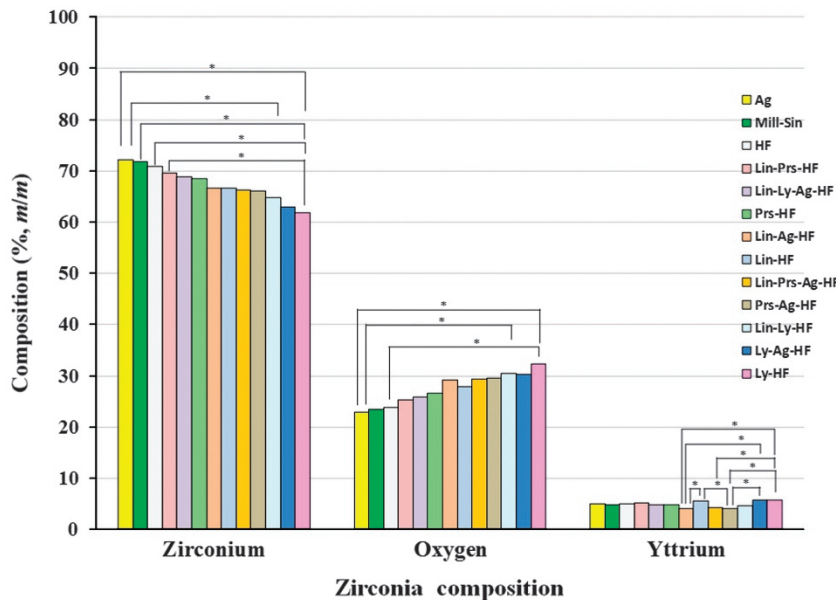

Figure 3 After the treatments specified in Figure 1 were complete, the composition of zirconium, oxygen, and yttrium for different groups as determined by EDS in weight percent. For zirconium, there was a statistical difference ($P < 0.05$) in the composition between Group Mill-Sin and Group Ly-HF, Group HF and Group Ly-HF, Group Lin-Ly-HF and Group Ag, Group Lin-Prs-HF and Group Ly-HF, Group Lin-Ly-HF and Group Ag, Group Ly-HF and Group Ag. For oxygen, there was a statistical difference ($P < 0.05$) in the composition between Group HF and Group Ly-HF, Group Lin-Ly-HF and Group Ag, Group Ly-HF and Group Ag. For yttrium, there was a statistical difference ($P < 0.05$) in the composition between Group Lin-HF and Group Lin-Ag-HF, Group Lin-HF and Group Prs-Ag-HF, Group Lin-Ag-HF and Group Ly-HF, Group Lin-Ag-HF and Group Ly-Ag-HF, Group Ly-HF and Group Lin-Prs-Ag-HF, Group Ly-HF and Group Prs-Ag-HF, Group Ly-Ag-HF and Group Prs-Ag-HF. EDS, energy dispersive spectroscopy.
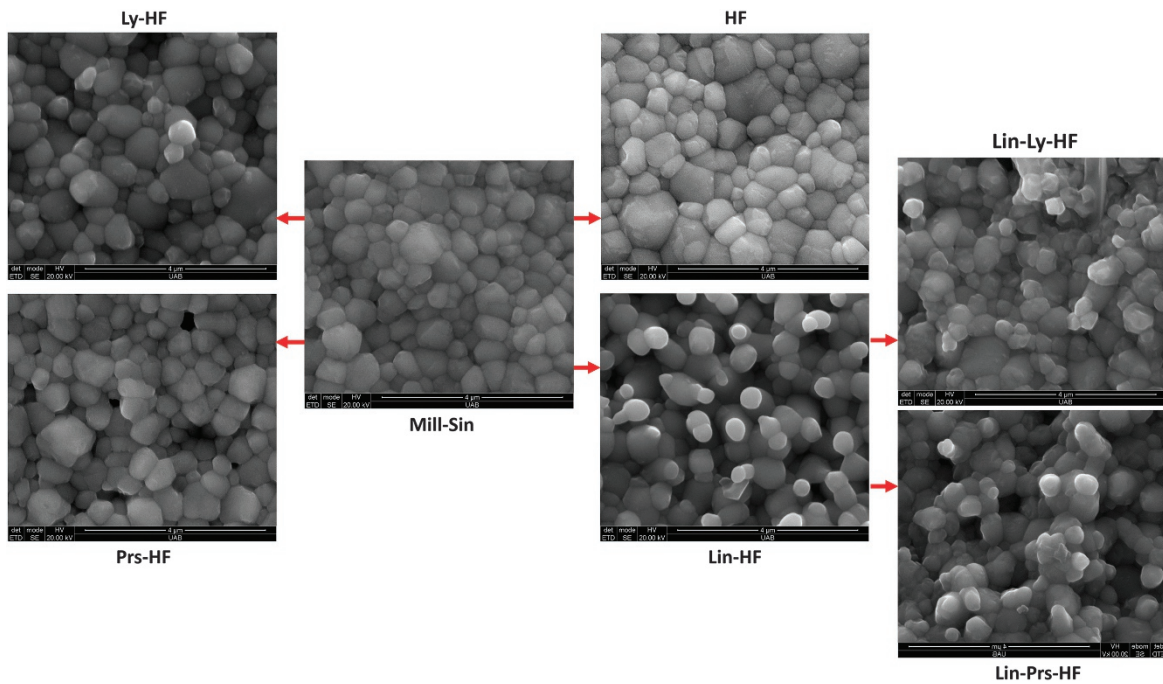
Figure 4 The group Mill-Sin had unaffected grains all over the microstructure which was not affected by etching with hydrofluoric acid (group HF) with the retention of the same grain size, shape, and contrast. However, when group Mill-Sin was covered with liner (group Lin-HF), there were many unetched grains. The number of affected grains was reduced when group Lin-HF was covered with porcelain (layered = group Lin-Ly-HF, pressed = group Lin-Prs-HF) with no difference in the microstructure between the two veneering techniques (groups Lin-Ly-HF, Lin-Prs-HF). There were some affected grains when the porcelain was layered (group Ly-HF) or pressed (group Prs-HF) on group Mill-Sin with no liner application.
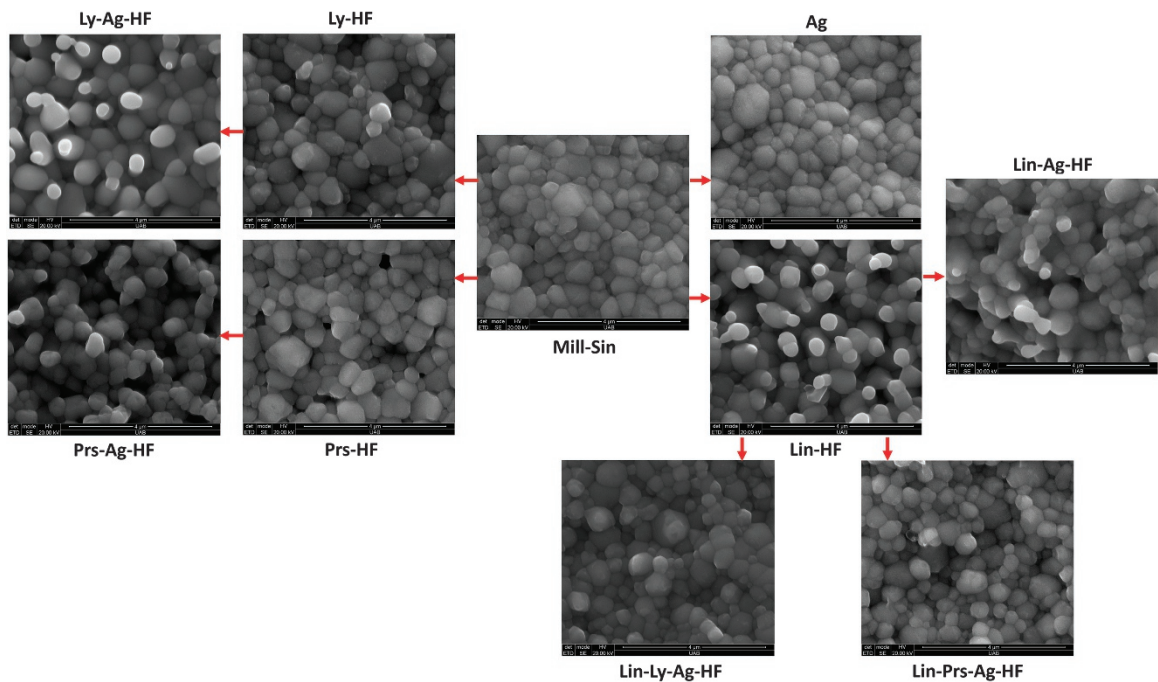
Figure 5 Group Ag had facets on the grains with the same shape and contrast of group Mill-Sin after aging. When the group Mill-Sin covered with liner, there were many affected grains, but with less number of affected grains when exposed to aging. Furthermore, the number of affected grains were reduced when group Lin-HF was covered with porcelain and then aged (layered porcelain = group Lin-Ly-Ag-HF, pressed porcelain = group Lin-Prs-Ag-HF) with no difference in the number of affected and unaffected grains between the veneering techniques. When group Mill-Sin covered with porcelain (layered porcelain = group Ly-HF, pressed porcelain = group Prs-HF), there was no difference in the number of affected and unaffected grains between the veneering techniques. When the layered porcelain (group Ly-HF), and pressed porcelain (group Prs-HF) were aged, there were more affected grains in the layered porcelain (group Ly-Ag-HF) than pressed porcelain (group Prs-Ag-HF).
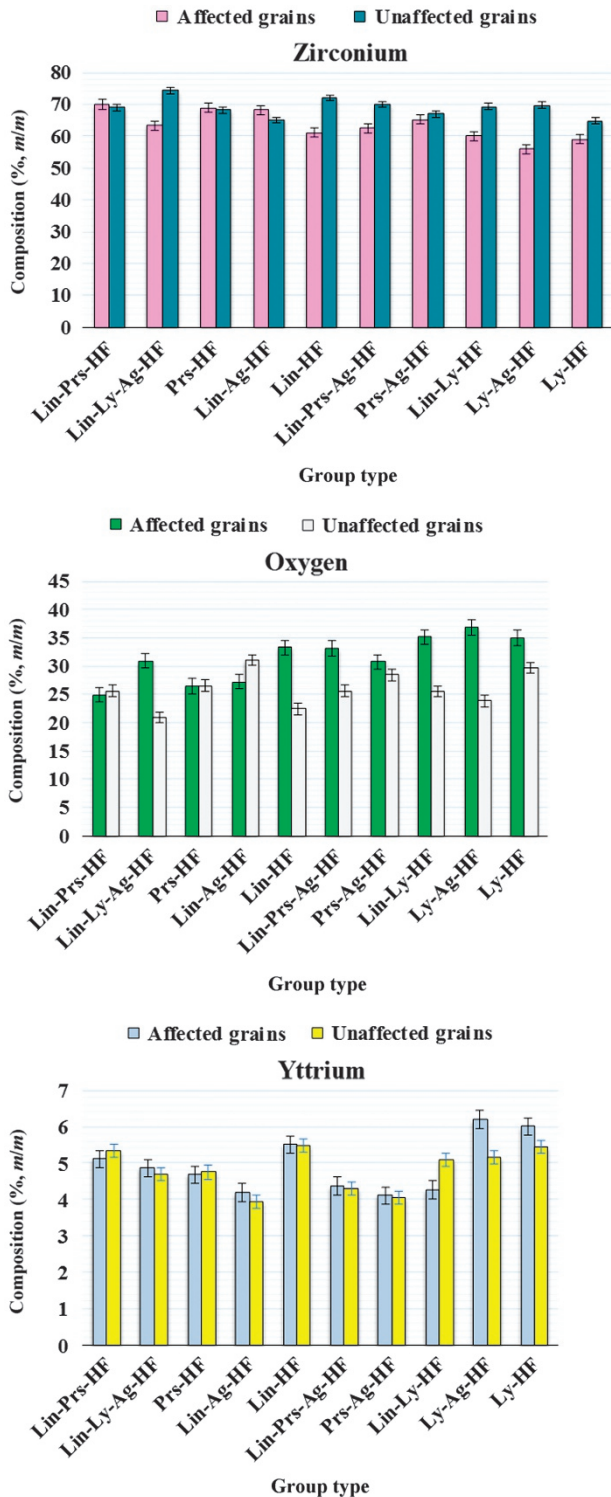
Figure 6 The composition of affected and unaffected grains of different groups for zirconium, oxygen, and yttrium as determined by EDS in weight percent. There was statistical difference ($P<0.05$) in the composition between affected and unaffected grains for zirconium in groups Lin-HF, Lin-Ly-HF, Lin-Ly-Ag-HF, Lin-Prs-Ag-HF, Ly-HF, and Ly-Ag-HF. There was statistical difference ($P<0.05$) in the composition between affected and unaffected grains for oxygen in groups Lin-HF, Lin-Ly-HF, Lin-Ly-Ag-HF, Lin-Prs-Ag-HF, Ly-HF, and Ly-Ag-HF. There was no statistical difference ($P>0.05$) in the composition between affected and unaffected grains for yttrium except for group Lin-Ly-HF. EDS, energy dispersive spectroscopy.

Mill-Sin was aged (group Ag), there were irregular grains with different sizes similar to Group Mill-Sin, but ledges were present on the grains. When Group Mill-Sin was covered with liner and then aged (Group Lin-Ag-HF), the affected zirconia structure was again present. The porcelain (with liner) applied with the two different veneering technique on Group Lin-HF and then aged (layering: Group Lin-Ly-Ag-HF, pressing: Group Lin-Prs-Ag-HF), the number of frequency of affected, flat grains decreased compared with Group Lin-HF with no difference in the microstructure between Groups Lin-Ly-Ag-HF and Lin-Prs-Ag-HF. When the porcelain (without liner) was applied on Group Mill-Sin and then aged (layered: Group Ly-Ag-HF, pressed: Group Prs-Ag-HF), there were many affected, flat grains similar to group Lin-HF and more than Group Prs-Ag-HF.

Composition differences between affected and unaffected grains (Zr, O, and Y)

The elemental analysis of the affected and unaffected grains of each sample group are illustrated in Figure 6. There was a statistical difference ($P<0.05$) in the composition between affected and unaffected grains for zirconium and oxygen. In general, the zirconium levels were higher in the unaffected structure, with a higher oxygen level being observed in the affected structure. There was a statistical difference ($P<0.05$) in the composition between affected and unaffected grains for zirconium in Groups Lin-HF, Lin-Ly-HF, Lin-Ly-Ag-HF, Lin-Prs-Ag-HF, Ly-HF, and Ly-Ag-HF. There was a statistical difference ($P<0.05$) in the composition between affected and unaffected grains for oxygen in Groups Lin-HF, Lin-Ly-HF, Lin-Ly-Ag-HF, Lin-Prs-Ag-HF, Ly-HF, and Ly-Ag-HF.

There was no statistical difference ($P>0.05$) in the composition between affected and unaffected grains for yttrium except for Group Lin-Ly-HF (affected grains 4% ± 0.4%, unaffected grains 5% ± 0.2%).

DISCUSSION

Effect of HF on the microstructure of zirconia

The microstructure of Group Mill-Sin, the control, was unchanged by exposure to HF. This confirms that there was no detectable effect of the acid on the microstructure as documented in our previous study[17] with little tetragonal to tetragonal transformation ($X_m = 0.8\%$). Thus, an HF effect during different surface treatments can be discounted.

The interpretation of the microstructure

Two distinct structures were observed after liner and porcelain application (layered and pressed) as in Groups Lin-HF, Lin-Ag-HF, Lin-Ly-HF, Ly-HF, Ly-Ag-HF, Lin-Prs-HF, Lin-Prs-Ag-HF, Prs-HF, and Prs-Ag-HF. Faceted grains that show a range in apparent size, typical of a fully-dense, equiaxed grain structure, are identical to Group Mill-Sin, the control. This microstructure has been referred to as unaffected as it is typical of thermally etched zirconia. In addition, a structure (referred to as "affected") that appears much brighter in secondary electron images is a result of the liner and porcelain application. The round, flat areas are the as-prepared surfaces and were unaffected by thermal and chemical etching. These features are higher than the equiaxed grains and have a large surface area, resulting in their higher brightness. A micrograph and schematic is shown in Figure 7.

The reaction layer is more oxygen-rich and, therefore, lower in zirconium than the equiaxed structure, which is the base material, as illustrated in Figure 6. Furthermore, when there is change in the elemental concentration, thermal and chemical etching may be
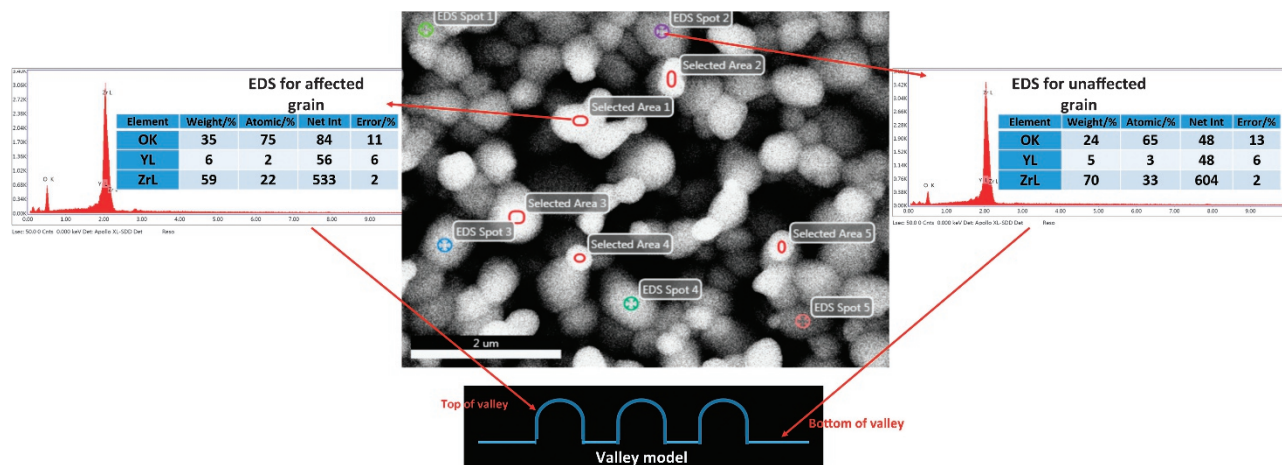
Figure 7 Interpretation of the affected and unaffected grains in the microstructure of zirconia. The EDS of the affected grains (5 points) were similar to the EDS to the unaffected grains (5 points), but with different concentrations. The composition of two different color grains can be implied in a valley model. The affected grains (closer to the viewer) will be the top of the valley and the unaffected grains (farther to the viewer) will be the bottom of the valley. The elements of the affected and unaffected grains are identical but with different composition. EDS, energy dispersive spectroscopy.

affected, which will cause a change in zirconia surface topography, which implies poor wetting.[34]

Pressing technique

The pressing technique pushes a ceramic ingot into the zirconia samples, which leads to a dense veneering porcelain with no defects and voids to promote diffusion at the pressed porcelain–zirconia interface. Furthermore, there was a minimal mismatch in CTE between the pressed porcelain (10.5×10^{-6} per °C) and zirconia (10.8×10^{-6} per °C). Therefore, there is no residual stress to further enhance the diffusion at the interface.[19–20] According to the reasons previously mentioned, there is no compositional difference between the affected and unaffected grains when the porcelain was pressed alone regardless of liner use and aging process (Groups Prs-HF, Lin-Prs-HF, Prs-Ag-HF) except for Group Lin-Prs-Ag-HF because when the pressed porcelain was combined with liner and then aged, not all the voids were eliminated during pressing; and this enhanced the diffusion by aging. The results of the present study support previous studies in which the use of liner decreased bond strength.[6–7,9,16,20,29]

Layering technique

During the layering technique, the residual stresses can likely accumulate during the heating and cooling firing procedures because of the cooling rate[18] and CTE mismatch between zirconia and layered porcelain.[19–20] In addition, the voids and defects resulting from the layering technique promoted movement of atoms, which enhanced the diffusion at the porcelain–zirconia interface. The process is further accelerated by having a higher concentration of oxygen and silicon compared with pressed porcelain. As a result, there was a difference in the composition between affected and unaffected grains; (Group Ly-HF) and the difference was further enhanced by the aging process (Group Ly-Ag-HF) by diffusion through the voids.

In addition, when the layered porcelain was combined with liner, the diffusion process was further enhanced (Group Lin-Ly-HF) compared with no liner application (Group Ly-HF) because of more residual stress accumulated by liner application. Therefore, the results

of the present study support the previous studies in which the use of liner decreased bond strength.[6–7,9,16,20,29]

There was no diffusion with pressing (Group Lin-Prs-HF) compared with layering (Group Lin-Ly-HF); therefore, results in the present project confirm the results from previous studies in which there were fewer failures to pressed porcelain compared with layered porcelain.[31] Therefore, the hypothesis that there will be no difference in the veneering technique for the interdiffusion process would be rejected.

Effect of aging on the microstructure of the control group

The crystalline microstructure of zirconia (Group Ag) had ledges after aging. This was caused by destabilization of the tetragonal phase with sever tetragonal to monoclinic transformation ($X_m = 70\%$) as documented in our previous study.[17] However, the ledges were not shown after aging when the zirconia samples were covered with porcelain (Groups Ly-Ag-HF, Prs-Ag-HF, Lin-Prs-Ag-HF, and Lin-Ly-Ag-HF). The microstructure confirms our previous study[17] in which porcelain coverage protects the zirconia from the microleakage at the porcelain–zirconia interface to cause a further tetragonal to monoclinic transformation and, thereby, formation of ledges on the surface of the grains. The hypothesis that the liner decreases the interdiffusion at the zirconia–porcelain interface would be rejected.

A limitation of this study is that testing of zirconia–porcelain bond strength after aging was not done to correlate with our SEM findings. Future proposed research will include a study of computer-aided design, computer-aided manufacture (CAD/CAM) generated veneering porcelain on zirconia samples after aging, and possibly, bond strength testing.

CONCLUSIONS

1. A liner should not be used before porcelain application especially when using the layering technique for zirconia restorations.
2. Pressing should be considered the technique of choice rather than layering the porcelain for zirconia restorations.

1 Fischer J, Stawarczyk B. Compatibility of machined Ce-TZP/Al2O3 nanocomposite and a veneering ceramic. *Dent Mater* 2007; **23**(12): 1500–1505.

2 Göstemeyer G, Jendras M, Borchers L *et al.* Effect of thermal expansion mismatch on the Y-TZP/veneer interfacial adhesion determined by strain energy release rate. *J Prosthodont Res* 2012; **56**(2): 93–101.

3 Göstemeyer G, Jendras M, Dittmer MP *et al.* Influence of cooling rate on zirconia/veneer interfacial adhesion. *Acta Biomater* 2010; **6**(12): 4532–4538.

4 Kim KY, Kwon TK, Kang TJ *et al.* Digital veneering system enhances microtensile bond strength at zirconia core-veneer interface. *Dent Mater J* 2014; **33**(6): 792–798.

5 He M, Zhang Z, Zheng D *et al.* Effect of sandblasting on surface roughness of zirconia-based ceramics and shear bond strength of veneering porcelain. *Dent Mater J* 2014; **33**(6): 778–785.

6 Freifrau Von Maltzahn N, Kleibe M, Stiesch M *et al.* Interfacial adhesion of zirconia/veneer bilayers with different thermal characteristics. *Dent Mater J* 2014; **33**(5): 583–590.

7 Ishibe M, Raigrodski AJ, Flinn BD *et al.* Shear bond strengths of pressed and layered veneering ceramics to high-noble alloy and zirconia cores. *J Prosthet Dent* 2011; **106**(1): 29–37.

8 Nishigori A, Yoshida T, Bottino MC *et al.* Influence of zirconia surface treatment on veneering porcelain shear bond strength after cyclic loading. *J Prosthet Dent* 2014; **112**(6): 1392–1398.

9 Wang G, Zhang S, Bian C *et al.* Effect of zirconia surface treatment on zirconia/veneer interfacial toughness evaluated by fracture mechanics method. *J Dent* 2014; **42**(7): 808–815.

10 Denry IL, Holloway JA. Microstructural and crystallographic surface changes after grinding zirconia-based dental ceramics. *J Biomed Mater Res Part B Appl Biomater* 2006; **76**(2): 440–448.

11 Kosmac T, Oblak C, Jevnikar P *et al.* Strength and reliability of surface treated Y-TZP dental ceramics. *J Biomed Mater Res* 2000; **53**(4): 304–313.

12 Koenig V, Vanheusden AJ, Le Goff SO *et al.* Clinical risk factors related to failures with zirconia-based restorations: an up to 9-year retrospective study. *J Dent* 2013; **41**(12): 1164–1174.

13 Sailer I, Fehér A, Filser F *et al.* Five-year clinical results of zirconia frameworks for posterior fixed partial dentures. *Int J Prosthodont* 2007; **20**(4): 383–388.

14 Durand JC, Jacquot B, Salehi H *et al.* Confocal Raman microscopic analysis of the zirconia/feldspathic ceramic interface. *Dent Mater* 2012; **28**(6): 661–671.

15 Stoner BR, Griggs JA, Neidigh J *et al.* Evidence of yttrium silicate inclusions in YSZ-porcelain veneers. *J Biomed Mater Res Part B Appl Biomater* 2014; **102**(3): 441–446.

16 Monaco C, Tucci A, Esposito L *et al.* Adhesion mechanisms at the interface between Y-TZP and veneering ceramic with and without modifier. *J Dent* 2014; **42**(11): 1473–1479.

17 Alghazzawi TF, Janowski GM. Evaluation of zirconia-porcelain interface using X-ray diffraction. *Int J Oral Sci* 2015; **7**(3): 187–195.

18 Guazzato M, Walton TR, Franklin W *et al.* Influence of thickness and cooling rate on development of spontaneous cracks in porcelain/zirconia structures. *Aust Dent J* 2010; **55**(3): 306–310.

19 Guess PC, Bonfante EA, Silva NR *et al.* Effect of core design and veneering technique on damage and reliability of Y-TZP-supported crowns. *Dent Mater* 2013; **29**(3): 307–316.

20 Canullo L, Micarelli C, Bettazzoni L *et al.* Shear bond strength of veneering porcelain to zirconia after argon plasma treatment. *Int J Prosthodont* 2014; **27**(2): 137–139.

21 Zeighami S, Mahgoli H, Farid F *et al.* The effect of multiple firings on microtensile bond strength of core-veneer zirconia-based all-ceramic restorations. *J Prosthodont* 2013; **22**(1): 49–53.

22 Bonfante EA, Rafferty B, Zavanelli RA *et al.* Thermal/mechanical simulation and laboratory fatigue testing of an alternative yttria tetragonal zirconia polycrystal core-veneer all-ceramic layered crown design. *Eur J Oral Sci* 2010; **118**(2): 202–209.

23 Millen CS, Reuben RL, Ibbetson RJ. The effect of coping/veneer thickness on the fracture toughness and residual stress of implant supported, cement retained zirconia and metal-ceramic crowns. *Dent Mater* 2012; **28**(10): e250–e258.

24 Mainjot AK, Schajer GS, Vanheusden AJ *et al.* Influence of zirconia framework thickness on residual stress profile in veneering ceramic: measurement by hole-drilling. *Dent Mater* 2012; **28**(4): 378–384.

25 Mainjot AK, Schajer GS, Vanheusden AJ *et al.* Influence of veneer thickness on residual stress profile in veneering ceramic: measurement by hole-drilling. *Dent Mater* 2012; **28**(2): 160–167.

26 Rosentritt M, Steiger D, Behr M *et al.* Influence of substructure design and spacer settings on the *in vitro* performance of molar zirconia crowns. *J Dent* 2009; **37**(12): 978–983.

27 Ramos CM, Cesar PF, Lia Mondelli RF *et al.* Bond strength and Raman analysis of the zirconia-feldspathic porcelain interface. *J Prosthet Dent* 2014; **112**(4): 886–894.

28 Belli R, Frankenberger R, Appelt A *et al.* Thermal-induced residual stresses affect the lifetime of zirconia-veneer crowns. *Dent Mater* 2013; **29**(2): 181–190.

29 Wang G, Zhang S, Bian C *et al.* Interface toughness of a zirconia-veneer system and the effect of a liner application. *J Prosthet Dent* 2014; **112**(3): 576–583.

30 Renda JJ, Harding AB, Bailey CW *et al.* Microtensile bond strength of lithium disilicate to zirconia with the CAD-on technique. *J Prosthodont* 2015; **24**(3): 188–193.

31 Christensen RP, Ploeger BJ. A clinical comparison of zirconia, metal and alumina fixed-prosthesis frameworks veneered with layered or pressed ceramic: a three-year report. *J Am Dent Assoc* 2010; **141**(11): 1317–1329.

32 Queiroz JR, Benetti P, Massi M *et al.* Effect of multiple firing and silica deposition on the zirconia-porcelain interfacial bond strength. *Dent Mater* 2012; **28**(7): 763–768.

33 Guess PC, Kulis A, Witkowski S *et al.* Shear bond strengths between different zirconia cores and veneering ceramics and their susceptibility to thermocycling. *Dent Mater* 2008; **24**(11): 1556–1567.

34 Benetti P, Della Bona A, Kelly JR. Evaluation of thermal compatibility between core and veneer dental ceramics using shear bond strength test and contact angle measurement. *Dent Mater* 2010; **26**(8): 743–750.

35 International Standard Organization. ISO 13356 *implants for surgery-ceramic materials based on yttria-stabilized tetragonal zirconia (Y-TZP)*. Geneva: International Standardization Organization, 2008.

36 Alghazzawi TF, Janowski GM. Correlation of flexural strength of coupons versus strength of crowns fabricated with different zirconia materials with and without aging. *J Am Dent Assoc* 2015; **146**(12): 904–912.