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Joining Dental Ceramic Layers With Glass

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Abstract

Objective—Test the hypothesis that glass-bonding of free-form veneer and core ceramic layers can produce robust interfaces, chemically durable and aesthetic in appearance and, above all, resistant to delamination.

Methods—Layers of independently produced porcelains (NobelRondo™ Press porcelain, Nobel BioCare AB and Sagkura Interaction porcelain, Elephant Dental) and matching alumina or zirconia core ceramics (Procera alumina, Nobel BioCare AB, BioZyram yttria stabilized tetragonal zirconia polycrystal, Cyrtina Dental) were joined with designed glasses, tailored to match thermal expansion coefficients of the components and free of toxic elements. Scanning electron microprobe analysis was used to characterize the chemistry of the joined interfaces, specifically to confirm interdiffusion of ions. Vickers indentations were used to drive controlled corner cracks into the glass interlayers to evaluate the toughness of the interfaces.

Results—The glass-bonded interfaces were found to have robust integrity relative to interfaces fused without glass, or those fused with a resin-based adhesive.

Significance—The structural integrity of the interfaces between porcelain veneers and alumina or zirconia cores is a critical factor in the longevity of all-ceramic dental crowns and fixed dental prostheses.

Keywords

glass bonding; interface; veneer; ceramic core; crown

INTRODUCTION

Dental crowns and bridges are generally laminar structures, with complex geometries [1–3]. Traditionally, an aesthetic porcelain is veneered onto a strong core material layer by layer. In the case of all-ceramic restorations, the core material is usually alumina or (more recently) zirconia. Alumina crowns tend to fail by bulk fracture initiating at the cementation surface [4,5]. Zirconia is considerably stronger so that failure is more likely to occur in the porcelain overlayer, by chipping or by spallation from the core [6]—the integrity of the structure then rests with the relative toughness of the porcelain overlayer and the veneer/core interface. While successful, current veneering techniques are painstakingly time consuming

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and expensive, and the interfacial bonding is often less than perfect. With the move toward increased automation in the dental industry, there is room for the introduction of novel, economical procedures.

A potential alternative fabrication route is free-form processing, in which each layer is shaped individually, e.g. by robocasting [7,8] or computer aided manufacturing [2], and then fused together. It is possible to join two components by fusion at elevated temperature, but for all-ceramic components the required temperatures are very high [9]. Also, the interfaces do not always wet or fuse perfectly, leaving weaknesses that can act as sources of failures. Conversely, one might use a polymeric resin to bond the components at room temperature, but the resultant interface is then relatively weak and subject to chemical degradation [10,11]. A reasonable compromise is a glass bond. Glass joining is a long established technology [12,13], widely used in vacuum seals for metal components, electronic packaging, fuel cells and coating applications [14]. Principal requirements for a successful join are: matching coefficients of thermal expansion (CTE, typically within $1 \times 10^{-6}/^{\circ}\text{C}$), to minimize residual stresses; good wetting and interlayer diffusion, to effect a strong bond; low firing temperature, to minimize any degradation of the veneer layer during processing; and bioinertness, to avoid adverse chemical degradation in a reactive environment. In the case of dental joins, the joining glass should be lead- and bismuth-free, to avoid toxicity concerns.

In this study we describe a procedure for using lead-free glasses to fuse freestanding porcelain layers to alumina and zirconia core layers. As indicated, in all-ceramic systems both veneer and core layers are vulnerable to fracture, most generally to cracks that traverse the layer thickness—so-called ‘transverse’ cracks. More importantly, the interlayer between the two layers is itself vulnerable. Can the glass bond prevent cracks in the veneer layer from penetrating into the core, or vice-versa? Above all, can the glass interlayer prevent veneer cracks from delaminating the interface? Our procedure was to select commercial porcelain and core alumina and zirconia plates, and to design and custom-fabricate matching glasses for bonding the layers with good wetting, low porosity and minimum CTE mismatch stress. Electron microprobe analysis was then used to characterize interdiffusion chemistry at the interfaces and simple mechanical testing with a Vickers indenter applied to characterize the bond integrity.

MATERIALS AND METHODS

Since we were concerned here only with the joining process itself, experiments were confined to flat layers, mindful that the techniques will ultimately need to be applicable to more complex geometrical shapes. The procedure was to choose commercially matched porcelain and core material plates and to design and custom-fabricate glasses for bonding the layers with minimum CTE mismatch. Two dental material systems were selected for study. The first was Procera alumina (Nobel BioCare AB, Stockholm, Sweden), with CTE-matching NobelRondo™ Press porcelain (Nobel BioCare AB, Stockholm, Sweden). The second was Cyrtina Dental yttria stabilized tetragonal zirconia polycrystal (Biozym, Cyrtina Dental, Netherlands), with CTE-matching Sagkura Interaction porcelain (Elephant Dental, The Netherlands). The alumina and zirconia core materials were obtained as blocks and cut and ground into plates with sides 10 mm and thickness 0.7 mm. The porcelains were received as powders, which were mixed into water-based slurries and poured into refractory molds with 7 mm sides. After drying, the molds were vacuum-fired to a peak temperature of 850 °C over a 20 min heating–cooling cycle, according to manufacturer specifications. The as-fired porcelain specimens were then ground to 1 mm thickness. The surfaces of both core and veneer plates were polished flat and parallel to 1 μm finish using diamond paste, followed in the case of zirconia with colloidal silica suspension to remove any strain-

induced transformations. Essential properties of the alumina, zirconia and porcelain components are shown in Table 1, using data obtained from manufacturer's specifications and routine in-house materials characterization (see below).

The choice of glass compositions for bonding core and veneer layers was less straightforward. Several commercially available lead-free glasses were investigated, but none matched our selected dental ceramics sufficiently to produce suitable quality joins. Accordingly, we used an in-house sol-gel wet chemistry fabrication route to produce custom non-toxic glass compositions with CTE values matching those listed in Table 1 for each veneer/core bilayer combination. The methodology used glass components with documented properties and rule-of-mixtures formulae to obtain compositions with requisite CTE, elastic modulus and softening temperatures. Details of this selection process are described elsewhere [15]. The tailored glass compositions and ensuing physical properties used here are shown in Table 2 for each veneer–core system. Dilatometry (Orton DIL 2016 STD, Westerville, OH) was used to determine CTE values for each glass.

The glasses were fired at 1200 °C then quenched into shards and ground into frit with maximum particle size of 38 µm, a upper limit for ensuing firing without inducing residual porosity in the glass. The frits were then mixed into 50/50 vol% water/ethanol slurries. The slurries were applied evenly to the top surfaces of each of the alumina and zirconia core and matching porcelain veneer plates. In this way coating layers 50 µm to 100 µm thick were built up. To wet the glasses onto the surfaces, a prefiring cycle was conducted for each specimen layer at a rate of 30 °C/min, with a 5 min hold at 750 °C for the alumina core and veneer layers and 700 °C for the zirconia layers. The specimens were then slowly cooled within the furnace to avoid crazing or porosity in the coating.

The coated surfaces of each core and veneer combination were then brought into mutual contact and vacuum heated at 40 °C/min under light pressure to 830 °C for the alumina system and 800 °C for the zirconia system, at a common hold time 30 min. These temperatures were sufficient to fuse the veneers to the cores without compromising the shape of the composite structures. Prescribed hold times of 30 min at peak temperature were examined. Comparative tests at 15 min and 45 min hold times showed little difference in the final results.

The fired specimens were sectioned with a diamond saw, followed by grinding and polishing to 1 µm finish, in order to view the bonded interface by optical microscopy. All the specimens survived the cutting and finishing processes, providing a useful initial screening test for bond integrity. Uniformity of thickness and lack of porosity were taken as further indicators of a 'good' interface.

Wavelength dispersive spectroscopy (JEOL JXA-8900 SuperProbe, Japan Electron Optics, Tokyo, Japan) with a 1 µm-wide electron beam was used to examine ion diffusion between the bonding glass and the ceramic sandwich layers. Intensity readings were taken every 1.5–2.8 µm and recorded as profiles across the interface. Special attention was given to mobile K⁺ ions, since these ions were originally present in the porcelains but absent in the glasses, thus providing a definitive marker for interdiffusion.

To explore bond toughness, Vickers indentations were placed across the sections at various prescribed distances from the bonding interfaces in each of the porcelain/alumina and porcelain/zirconia layer systems using a microindentation tester (Zwick, Riverview, Michigan USA). Some indents were made in separate alumina, zirconia and porcelain plates as comparative controls. Different loads were used in the various layer materials, to maintain indentations with well-defined cracks without chipping: in the porcelains, $P = 10$ N; in alumina, $P = 10$ N; in zirconia, $P = 40$ N. In the layer structures, corner cracks were aligned

parallel and perpendicular to the glass interface, so that the lead transverse crack (at the corner closest to the interface) may intersect the interface itself. For each indent, a high power microscope was used to measure the lead arm crack size c measured from the indent center and tip location x measured relative to the glass/core interface.

RESULTS

Figure 1 shows images of glass-bonded (a) porcelain/alumina and (b) porcelain/zirconia layer structures. These images are typical of some 10 specimens of each material combination. The joins shown are at the low end of the interface thicknesses achieved, viz. 30 μm to 100 μm . The glasses appear to have good wetting, and low porosity. The interfaces between the porcelains and glasses are not easily discerned in the original micrographs, and so are highlighted here by superimposed white lines. This similarity in optical properties between the veneers and glasses lends itself to good aesthetics.

Microprobe analysis profiles were conducted on the fired glass join interfaces. Although profiles were obtained for all ionic species in the glasses and adjoining ceramic layers, specific attention was given to K^+ . Since the glasses for all the glass joins were formulated without this ionic component, any presence of K^+ in the glass provides definitive evidence of diffusion from the porcelain into the interface. Typical profiles are shown in Fig. 2. The diffusion distances in the profiles are substantial, particularly in the zirconia. No such evidence within the limits of resolution of the instrument (typically 1% in concentration) was found for diffusion of any ionic species from the glasses into the alumina or zirconia cores, or vice versa, consistent with the much lower diffusivity of these core materials. Nevertheless, the evidence for mobility of the K^+ ions, in conjunction with the optical microscopy observations, is indicative of good wetting.

Vickers indentations were made in polished sections of each glass-bonded veneer/core system. The first indents were placed well away from the interfaces, i.e. with their centers distant at least 3 times the lengths of the largest corner cracks. These indentation patterns were essentially symmetrical with equi-sized cracks. The average crack lengths of the indents in each layer differed by less than 10% relative to those in corresponding monolithic control materials at the same load, indicating negligibly small residual stresses < 10 MPa [9,16]. These indentations usefully provided the values of hardness H (from plastic impression size) and toughness T (from corner crack size) listed for each material in Table 1 [17].

As the indent centers were placed closer to the interface the crack patterns became distorted, with the lead transverse crack in particular sensing the modulus mismatch influence of the adjacent ceramic layer. Figure 3 shows an example for near-interface indents in (a) porcelain and (b) zirconia layers. Lead transverse corner cracks from indents in the porcelain became shorter, ultimately entering the glass interlayer without apparent discontinuity (Fig. 3a). For even closer indents, the lead cracks arrested at the core interface. Conversely, lead corner cracks from indents in the zirconia became longer until, at sufficiently close locations, the cracks crossed into the bonding glass and veneer, at which point they noticeably elongated (Fig. 3b). In none of the specimens was delamination observed at the glass interfaces, even for the closest of veneer or core indents, suggesting good bonding. Similar crack-interface interactions were observed in the alumina system.

A simple fracture mechanics relation enabled some elementary quantification of these observations. For Vickers indentations, the driving force for generation of corner cracks can be defined by a so-called 'stress intensity factor' [17,18]

$$K = \zeta(E/H)^{1/2} P/c^{3/2} \quad (1)$$

where c is corner crack length (measured from the indent center), E is Young's modulus and H hardness of the material containing the indent, and $\zeta = 0.016$ is a dimensionless coefficient. In monolithic materials, K identifies with the intrinsic crack resistance of the material, the toughness T . Since the tests in our experiments were conducted in air, where moisture can cause slow crack growth, values obtained in this way are likely to overestimate the intrinsic toughness for inert (dry) environments. However, that is not a major concern here, because we are interested principally in relative values between constituent layers. Thus, in the layer structures themselves, the quantity K evaluated from the length c of the lead crack can be taken as an 'effective toughness' [9]. By emplacing several indents at different locations across the specimen sections, the variation of K could be plotted out as a function of tip location x measured relative to the glass/core interface (with positive direction of x away from indent center). Such plots are shown in Fig. 4 for the glass-bonded porcelain/zirconia system. Data points represent individual indents, curves are empirical fits, shaded bands indicate the glass interlayer. The vertical dashed lines are asymptotic toughness values for monolithic porcelain and zirconia. For indents in the porcelain (Fig. 4a), the effective toughness increases slightly as the crack tip approaches the core interface (decreasing x) and senses the stiffer and tougher adjoining zirconia layer, indicating increasing inhibition of crack extension. For indents in the zirconia (Fig. 4b), the effective toughness decreases markedly as the crack tip approaches the core interface (increasing x), and then drops precipitously as the crack penetrates into the veneer.

Again, tests on the alumina system showed similar behavior to that in Fig. 4. A plot of $K(x)$ for porcelain/alumina is shown in Fig. 5.

Quantification of the above observations may be taken one stage further, using a well-documented analysis of crack interface deflection to determine a lower bound to the toughness of our bonded interfaces [19]. Basically, for a transverse crack approaching an interface, delamination will occur preferentially over penetration if the interfacial toughness is less than about one half that of the adjacent layer material. For indents in the core, the lead corner cracks always penetrated into the veneer without delamination, meaning that the toughness of the glass/core interfaces was at least one half that of the bulk veneer (Table 2.1), i.e. greater than $0.4 \text{ MPa m}^{1/2}$.

DISCUSSION

This study has demonstrated the feasibility of joining porcelain veneers to ceramic cores using a glass bonding approach. The primary advantage of this approach is that matching veneers and cores can be prepared as individual freeform layers using modern-day fabrication and machining technologies, without painstaking layer-by-layer painting-on of the porcelain. A key element in choosing the bonding glass is matching of the coefficient of thermal expansion to the veneer and core, to avoid residual stresses. Another important element is the avoidance of potentially toxic components, especially lead but also bismuth. Once the glass composition is chosen and prepared in frit form the joining process is straightforward—simply mix the frit into a slurry, paint onto each veneer and core layer separately, prefire to wet the coated surfaces, then fire the layer composites in a furnace at a slightly higher temperature to fuse the interface. The firing temperature is not excessive (typically 850°C), so the porcelains do not melt or creep. The glasses provides good wetting of the veneer and core surfaces. And the glasses have similar optical properties to those of porcelains, without noticeable interface porosity, lending themselves to favorable aesthetics.

Chemical characterization of the ensuing interfaces confirmed the integrity of the glass bonding. Scanning electron microprobe analysis revealed interdiffusion of ionic species across the glass/veneer interface. The diffusion of K^+ ions was of particular interest, because the glass compositions initially contained no potassium component. The presence of K^+ in the glass after firing is therefore definitive evidence for ionic interdiffusion, indicative of good chemical bonding. Other ionic species were also observed to diffuse across the glass/veneer interfaces. However, analogous diffusion across the glass/core interfaces was not detectable, attributable to the low diffusivity in the alumina and zirconia ceramics.

Mechanical characterization was used to test the joined interfaces for strength. Corner cracks from indentations were directed into the interfaces. Transverse cracks originating from indents in the veneer arrested at the core, without deflecting into the interface. Similar cracks originating from indents in the core penetrated into the glass interface and veneer, again without delamination. In the latter case, a lower bound to the glass/core interface toughness was estimated at $0.4 \text{ MPa m}^{1/2}$, a most respectable toughness for any interface, confirming the mechanical integrity of the glass bonding. The absence of delamination contrasts with previous observations in similarly fused porcelain/ceramic interfaces but without a glass bond [9]. The measured interface toughness is also substantially higher than that achievable with polymer-based adhesives [10,11]. Glass-fused interfaces are also less susceptible than their resin-based counterparts to chemical degradation, and are more resistant to thermal and mechanical fatigue. One further advantage of glass joins is that the elastic modulus of the glass can be matched more closely to that of the typical dental porcelain, eliminating the prospect of catastrophic flexure-induced radial cracking of the veneer on a compliant interface support [20].

Future development of glass bonding technology in dental applications may include the design of interfaces with more heavily graded interfaces, to redistribute interfacial stresses and enhance strength [21]. Also, extension to more complex, anatomically correct shapes is a further goal.

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Certain equipment, instruments or materials are identified in this paper in order to specify experimental details, and do not imply recommendation by the National Institute of Standards and Technology.

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Figure 1. Showing glass bonded interface in (a) alumina and (b) zirconia core systems. Superimposed white horizontal lines are used to highlight the interfaces, especially between the glass and porcelain.

Figure 2. Microprobe scan profiles of K^+ ion concentration across glass-bond interfaces, for alumina and zirconia systems. Glass interlayer thickness 100 μm for alumina system, 50 μm for zirconia system.

Figure 3. Vickers indentations glass-bonded zirconia core system: (a) indent in porcelain, (b) indent in zirconia. Distances of indent center c and lead crack tip x measured relative to glass/zirconia interface.

Figure 4.

Stress intensity factor K as function of distance x of lead Vickers corner crack from glass/core interface, for zirconia core system. Data points are individual indents ($N = 25$). Inset indicates layer in which indentation is contained and direction of lead corner crack. Solid curves are empirical fits, shaded bands indicate glass interlayer, asymptotic dashed lines are toughness bounds in each layer.

Figure 5.

Stress intensity factor K as function of distance x of lead Vickers corner crack from glass/core interface, for alumina core system. Data points are individual indents ($N = 57$). Inset indicates layer in which indentation is contained and direction of lead corner crack. Solid curves are empirical fits, shaded bands indicate glass interlayer, asymptotic dashed lines are toughness bounds in each layer.

Table 1

Properties of core ceramics and matching porcelains used in this study. Modulus values from manufacturer, hardness and toughness from indentation measurements, and coefficients of thermal expansion from dilatometry.

Alumina system	Function	Supplier	Modulus, <i>E</i> (GPa)	Hardness, <i>H</i> (GPa)	Toughness, <i>T</i> (MPa m ^{1/2})	CTE (10 ⁻⁶ /°C)
Procera	Core	Nobel Biocare	370	13.5	3.1	7.15
Rondo	Veneer	Nobel Biocare	65	6.4	0.8	7.20

Zirconia system	Function	Supplier	Modulus, <i>E</i> (GPa)	Hardness, <i>H</i> (GPa)	Toughness, <i>T</i> (MPa m ^{1/2})	CTE (10 ⁻⁶ /°C)
BioZyram	Core	Cytina Dental	205	12.0	5.3	10.5
Sakura Interaction	Veneer	Elephant Dental	65	6.2	0.8	9.9

Table 2

Glass compositions used in this study.

System	SiO ₂ (mol%)	Al ₂ O ₃ (mol%)	CaO (mol%)	Na ₂ O (mol%)	BaO (mol%)	B ₂ O ₃ (mol%)	CTE (10 ⁻⁶ /°C)
Alumina system	60	3.03	8.37	6.41	6.05	16.14	7.0
Zirconia system	60	3.13	9.4	14.64	6.56	6.27	10.4