Research paper

**Al\textsubscript{2}O\textsubscript{3}/GdAlO\textsubscript{3} fiber for dental porcelain reinforcement**

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**A R T I C L E I N F O**

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**A B S T R A C T**

The aim of this study was to test the hypothesis that the addition of continuous or milled GdAlO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} fibers to a dental porcelain increases its mechanical properties. Porcelain bars without reinforcement (control) were compared to those reinforced with long fibers (30 vol%). Also, disk specimens reinforced with milled fibers were produced by adding 0 (control), 5 or 10 vol% of particles. The reinforcement with continuous fibers resulted in significant increase in the uniaxial flexural strength from 91.5 to 217.4 MPa. The addition of varied amounts of milled fibers to the porcelain did not significantly affect its biaxial flexural strength compared to the control group. SEM analysis showed that the interface between the continuous fiber and the porcelain was free of defects. On the other hand, it was possible to note the presence of cracks surrounding the milled fiber/porcelain interface.

In conclusion, the reinforcement of the porcelain with continuous fibers resulted in an efficient mechanism to increase its mechanical properties; however the addition of milled fibers had no significant effect on the material because the porcelain was not able to wet the ceramic particles during the firing cycle.

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**1. Introduction**

One of the most challenging structural applications of ceramics in dentistry is the fixed partial denture (FPD) because of the high stresses to which this structure is subjected in the posterior region of the oral cavity. The low fracture toughness of ceramic materials is in part responsible for the observed failure rates of ceramic FPDs, which have been reported to be as high as 35% after 3 years (Kelly et al., 1995). One way to improve the performance of such structures is tailoring of the material’s microstructure in order to improve resistance to crack propagation (Guazzato et al., 2004a,b). In this regard, many core materials have been developed in the past years to build FPDs, such as glass-ceramics, glass-infiltrated alumina, alumina polycrystal and yttrium oxide partially-stabilized tetragonal zirconia polycrystals. These core materials are usually used to build a framework that is veneered with a dental porcelain.

Dental porcelains have been used very successfully for many years associated with metal substructures to produce bridgeworks. Due to their low fracture toughness (around 1.0 MPa m\textsuperscript{1/2}) (Cesar et al., 2005), they are not primarily
indicated to be used alone in a bridgework. One way to use only porcelain to produce a bridgework is by means of reinforcing the material so that it can be used without the metal framework to construct more conservative FPDs, like the “inlay-anchored adhesive fixed partial denture”. This type of prosthesis is a useful conservative prosthodontic treatment option especially when an esthetic single-tooth replacement with a minimally invasive tooth reduction is desired and an implant is either contraindicated or refused by the patient (Magne et al., 2002). No reports were found in the literature regarding the use of reinforced porcelains to construct FPDs, however it is expected that their mechanical properties are sufficient to withstand the stresses of the oral cavity, and their cost is expected to be lower than that of structures involving core materials.

One of the most efficient ways to improve the mechanical properties of a ceramic matrix is to add long fibers to the structure, creating a continuous fiber-reinforced ceramic matrix composite (CFCMC) (Kamino et al., 1996; Mamiya et al., 2000; Shin and Tanaka, 1994). The improvement on the mechanical properties of such a fiber-reinforced material is related to several toughening mechanisms such as crack bridging at the crack wake, microcrack toughening, and the absorption of energy by means of plastic deformation and fracture of the fibers (Dutton et al., 2000). Various factors may influence the degree of reinforcement obtained by the addition of a continuous fiber to the ceramic matrix. The thermal compatibility is one of them, since the fiber and the matrix must be thermally compatible so as to avoid the growth of undesirable cracks during cooling. Other factors also play an important role such as the volume fraction, orientation, distribution, anisotropy and interfacial bonding of the fiber phase (Bhatt et al., 1992).

One candidate material to reinforce porcelains is the eutectic GdAlO$_3$/Al$_2$O$_3$ fiber composite (Waku et al., 1997). This fiber is obtained by directional solidification, such as the laser heated pedestal growth (LHPG) technique, and does not have pores or cracks, resulting in mechanical strength of about 1780 MPa (−25 times higher than the mean strength of dental porcelains) and high thermal stability at elevated temperatures (Medeiros et al., 2007). The high strength of this type of fiber is also related to the alternation of phases in the eutectic microstructure, which increases the energy required for crack propagation (Lee et al., 2001a,b). Another important property of this fiber is the coefficient of thermal expansion (CTE) of 8.8 \times 10^{-6} \, ^\circ C^{-1} which is close to the average CTE of vitreous porcelains (7.8 \times 10^{-6} \, ^\circ C^{-1}) used as veneering materials over alumina-based cores (Medeiros, 2004).

The aim of this study was to test the hypothesis that the addition of continuous GdAlO$_3$/Al$_2$O$_3$ fibers to a vitreous porcelain will significantly increase its flexural strength so that it can be indicated to construct FPDs. Additionally, the work tested the hypothesis that adding different amounts of GdAlO$_3$/Al$_2$O$_3$ particles (obtained by milling) to a dental porcelain will improve its mechanical properties so that it can be used to construct stronger inlays, onlays, veneers and crowns. The second hypothesis is based on the fact that some studies have shown improvements in mechanical properties of alumina-based core ceramics after the addition of alumina particles or silicon carbide whiskers (Tan et al., 2001; Tanimoto and Nemoto, 2004).

2. Material and method

2.1. Production of GdAlO$_3$/Al$_2$O$_3$ fibers

To produce the eutectic gadolinium aluminate/alumina fibers, primary Al$_2$O$_3$ (Alfa Aesar, 5N) and Gd$_2$O$_3$ (Reacton, 6N) powders were used as starting materials and mixed in the eutectic composition (77 mol% of Al$_2$O$_3$ and 23 mol% of Gd$_2$O$_3$). To ensure compositional homogeneity, the oxides were ball milled for 24 h prior to preparing 50 \times 10 \times 10 \, mm$^3$ green-ceramic bars. These bars were pre-sintered at 1300 °C for 4 h and then cut into 1 mm \times 1 mm transversal sections to produce the pedestals for the LHPG pulling process. The experiments were performed without crystallographically oriented seeds (the pedestal was also used as a seed) in air atmosphere, without pedestal rotation, at a fiber pedestal pulling ratio of 1.0. Details of the LHPG pulling process are described elsewhere (Andreatta et al., 2002b).

2.2. Continuous fiber-reinforced porcelain

A commercial dental porcelain (Cerabien, Noritake) shade D4 was used in this study. Bar specimens were produced using a stainless steel mould with dimensions of 25 \times 5 \times 2 \, mm$^3$. Eight fiber-reinforced specimens were produced by adding three GdAlO$_3$/Al$_2$O$_3$ fibers (diameter of 0.8 mm and length of 23 mm) to the porcelain. Fibers were positioned parallel to each other at 0.5 mm from the tensile surface. One fiber was placed in the center of the bar, and the other two were positioned at the midpoint between the center fiber and the margin of the bar. The final fiber content was 30% in volume (53 wt%) (Fig. 1). The continuous fiber-reinforced specimens were sintered according to the porcelain manufacturer recommendations (Table 1). Due to firing shrinkage, the final thickness was reduced to 1.8 mm after the sintering cycle. The four surfaces of the bar were ground and the tensile surface was polished sequentially, with 300, 600, 1200-grit silicon carbide abrasive papers, and diamond paste of 1 \, µm as the final abrasive. The final specimen dimensions were 23.0 \times 3.5 \times 1.4 \, mm$^3$, and the final distance of the fiber from the tensile surface was 0.2 mm. Another eight specimens were produced using the same methodology but without the addition of fibers (control).

2.3. Particle-reinforced porcelain

GdAlO$_3$/Al$_2$O$_3$ fibers were milled in a tungsten carbide rings mill (Shatterbox, Spex 8500) in order to obtain particles with diameter of approximately 11 \, µm. Two different volume fractions of these particles were added to the porcelain powder (Cerabien, Noritake): 5 and 10 vol%. Seven disc specimens (20 mm in diameter and 3 mm in thickness) were produced for each particle content by the vibration-condensation method and sintered in a dental porcelain furnace following the firing schedule recommended by the manufacturer (Table 1). After firing, the specimens were machined and one of the surfaces was mirror polished using a polishing machine (Ecomet 3, Buehler, Lake Buff, USA) with diamond suspensions (45, 15, 6 and 1 \, µm). No color changes were visible to the naked eye in the fiber-reinforced
shows that the interface between the continuous fiber and the porcelain is free of defects at the level of sub-micrometric scale. In this figure, it is also possible to note the irregular microstructure of the GdAlO/

For the disc specimens, the Young's modulus, the values obtained for the continuous fiber-reinforced specimens were 28% higher than those of the control group ($p < 0.001$). The elastic modulus varied significantly depending on the particle content so that the higher the fiber content, the lower the elastic modulus ($p < 0.0001$).

Fig. 3 shows that the interface between the continuous fiber and the porcelain is free of defects at the level of sub-micrometric scale. In this figure, it is also possible to note the irregular microstructure of the GdAlO/

Fractographic analysis showed that fractured surfaces were

where, $f$ is the fracture load, $l$ is the span distance, $w$ is the specimen's width and $h$ the specimen's thickness.

For the disc specimens, the specimens were fractured in bi-axial flexure test by means of the piston-on-3-balls technique in a universal testing machine. The disks were supported on three steel balls (each 1.6 mm in diameter) that were equally spaced around a support circle having a radius of 4 mm. The specimens were loaded to failure by a flexural load applied by a steel cylinder with a diameter of 1.6 mm. The biaxial fracture stress ($\sigma_b$) was calculated according to the following formula:

$$
\sigma_b = \frac{3P(1+\nu)}{4\pi l^2}
\left[ 1 + 2 \ln \frac{a}{b} + \frac{(1-\nu)}{(1+\nu)} \left( 1 - \frac{b^2}{2a^2} - \frac{a^2}{2b^2} \right) \right]
$$

where, $P$ is the fracture load, $l$ the thickness of the support circle, $b$ is the radius of the steel cylinder, $\nu$ is the Poisson's ratio, and $R$ is the specimen's radius. The uniaxial test was selected for specimens with long fibers because its design resembles more accurately the stress state of a FPD connector. The biaxial test was chosen for the particle-reinforced specimens since this type of composite is not primarily intended to construct a FPD connector and this test is not influenced by edge defects, making specimen preparation easier.

Fractographic analysis of fractured surfaces was performed in the SEM. All data were analyzed by one-way analysis of variances (ANOVA) and multiple comparisons were performed using Tukey's post-hoc test at a pre-set significance level of 5%.

### 3. Results

Table 2 shows that the reinforcement of porcelain bars with continuous GdAlO/Al$_2$O$_3$ fibers resulted in an increase of 137% in the flexural strength ($p < 0.0001$). All specimen showed brittle fracture, as it can be noted by the single peak shown in the force–displacement curves in Fig. 2. With respect to the Young's modulus, the values obtained for the continuous fiber-reinforced specimens were 28% higher than those of the control group ($p < 0.001$).

The addition of varied amounts (5 and 10 vol%) of milled GdAlO/Al$_2$O$_3$ particles to the porcelain did not significantly affect the biaxial flexural strength when compared to the control group (0%) ($p = 0.08$). However, the particle-reinforced materials tended to show lower strength compared to the control. The elastic modulus varied significantly depending on the particle content so that the higher the fiber content, the lower the elastic modulus ($p < 0.0001$).

Fig. 3 shows that the interface between the continuous fiber and the porcelain is free of defects at the level of sub-micrometric scale. In this figure, it is also possible to note the irregular microstructure of the GdAlO/Al$_2$O$_3$ fiber, also referred to as “Chinese Script” (letter F) because it resembles the characters of this language (Andreeta et al., 2002a; Medeiros et al., 2007; Yoshikawa et al., 1999). Fig. 4 shows the interface between the milled GdAlO/Al$_2$O$_3$ fibers and the porcelain. It is possible to note the presence of cracks surrounding the entire milled fiber/porcelain interface (arrow). Fractographic analysis showed that fractured surfaces were
Table 2 – Density, flexural strength and elastic modulus of continuous fiber-reinforced and particle (milled fiber) reinforced porcelain as a function of the fiber content. Values with the same superscript are statistically similar (p > 0.05).

<table>
<thead>
<tr>
<th>Material</th>
<th>Fiber content</th>
<th>Density (g/cm³)</th>
<th>Flexural strength (MPa)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous Fiber-reinforced</td>
<td>No fibers</td>
<td>2.67 (0.26)</td>
<td>91.5 (7.1)</td>
<td>70.4 (5.8)</td>
</tr>
<tr>
<td></td>
<td>3 long fibers</td>
<td>4.99 (0.42)</td>
<td>217.4 (23.6)</td>
<td>90.2 (7.5)</td>
</tr>
<tr>
<td>Particle-reinforced</td>
<td>No fibers</td>
<td>2.47 (0.04)</td>
<td>105.2 (15.3)</td>
<td>73.5 (2.0)</td>
</tr>
<tr>
<td></td>
<td>5 vol%</td>
<td>2.64 (0.01)</td>
<td>92.7 (15.7)</td>
<td>69.2 (2.2)</td>
</tr>
<tr>
<td></td>
<td>10 vol%</td>
<td>2.64 (0.13)</td>
<td>87.1 (17.6)</td>
<td>53.6 (1.0)</td>
</tr>
</tbody>
</table>

Fig. 2 – Load versus extension curves for continuous fiber reinforced porcelain and control (no reinforcement).

very rough and had different planes in the porcelain region (Fig. 5(a)), indicating that multiple cracks propagated simultaneously because of the high elastic energy stored by the composite during loading. The exposed parts of fibers were a consequence of fiber/matrix interface debonding, and are indicative that a “fiber pull-out” toughening mechanism may have acted during fracture propagation. Exposed fiber surfaces revealed some small voids, which were not present on the surface of fresh pulled fibers, indicating that they were formed during sintering. The cause of the interface void formation could not be determined, since no reaction between fiber and glassy matrix could be observed (Fig. 2).

The complex fracture surfaces of the specimens hindered the analysis of fracture paths and the identification of fracture origins. For the specimen in Fig. 5, however, it was determined that the fracture was associated with the central fiber. The arrows in Fig. 5(b) indicate the fracture origin is an interfacial void near the area where the tensile stress in the fiber is maximum. The fracture path in the surrounding glassy matrix was almost co-planar with the fracture surface of the fiber. This fracture also started at the fiber-matrix interface (indicated by the dotted line in Fig. 5(b) and propagated in the direction of the surface under tension. These results indicated that the main fracture path started at the central fiber and then propagated through the porcelain matrix.

4. Discussion

The first hypothesis of this study was accepted since the addition of continuous GdAlO₃/Al₂O₃ fibers to the porcelain tested significantly increased its flexural strength and elastic modulus. Such improvement on the mechanical properties is related to several toughening mechanisms associated to the use of long fibers, such as crack bridging at the crack wake, microcrack toughening, and the absorption of energy by fracture of the fibers (Dutton et al., 2000). The occurrence of fiber pull-out, as seen in Fig. 5(a), suggested that there
are frictional or mechanical interlocking forces so that more elastic energy is consumed before catastrophic failure.

Another factor that contributed to the observed improvement in mechanical properties was the fact that the fibers and the porcelain used in the present study were thermally compatible, reducing undesirable crack formation during cooling. In fact, the microstructural analysis of the reinforced specimens (Fig. 3) did not show cracks related to thermal incompatibility in the interface between the continuous fibers and the porcelain. It was also possible to note in Fig. 3 that interfacial bonding between the fiber and the glassy matrix was strong enough to allow satisfactory load transfer, but it was not so strong to inhibit interfacial debonding during fracture propagation, leading to the occurrence of fiber pullout. The single peak observed in the load–displacement curve of the reinforced material (Fig. 2) is also evidence that the elastic energy was efficiently transmitted from the matrix to the fibers during loading, since the specimens fractured in only one stage, in a behavior similar to that of the porcelain without fibers. This result indicated that there is no damage accumulation during loading of the composite and fracture starts to propagate unstably when one or more fibers fracture suddenly. This interpretation is also supported by the fractographic analysis presented in Fig. 4(b).

The relatively high mean flexural strength obtained by the porcelain reinforced with long fibers (217.4 MPa) is an indication that this composite may be used to construct inlay-anchored FPDs. Moreover, the 28% increase in the elastic modulus after addition of long fibers is an important improvement, since a more rigid connector is beneficial for this type of dental application. In the present study, the long continuous fibers were placed very close to the tensile surface of the specimens in order to provide optimum usage of the fibers. It is important to note that this design can also be used to reinforce porcelain FPDs since the fibers can be placed in the connector area close the gingival embrasure.

Theoretical upper and lower limits \[ P_C(u) \] and \[ P_C(l) \] for flexural strength were calculated for the continuous fiber-reinforced porcelain based on the Voigt and Reuss law (Callister, 2000):

\[
P_C(u) = P_m f_m + P_f f_f
\]

\[
P_C(l) = P_m f_m + P_m f_f
\]

where \( P_C \) is the theoretical property of the composite material, \( P_m \) is the matrix property, \( f_m \) is the matrix volume fraction, \( P_f \) is the fiber property, and \( f_f \) is the fiber volume fraction. Fig. 6 shows how the flexural strength obtained experimentally is related to \( P_C(u) \) and \( P_C(l) \). It is possible to note that the composite's strength still can be improved since it is close to the lower limit predicted by Eq. (4). Interfacial voids formed on the fiber surfaces during sintering (Fig. 4(a)) seemed to have caused the premature fracture of the fibers, lowering their strength (Fig. 4(b)). Therefore, a study about defect formation during sintering is necessary to understand how to avoid them in order to improve the composite's strength. Moreover, other microstructural features like fiber diameter and chemical composition of glassy matrix, can be optimized to improve mechanical reinforcement.

The increase in strength observed after the addition of the long fibers to the porcelain is also related to the increase in the Young's modulus, \( E \). The calculated \( E \) value for the fiber was 343 GPa, considering the volumetric fraction of the \( \text{GdAlO}_3 \) phase of 0.61 (obtained in an image analyzer) and the
5. Conclusion

Within the limits of this study, it was possible to conclude that the reinforcement of a ceramic with continuous GdAlO$_3$/Al$_2$O$_3$ fibers resulted in increased strength and elastic modulus compared to the control group. However, the addition of varied amounts (5 and 10 vol%) of milled GdAlO$_3$/Al$_2$O$_3$ fibers to the porcelain did not improve its mechanical properties compared to the control group. This result was explained by the microstructural analysis which showed that the porcelain was not able to wet the ceramic particles during the firing cycle. From the clinical point of view, it is possible to conclude that the long fibers are good candidates to reinforce the connector of inlay-anchored FPDs, leading bridgeworks with longer lifetimes. However, the addition of milled fibers to the porcelain in the conditions of this study can not improve the mechanical behavior of inlays, onlays and crowns.

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References


