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Designing functionally graded materials with superior load-bearing properties

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Abstract

Ceramic prostheses often fail from fracture and wear. We hypothesize that these failures may be substantially mitigated by an appropriate grading of elastic modulus at the ceramic surface. In this study, we elucidate the effect of elastic modulus profile on the flexural damage resistance of functionally graded materials (FGMs), providing theoretical guidelines for designing FGM with superior load-bearing property. The Young's modulus of the graded structure is assumed to vary in a power-law relation with a scaling exponent n ; this is in accordance with experimental observations from our laboratory and elsewhere. Based on the theory for bending of graded beams, we examine the effect of n value and bulk-to-surface modulus ratio (E_b/E_s) on stress distribution through the graded layer. Theory predicts that a low exponent ($0.15 < n < 0.5$), coupled with a relatively small modulus ratio ($3 < E_b/E_s < 6$), is most desirable for reducing the maximum stress and transferring it into the interior, while keeping the surface stress low. Experimentally, we demonstrate that elastically graded materials with various n values and E_b/E_s ratios can be fabricated by infiltrating alumina and zirconia with a low-modulus glass. Flexural tests show that graded alumina and zirconia with suitable values of these parameters exhibit superior load-bearing capacity, 20% to 50% higher than their homogeneous counterparts. Improving load-bearing capacity of ceramic materials could have broad impacts on biomedical, civil, structural, and an array of other engineering applications.

Keywords

biomechanical prostheses; functionally graded ceramics; modulus gradients; stress dissipation; load-bearing capacity

1. Introduction

Ceramics are widely used in load-bearing biomedical applications due to their excellent biocompatibility, wear resistance and aesthetics [1-3]. Ceramic bearings for total hip and

knee replacements are a notable case [4-8]. All-ceramic dental restorations are another excellent example [9-11]. However, ceramics are susceptible to flexural fracture which accounts for millions of dollars annually in replacement costs and can cause significant patient discomfort and reduced quality of life [12-15]. We propose to improve the resistance to flexural fracture of ceramics by grading ceramic surface with a low-modulus glass [16-18].

Traditionally, strengthening ceramics and improving their resistance to contact damage relies on the introduction of a compressive residual stress layer at the ceramic surfaces by tempering [19], chemical treatments (e.g. ion-exchange or partial leaching) [20], introduction of second-phase particles [21], or infiltrating glass with a lower coefficient of thermal expansion (CTE) [22, 23]. However, surface compressive stresses are inevitably accompanied by tensile stresses in the bulk of ceramics, which can promote cracking [24]. More recently, Suresh, Padture and co-workers have introduced a new concept of improving the contact damage resistance of ceramics by infiltrating the ceramic surface with a low-modulus glass of matching CTE and poisson's ratio, producing an elastically graded surface without any long-range residual thermal stresses [25-30]. Such modulus gradient can improve contact damage resistance of ceramic materials by diminishing tensile stresses at the outer surface of the diffuse layers. We have extended this concept to the flexural damage resistance of ceramics [17]. To date, only a few such studies have been published, all relating to biomedical applications [16, 18, 31] However, the effect of elastic modulus profile on the stress dissipation remains elusive.

A recent study conducted in our laboratory has shown that a low-modulus surface can effectively reduce the surface stress while diminishing and transferring the maximum stress from the surface to the interior of a bending beam or plate [18]. In that study, explicit flexure formulas have been derived to compute bending stress states across the section of a graded sandwich beam [18]. This was done by solving integrals of the moment-curvature relationship for a power-law modulus gradient—low modulus at the surface and high modulus within. Our analysis showed that such modulus gradients can effectively reduce surface tensile stresses and transfer them into the interior [16, 18]. However, our stress analysis was based on a power-law modulus function with a given scaling exponent n value, determined from a model graded glass-zirconia system. The optimal condition for stress dissipation in relation to various modulus functions with different n values and bulk-to-surface modulus ratios has not been previously examined.

In this study, we elucidate the effects of modulus profile (power-law function with various n values) and ratio (bulk-to-surface Young's modulus ratio, E_b/E_s) on the stress dissipation in graded beams and plates. Experimentally, we demonstrate that graded structures with various modulus profiles can be fabricated by glass-infiltration of ceramic templates with various porosities. In addition, by infiltrating ceramics with marked difference in elastic modulus, we can alter the bulk-to-surface modulus ratio [17, 32]. Flexural tests show significantly improved load-bearing properties imparted by the appropriate surface elastic grading of alumina and zirconia ceramics. In practice, such graded materials can also be fabricated using a robocasting technique, where structures consisting of thin layers with predetermined compositions and moduli can be printed [33-36]. Thus, our study provides a guideline for designing graded structures with appropriate modulus profiles for superior load-bearing capacities.

2. Generalized Stress Analysis In Graded Structures

Detailed derivation of closed-form flexure formulas for computing the bending stress distributions in simply supported graded sandwich beams subject to transverse center loads

was presented in the earlier paper [18] and will not be repeated here. For readers' convenience, below we briefly summarize the key findings. But first we define the coordinates and parameters required for stress analysis (Fig. 1). The beam consists of a uniform core with graded layers at both top and bottom surfaces. h_2 and h_1 represent the half thicknesses of the beam and its homogeneous core, respectively, while $h (= h_2 - h_1)$ is the thickness of each graded layer. b is the width of the beam. Assuming the elastic modulus changes with respect to the spatial coordinates according to a power-law relation, the stress distribution in the uniform core and graded layers can be expressed in equations 1a and b, respectively [18].

$$\sigma_{xgu} = - \frac{ME_b}{E_b I_{gu} + E_s I_{gg1} + (E_b - E_s) I_{gg2}} y \quad (0 \leq y < h_1) \quad (1a)$$

$$\sigma_{xgg} = - \frac{M \left[E_s + (E_b - E_s) \left(\frac{h_2 - y}{h} \right)^n \right]}{E_b I_{gu} + E_s I_{gg1} + (E_b - E_s) I_{gg2}} y \quad (h_1 \leq y \leq h_2) \quad (1b)$$

where E_b is the Young's modulus of the uniform core, E_s is the surface modulus of graded layers, y is the perpendicular distance to the neutral axis (NA), n is the scaling exponent of the modulus function, and $t = (h_2 - y)$ is the distance from the surface. The gradient of modulus may be described by a power-law relation [18]:

$$E = E_s + (E_b - E_s) \left(\frac{h_2 - y}{h} \right)^n \quad (2)$$

The bending moment, M , and moment of inertia, I_{gu} , I_{gg1} and I_{gg2} , are:

$$M = \frac{FL}{4} \quad (3)$$

$$I_{gu} = \frac{2bh_1^3}{3} \quad (4)$$

$$I_{gg1} = \frac{2b(h_2^3 - h_1^3)}{3} \quad (5)$$

$$I_{gg2} = \frac{2b(h_2 - h_1)^{(n+1)}(h_1^2 n^2 + 2h_2 h_1 n + 3h_1^2 n + 2h_2 h_1 + 2h_2^2 + 2h_1^2)}{(n+3)(n+2)(n+1)h^n} \quad (6)$$

As can be seen from the above equations, three key factors govern the stress state in a graded structure: the total beam thickness to graded layers ratio ($2h_2/2h = h_2/h$); exponent n

of the modulus function; and bulk-to-surface modulus ratio (E_b/E_s). Our previous study has examined the effect of total layer thickness to graded layers ratio on the stress distribution. It was found that a small thickness ratio ($h_2/h < 5$) is more likely to reduce the maximum stress. However, the previous study for a glass-infiltrated zirconia system was done using a fixed $n = 0.32$ (determined by nanoindentation) and $E_b/E_s = 3.2$ ($E_b = 240$ GPa for zirconia and $E_s = 75$ GPa for glass-zirconia graded surface). The effects of n value and modulus ratio on stress state have not been evaluated analytically, due mainly to the labor-intensive nature of such exercise. In the present study, we created a C++ code using the analytical equations 1 – 6 to search for an optimal n value in reducing the maximum stress for any given h_2/h thickness ratio with constant $E_b/E_s = 3.2$. Once an optimal n value for a given thickness ratio was determined, we extended our study to investigate the effect of E_b/E_s ratio on the stress distribution.

3. Materials & Methods

3.1. Materials

To demonstrate the feasibility of fabricating graded materials with different elastic modulus profiles and bulk-to-surface modulus ratios, two ceramic systems—alumina and Y-TZP—are selected. Accordingly, two glass compositions are developed to infiltrate alumina and Y-TZP. The infiltrating glass and ceramic substrate have identical CTE, so that no long-range residual thermal stress is introduced to the systems from glass infiltration. This makes them ideal systems for the experimental determination of elastic gradients effect on the critical load for flexural fracture. The elastic modulus of the two infiltrating glasses is ~67 GPa, while the bulk modulus for alumina and zirconia is 410 GPa and 240 GPa, respectively. Note that the modulus values quoted above are based on nanoindentation test. Thus, by infiltrating different ceramic materials, graded structures with various E_b/E_s values can be fabricated.

Fully sintered, 99.5% pure, alumina plates (AD995, CoorsTek, Golden, CO) were obtained. The alumina plates (20 mm in diameter) were ground to 1.5, 1.0, 0.7 mm thick (12 specimens for each thickness), polished with successive grits to 0.5 μm finish. Six plates from each thickness group were randomly selected for glass-infiltration, producing graded glass-alumina structures (GAG). An in-house prepared powdered glass slurry was applied on both top and bottom surfaces of these plates. Glass infiltration was carried out at 1550 °C for 2 h with a heating and cooling rate of 8 °C per min. The selected glass infiltration temperature was below the sintering temperature (1600 °C) of alumina, avoiding significant grain growth. The main composition of the infiltrating glass (> 1 weight %) contained: SiO₂ (71.60%), Al₂O₃ (10.55%), K₂O (8.00%), Na₂O (6.89%), CaO (1.34%). The glass was formulated to create a CTE of $8.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ (between 25 – 450 °C), identical to that of alumina [32].

Y-TZP plates, fabricated from a commercial zirconia powder (TZ-3Y-E grade, Tosoh, Tokyo, Japan), were heat-treated at 1350 °C for 1 h. The heat-treated plates were then polished and infiltrated with a silicate glass at 1450 °C for 2 h. The main composition of the infiltrating glass (> 1 weight %) contained: SiO₂ (65.5%), Al₂O₃ (11.7%), K₂O (10.0%), Na₂O (7.3%), CaO (3.0%), and Tb₄O₇ (1.9%). The glass was formulated to create a CTE of $10.4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ (between 25 – 450 °C), similar to that of Y-TZP [17]. We combined the glass infiltration and densification of Y-TZP in one process, this way the grain growth [37] and/or destabilizing of the tetragonal zirconia phase [38] associated with the post-sintering heat treatment could be prevented. Glass infiltrated zirconia (GZG) plates with thickness of 1.0, 0.7, 0.4 mm (6 specimens per thickness) were fabricated. In parallel, Y-TZP plates of identical thickness were synthesized at 1450 °C for 2 h. A heating and cooling rate of 14 °C per min was used for glass infiltration and densification of Y-TZP.

3.2. Characterization

At least 3 specimens from each infiltrated group were subjected to scanning electron microscopy (SEM) and nanoindentation analyses. Specimens were sectioned along the modulus gradients using a water cooled low speed diamond saw (Isomet, Buehler, Lake Bluff, IL). The cross-sections were polished down to 0.5 μm finish. To reveal the microstructure of the graded glass/ceramic layers, the polished sections were subjected to chemical etching using 10% hydrofluoric acid for 5 mins. To unveil the microstructure of the dense ceramic cores, additional specimens were thermally etched at 1500°C (alumina) and 1250°C (zirconia) with a dwell time 20 mins and a heating and cooling rate of 8°C per min. The selected thermal etching temperatures were significantly lower than the sintering temperatures for alumina (1600°C) and Y-TZP (1450°C), so that no significant grain growth anticipated. The chemically and thermally etched sections were carbon coated prior to SEM examination (Hitachi 3500N, Japan).

To identify the crystalline phase present in the external surface residual glass and the subsequent graded layers, as infiltrated glass-alumina and glass-zirconia graded surfaces (with an external glass layer) were subjected to x-ray diffraction (XRD, Philips X'Pert System, Almelo, Overijssel, Netherlands) analysis with nickel filtered Cu K_α radiation at 45 kV and 45 mA. Data was collected from 15° – 70° at a scanning rate of 1°/min and a step size of 0.02°. Spectrum was analyzed for homogenous ceramics (alumina and Y-TZP), the graded layers, and the external glasses to show the amorphous glass phase expected on the surface and to ensure that no phase change occurs within the alumina and Y-TZP. This also confirmed that no additional crystal phase is formed on the surface upon cooling from the glass infiltration temperature. In addition, energy-dispersive x-ray (EDX) analysis was conducted on infiltrated and uninfiltrated glasses as well as on glass bars for CTE measurements to detect any compositional change induced from glass infiltration.

The Young's moduli and hardness values of the graded structures were determined using nanoindentations (3D Omniprobe TriboIndenter, Hysitron, Minneapolis, MN). Three specimens from each infiltrated material were embedded in an epoxy resin and sectioned and polished down to 0.5 μm finish. Measurements were taken along the graded cross section, from the surface to interior, with a Berkovich indenter with a step size of 3, 10 or 20 μm . The tip area function and machine compliance were determined using fused silica samples. The maximum indentation load used were 40 and 400 mN for graded zirconia and 500 mN for graded alumina. A loading and unloading rate of 5 mN/s was employed in all cases. The reduced modulus was determined by the Oliver-Pharr approach from the indentation curve [39]. The Young's modulus of the specimen was computed using the measured reduced modulus. The reduced modulus, E_r , is described by the relationship

$$\frac{1}{E_r} = \frac{(1 - \nu_i^2)}{E_i} + \frac{(1 - \nu_s^2)}{E_s}$$
 where E and ν are the Young's modulus and Poisson's ratio, respectively, of the target material, while E_i and ν_i are the elastic modulus and Poisson's ratio of the diamond indenter. We use $\nu = 0.3$ for Y-TZP and $\nu = 0.22$ for alumina, $E_i = 1040$ GPa and $\nu_i = 0.07$ for the diamond indenter [18].

To elucidate the effect of modulus gradients on the bending stress distribution, we compared the critical load for flexural fracture of graded with ungraded plates. In addition, to explicate the effect of total thickness to graded layers ratio on stress distribution in graded plates, we fabricated test plates with various thicknesses (ranging from 0.4 – 1.5 mm) while holding graded layer thickness constant for each material system. Since the minimum thickness for a bending bar or biaxial disc is 1.2 mm [40], we adopted a ball-on-ceramic/polymer bilayer method to determine the critical fracture load of a bending plate (Fig. 1b) [41, 42]. The ball-on-flat bilayer indentation flexural test produces bending stresses in the ceramic layer just

like those generated by a biaxial or 3-point bend test, and yet is more tolerant to the specimen dimensions, capable of testing specimens with thinner thicknesses and irregular shapes.

All ceramic plates were polished with successive diamond grits and finished with 0.5 μm disk. For graded plates, specimens were abraded with a 6 μm diamond disk to remove the external surface glass, and then finished with a 0.5 μm disk to normalize the surface morphology. The plates were bonded to a polycarbonate base (12.5 mm thick, Hyzod, AlN Plastics, Norfolk, VA) with a thin epoxy layer ($\sim 20 \mu\text{m}$) (Harcos Chemicals, Bellesville, NJ). The epoxy adhesives were cured. The ceramic/polycarbonate bilayers were loaded at their top surfaces with a tungsten carbide (WC) indenting sphere of radius 3.18 mm mounted into the cross head of a screwdriven universal testing machine (Model 5566, Instron Corp., Canton, MA). The load was increased monotonically at a 1 mm/min rate; load data were recorded electronically at intervals of 0.002 s. Critical loads for the onset of flexural fracture in the ceramic plates were determined from a load drop in the load-deflection curve.

4. Results

4.1 Experimental results

The representative micro structures of graded alumina (GAG) and zirconia (GZG) are shown in Fig. 2. Images for the graded layers were acquired in the backscattered electron (BSE) mode on polished cross-sections, while those for the homogeneous cores were obtained in the secondary electron (SE) mode on thermally etched specimens. In both materials, the graded surfaces consisted of relatively high glass content, which decreased gradually as the distance from the surface increased and eventually diminished in the high crystalline ceramic cores. At this BSE mode (Fig. 2b), it seems that glass infiltration has resulted in significant growth of zirconia grains at the graded surface. Higher resolution SEM image on hydrofluoric acid (10%, 15 mins) etched surface of GZG showed that the “large” surface grains were in fact consisted of multiple Y-TZP particles, typically 8 – 15 particles with size around 0.2 μm or less (Fig. 3). However, this was purely based on SEM observations. In order to better understand the effect of glass infiltration on particle size, morphology, and composition, we are currently conducting TEM and XRD analyses on graded and ungraded ceramics.

XRD spectra of the surface and interior of graded GAG and GZG structures are shown in Fig. 4. Analysis confirmed that the graded surface of GAG consisted of a α alumina phase and small amount of glass. For GZG, the surface consisted of a tetragonal zirconia phase and an amorphous glass phase, no monoclinic phase was determined. In the interior of the graded materials, α alumina and tetragonal zirconia were the only phase present in GAG and GZG, respectively. EDX analysis revealed identical compositions in uninfiltrated and infiltrated glasses for both alumina and zirconia systems.

The Young's moduli, E , for GAG and GZG as a function of the distance from the surface, $t = h_2 - y$, are plotted in Fig. 5. In both cases, the elastic modulus increases as the distance from the surface increases. The infiltrating glass at the external surfaces of both materials had a modulus ~ 67 GPa, similar to that of dental porcelains or soda-lime glass. The graded glass-ceramic surface possessed a modulus of ~ 80 GPa and ~ 75 GPa for GAG and GZG, respectively. The bulk alumina and zirconia exhibited a modulus of 410 and 240 GPa, respectively. These indentation Young's modulus values were 10% to 15% higher than the previously reported value 372 GPa for alumina [43] and 214 GPa for Y-TZP (measured using a sonic resonance method). This discrepancy could be due to the calibration error of the nanoindenter and the Poisson's ratio value for various constituents used to compute the Young's modulus. Hopefully, with further development of the indentation instrumentations,

we could have better interpretation of the modulus values. Since nanoindentation is a relatively simple and straightforward method to determine the elastic modulus profile as a function of the depth from the surface, we decided to utilize the indentation modulus data. We fitted the $E-t$ data with a power-law relation using equation 2. It was found that $n = 0.17$ and 0.32 resulted in a best fit to the experimental data for GAG and GZG, respectively.

Critical loads for the onset of fracture in graded alumina and zirconia plates relative to their homogeneous counterparts are shown in Fig. 6. Loads required to fracture GAG plates were 1260 ± 170 (mean $\pm$ SD), 675 ± 74 , and 404 ± 16 N for $d = 1.5$, 1.0 , and 0.7 mm thickness, respectively, which were 37%, 40%, and 45% higher than their homogeneous alumina counterparts (798 ± 130 , 403 ± 70 , and 222 ± 39 N). Loads to fracture for GZG plates were 1081 ± 140 , 648 ± 39 , and 227 ± 20 N for $d = 1.0$, 0.7 , and 0.4 mm, which were 17%, 25%, and 50% higher than their homogeneous Y-TZP counterparts (894 ± 85 , 487 ± 78 , and 113 ± 10 N).

4.2 Theoretical analysis

Our experimental observation demonstrates that it is possible to tailor the n value of the modulus function and the bulk-to-surface modulus ratio (E_b/E_s) by using various glass-ceramic infiltration pairings (Fig. 5). Previous study has shown that for a given n value and E_b/E_s ratio, the total thickness to graded layers ratio (h_2/h) plays a governing role in reducing the maximum tensile stress and transferring it deep into the bulk, away from the source of failure-inducing surface flaws [18]. Building on our experimental observations and previous theoretical analysis, we systematically investigate the effect of these parameters on the stress dissipation in graded materials. Examples of modulus gradients for various n values are presented in Fig. 7. Moduli E are normalized relative to surface modulus E_s , and gradation distances, $t = h_2 - y$, are normalized relative to graded layer thickness h .

The stress distribution in an elastically graded structure of a given elastic modulus function can be computed using equation 1. To determine the effectiveness of n value in reducing the maximum stress, we have created a C++ code using the analytical equations 1 – 6. We fix $E_b/E_s = 3.2$ (similar to that seen in the GZG system) but let n vary from 0.01 to 4 in incremental steps of 0.01. We determine the lowest maximum stress and its relative location with respect to the surface for $h_2/h = 1.5$ to 10 in incremental steps of 0.1.

The maximum stress (σ_{g-max}) and its location as well as the surface stress (σ_{g-surf}) in the graded plates before fracture are plotted as a function of the n value (Fig. 8). The maximum and surface stresses are normalized by the maximum stresses (σ_{u-max}) occurring at the surface of their homogeneous counterparts. Solid and gray curves represent the normalized maximum and surface stresses, respectively, in graded plates of various thickness ratios ($h_2/h = 10, 5.8, 4.2, 2.5$, and 1.7) but constant bulk-to-surface modulus ratio ($E_b/E_s = 3.2$). From Fig. 8a, it can be noted that controlled gradients of the surface elastic property can effectively reduce the maximum bending stress in a plate or beam. A small h_2/h ratio is more effective to reduce the maximum stress, but it also results in a relatively high surface stress. A small n value can, however, diminish both the maximum stress and surface stress. The greatest reduction of maximum and surface stresses occurs when $n < 1$ for most of the thickness ratios examined (see shaded region in Fig. 8). In fact, for $h_2/h > 2.5$, the most effective stress reduction n values lies below 0.5, well within the range of the current GAG ($n = 0.17$) and GZG ($n = 0.32$) materials.

The location of the maximum stress is also an important factor that dictates the fracture behavior. The distance of the maximum stress from the surface in graded plates of various h_2/h ratios as a function of the n value is plotted in Fig. 8b. The maximum stress location, $t = h_2 - y$, is normalized by dividing by the graded layer thickness h . The maximum stress

occurs at the surface of graded plates when $n = 0.01$. However, it quickly shifts toward a diffused zone of the graded layer as the n value increases, especially for large thickness ratios, i.e. $h_2/h > 2.5$. A $n \approx 0.15 - 0.5$ is able to significantly shift the maximum stress from the surface into the interior of a graded plate.

The normalized maximum stress and its location as well as the surface stress in the graded plates with various E_b/E_s ratios as a function of the thickness ratio are plotted in Fig. 9. The corresponding n values are the most effective value for diminishing the maximum stress in a graded plate of given h_2/h and E_b/E_s ratios, determined using our created C++ code. Solid and gray curves in Fig. 9a represent the normalized maximum and surface stresses, respectively, in graded plates of various modulus ratio ($E_b/E_s = 10, 8, 6, 5, 4, 3$, and 2). As can be seen from Fig. 9a, a small E_b/E_s ratio coupled with a small h_2/h value is more effective to reduce the maximum stress. However, small E_b/E_s and h_2/h ratios are less effective in transferring the maximum stress into the bulk of the material (Fig. 9b). They also result in a relatively high surface stress (Fig. 9a). Thus, a modulus ratio $E_b/E_s = 3 - 6$ and a thickness ratio $h_2/h = 2 - 8$ are most desirable for both reducing the maximum stress and transferring it into the bulk while keeping the surface stress low.

5. Discussion

Our study demonstrates that improvement in load-bearing capacity of ceramics can be achieved by grading the surface of ceramics with low-modulus glass compositions. Theoretically, elasticity analysis show that the scaling exponent n of the modulus profile, bulk-to-surface modulus ratio, and total plate to graded layers thickness ratio all play a significant role in determining through-thickness bending stress distribution in a graded plate or beam subjected to transverse load. Experimentally, we confirm that graded glass-alumina and glass-zirconia plates with various surface modulus gradients and plate to graded layer thickness ratios exhibit improved load-bearing property relative to their homogeneous counterparts. Below, we establish the correlation between the elastic modulus function and load-bearing property of functionally graded ceramics.

Taking together Figs. 8 and 9, for thickness range $h_2/h = 2 - 10$, a modulus profile with $0.15 < n < 0.5$ and $3 < E_b/E_s < 6$ is most desirable for reducing the maximum stress and for shifting it away from the surface into the graded zone, while keeping the surface stress low. It is important to note that the n value and E_b/E_s ratio for graded alumina and zirconia are 0.17 and 0.32 and 5.1 and 3.2 , respectively, well within the above-indicated range. In addition, the plate thickness ($2h_2$) examined here ranges from $0.4 - 1.5$ mm. Given the thickness of the graded layers $h = 0.08$ and 0.12 mm for alumina and zirconia respectively, the equivalent h_2/h for the thickness range examined lies between 1.7 and 9.6 , again overlaps with the above-mentioned most desirable thickness range $h_2/h = 2 - 10$. Thus, both graded alumina and zirconia plates have withstand transverse loads 37% to 45% and 17% to 50% higher than their homogeneous alumina and zirconia counterparts. A typical dental prosthesis also has a thickness range of $0.4 - 1.5$ mm, suggesting that by grading the ceramic surface, we can significantly improve the load-bearing capacity of alumina and zirconia restorations, averting flexural bulk fracture that happens all too often in all-ceramic crowns and bridges [13].

Flexural fracture of a homogeneous ceramic plate or beam occurs at the tensile surface where maximum stress exerts. By grading the ceramic surface, the surface flexural stress can be dramatically diminished. For the graded alumina and zirconia plates examined here, the surface stresses are below 25% and 45% , respectively, of those in their homogeneous counterparts. In addition, graded surface is able to reduce the maximum stress by 10% to 15% and 15% to 20% , and to transfer the maximum stress $60 - 70 \mu\text{m}$ and $30 - 100 \mu\text{m}$

away from the surface into the graded glass-alumina and glass-zirconia layers, respectively. Although, in some cases, the graded structures may only reduce the maximum stress by as small as 10% and transfer the maximum stress 30 μm (Y-TZP) or 60 μm (alumina) below the surface. The absence of large internal flaws of these fine-grained ceramics, coupled with the somewhat diminished effectiveness of any such internal flaws as stress concentrators [44], renders the graded material more flaw-tolerant and resistant to higher loads.

Biomechanical prostheses are often subjected to contact-slide fatigue loading, which require superior wear resistance. Our previous studies have shown that the resistance to sliding-contact fatigue is at least as high for the graded alumina and zirconia as for their ungraded counterparts, thus the mechanical integrity is not compromised by the infiltration [32, 45-47].

It is possible that the glass, both in the external surface glass layer and in the graded glass-ceramic layer, may undergo compositional change and/or crystallization during the infiltration process. In addition, new crystalline phase may form due to possible ion exchange between glass and ceramic, or simply, phase transformation of the ceramic induced from temperature and/or stress. All these can change the CTE of the glass and the ceramic, introducing residual stresses to the graded material and hence altering its strength. XRD analysis of the as infiltrated glass-alumina and glass-zirconia surfaces revealed a small amount of glass phase in the external glass and graded layers. There was no detectable secondary crystalline phase present in addition to the α -alumina or *t*-Y-TZP phase, at least within the detection limit of XRD (i.e. ~ 3 vol.%). EDX analysis showed identical compositions in uninfiltrated and infiltrated glasses as well as in glass bars for CTE measurements. Although EDX is only semiquantitative, this suggests that there was no essential change in glass composition during infiltration. Therefore, it is unlikely that significant residual stresses have developed in the graded materials. The observed strengthening effect is then due predominantly to the surface elastic grading.

We acknowledge that it is possible a small amount of residual stresses could have still developed in the graded layer. This is because the glass penetrates the grain boundaries and gradually separates the ceramic grains, leading to an increase in volume accompanied by localized compressive stresses at the surfaces of graded materials. We are currently conducting residual stress measurements of graded structures by micro-x-ray analysis using the “ $\sin^2\psi$ ” technique [48, 49]. Preliminary results have revealed no significant residual stresses at the graded glass-zirconia surface or in the center of the zirconia core, suggesting that the strengthen effect is indeed induced from the surface grading.

6. Conclusions

Using a composite beam theory, we have examined the effect of modulus profile on stress dissipation in functionally graded materials. Theory predicts that modulus functions with a low exponent value ($0.15 < n < 0.5$) coupled with a relatively small bulk-to-surface modulus ratio ($3 < E_b/E_s < 6$) are most effective in reducing the maximum stress and transferring it into the interior, while keeping the surface stress low. Experimentally, we have demonstrated that elastically graded ceramics with suitable *n* values and E_b/E_s ratios exhibit superior load-bearing capacity, 20% to 50% higher than their homogeneous counterparts. In a broader context, improving load-bearing property of ceramic materials could expand the indications for ceramics in biomedical applications, foreshadowing civil, structural, and other engineering applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Cross section of graded sandwich structures. (1) A symmetrically graded sandwich beam of width b and thickness $2h_2$. h is the graded layer thickness, h_1 the distance from neutral axis (NA), z to graded layer/core interface, and $t = (h_2 - y)$ the distance from surface. (2) A ball-on-ceramic/polymer bilayer test, which produces a through-thickness bending stress distribution in the ceramic plate, similar to that produced by a three-point bend or a biaxial test. P is the applied load; r is the radius of the indenter; R denotes the flexural radial cracks; and Y_D represents yield of polymer support.

Figure 2. Backscattered electron (BSE) images showing cross-sectional view of a graded glass-alumina and glass-zirconia structure [see left frames in (a) and (b), respectively]. Secondary electron (SE) images revealing the microstructure of thermally etched ceramic cross-sections near the center of the cores. Note: the glass content (dark phase) gradually decreased as it proceeded towards the interior.

Figure 3.
SEM micrograph revealing the microstructure of zirconia grains at the surface of a chemically etched glass-zirconia layer.

Figure 4. XRD spectra of graded (with an external residual glass layer) and ungraded surfaces of (a) alumina and (b) zirconia. Note: α and T represent the α -alumina and tetragonal zirconia phases, respectively.

Figure 5.

Variations of elastic modulus as a function of the depth below the surface. The individual points are the Young's modulus data obtained from nanoindentation. The solid curves are semi-empirical fit to the Young's modulus data, E , in the graded layers using a power-law

relation: $E = E_s + (E_b - E_s) \left(\frac{h_2 - y}{h} \right)^n$, where $E_s = 75$ and 80 GPa are the surface and $E_b = 240$ and 410 GPa are the bulk moduli of graded zirconia and alumina, respectively; h is the thickness of the graded layer; h_2 is the half thickness of the plate; y is the distance from the neutral axis; and $t (= h_2 - y)$ is the distance from the surface.

Figure 6.

Bar chart showing critical loads for flexural fracture of ceramic plates on polycarbonate support subject to Hertzian indentation.

Figure 7. Normalized elastic modulus E/E_s through the thickness of the graded layer t/h . The number 0.1, 0.2,... 4 denote various scaling exponents n of the modulus profile.

Figure 8.

Normalized maximum and surface stresses and their locations in the graded plates of various thicknesses. (a) Maximum stress ratio ($\sigma_{g-max}/\sigma_{u-max}$, black curves) and surface stress ratio ($\sigma_{g-surf}/\sigma_{u-max}$, gray curves) of graded plates with various plate thickness to graded layers ratios (h_2/h) as a function of the scaling exponent n . (b) Normalized distance of the maximum stress from the surface, t/h , in graded plates of various h_2/h ratios as a function of the n value.

Figure 9. Plots of (a) normalized maximum and surface stresses and (b) maximum stress location in the graded plates with various E_b/E_s ratios as a function of the thickness ratio and its corresponding n value.