Crystallization of High-strength Fine-sized Leucite Glass-ceramics

INTRODUCTION
Leucite glass-ceramics are widely used in dentistry to produce dental restorations by a variety of fabrication routes (Cattell et al., 2005), making these materials extremely versatile. Methods of manufacturing these materials include the blending of high- and low expansion powdered frits (Weinstein et al., 1962), or of synthetic leucite with glasses (Burk and Burnett, 1978) by fusion methods. The controlled heating of a glass and its surface crystallization has also been used (Höland et al., 2003), although not optimized. Commercial production methods produce glass-ceramics with up to 45% leucite volume fraction (Cattell et al., 2005), and with microstructures that lack homogeneity. Microcracking often results around large, irregular leucite crystals and clusters (>10 μm), inhomogeneously distributed in a glass matrix (Barreiro et al., 1989). Crystal-matrix microcracking and crystal twinning (Palmer et al., 1988) are associated with a temperature dependent (605-625°C) cubic to tetragonal phase transformation (Mackert, 1988). This is in conjunction with a thermal expansion (TEC) change from 10.1 to 25.1 x 10^-6 K^-1 (Rouf et al., 1978) and a reversible 1.2% volume change (Mackert, 1988). These processes can introduce stress-raising flaws or decouple the leucite crystals from the glass matrix (Binnis, 1983). This can reduce the elastic-stored strain energy of the thermal expansion anisotropy and deplete tangential compressive stresses around the crystals, which are key to strengthening in feldspathic dental porcelains (Denny et al., 1996). A critical particle size for glass-ceramic microcracking was explained by a Griffith-type energy balance criterion (Davidge and Green, 1968). In agreement with this theory, microcracking was minimized in tetragonal leucite glass-ceramics by a reduction in the mean leucite particle diameter (<4 μm) (Mackert et al., 2001). This type of fine-grained microstructure can be achieved by fine powder milling and controlled heat treatments (Cattell et al., 2006), because leucite crystallization is surface-nucleated (Höland et al., 1995). Several studies indicated that a reduction in leucite crystal size, uniformity of microstructure, and minimal matrix microcracking produced flexural strength increases up to 160 MPa (Sharpe et al., 1994; Cattell et al., 2001). However, flexural strength values of 200-300 MPa have been found in fine-grained (0.1-1 μm) leucite glass-ceramics (Rouf et al., 1978), although the glass opacity and high viscosity limit their processing and use for aesthetic restorations. In the present work, the objectives were to use a more controlled processing and crystallization regimen of a designed glass to produce translucent high-strength (>200 MPa) leucite glass-ceramics with......
fine-grained microstructures. These materials were designed with the objectives of reducing the incidence of restoration fracture, reducing enamel wear (Menzler et al., 1999), and increasing translucency (Beall and Duke, 1969). The hypotheses were that a fine crystal size (< 1 μm) and uniform microstructure in a thermally matched glass were associated with an increased biaxial flexural strength.

MATERIALS & METHODS

Glass/Glass-ceramic Synthesis

The glass batch composition was (mol%): 72.6% SiO₂, 10.7% Al₂O₃, 7.9% K₂O, 2.1% CaO, 0.3% TiO₂, 4.7% Na₂O, 1.1% Li₂O, and 0.5% MgO. The glass batch was heated in an electric kiln (Fredrickson Kiln Co., Alfred, NY, USA) at 10°C/min to 1316°C (7 hours hold), and then the frit was cooled and ground to 125 μm (glass A). Glass A was then wet-ground (distilled water) in an Attritor Mill (Model I-S Lab Attritor, Union Process, Akron, OH, USA) with 5 mm yttria-stabilized zirconia (YTZ) grinding media (Tosoh Inc., Grove City, OH, USA) at 400 rpm. Glass slurry was withdrawn after 15, 30, 45, 60, 90, and 120 minutes of milling. The 120-minute-milled slurry and the glass A materials were then milled according to the regimens shown in Figure 1a, to produce glasses M1A and M2A. Glasses were heat-treated in a furnace (RHF 1600, Carbolite, Hope Valley, UK) from 23°C at a rate of 10°C/min to 650°C (1 hour hold), then ramped to 1200°C (1 hour hold) and air-quenched.

Glass particle size was measured in a Mastersizer/E particle analyzer (Malvern Instruments, Malvern, Worcestershire, UK). Quantitative elemental analysis of the glass powders was carried out following attritor milling, by inductively coupled plasma mass spectrometry (ICP-MS, Elan 9000, Perkin Elmer, Norwalk, CT, USA).

X-ray Diffraction Analysis

X-ray diffraction (XRD) was carried out on the glasses and glass-ceramics by means of an X'Pert Pro X-ray diffractometer (PANalytical, Almelo, The Netherlands). Flat plate 0/0 geometry and Ni-filtered Cu-Kα radiation (λ₁ = 0.1540598 Å and λ₂ = 0.15444260 Å) were used. Data were continuously collected from 5° to 120° (20 range) with a step size of 0.0334° and a step time of 200.03 sec. Calibration was carried out using NIST standard reference material 660a (lanthanum hexaboride). The structural model of tetragonal leucite (ICDD: 00-038-1423) was used for phase identification. Crystal strain calculations were performed with the XRD data and Eq. 1 (Cullity and Stock, 2001):

$$e = \frac{a - a_0}{a_0}, e = \frac{c - c_0}{c_0}$$

where e and ε are the strain of leucite in the a-axis and c-axis, a and c are the mean unit cell dimensions of tetragonal leucite for the tested glass-ceramics, and a₀ and c₀ are the unit cell dimensions of the reference tetragonal leucite (ICDD: 00-038-1423).

Biaxial Flexural Strength Specimen Preparation

The glass-ceramic powders (A, M1A and M2A) were used to fabricate disc specimens (30 per group) by moistening 1.0 g of powder with 0.3 mL of modeling liquid (CH B: 24066, VITA, Bad Söckingen, Germany) and compacting in a cylindrical steel mold with a plunger. Discs were placed in a pre-heated (538°C) porcelain furnace (Multimat MCII, Dentsply, Konstanz, Germany) and sintered at a rate of 38°C/min to 1040°C for 2 min under vacuum. Specimens were next wet-ground to P1000 grade silicon carbide paper. One simulated stain firing in air from 538°C at a rate of 55°C/min to 780°C without hold and one simulated overglaze firing in air from 538°C at a rate of 55°C/min to 860°C with a 0.3 min hold were then applied.

Thirty IPS Empress Esthetic glass-ceramic (Lot: H2624, ETC2, Ivoclar-Vivadent, Schaan, Liechtenstein) specimens were prepared by spraying Perspex discs (14 mm x 2 mm) onto muffle bases and investing, pre-heating, and heat-extending in an Optomax press furnace (Jeneric/Pentron, Wallingford, CT, USA) according to the manufacturer's instructions. The investment was removed by sandblasting with 50 μm glass beads (Bracon Ltd., Etchingham, East Sussex, UK) at 1.5 x 10⁶ Pa pressure. The specimens were wet-ground to P1000 grade silicon carbide paper on the compressive test surface only and fired in a porcelain furnace (Multimat MCII, Dentsply) according to the manufacturer's recommended (simulated) firing cycles (2 stain and 2 overglaze firings).

Biaxial Flexural Strength Testing

The biaxial flexural strength was determined using the ball-oring ring fixture test. Disc specimens (14 x 2 mm) were centrally loaded on a 10 mm diameter knife-edge support, via a 4 mm diameter spherical ball indenter, at a crosshead speed of 1 mm/min. The BFS was calculated by Eq. 2 (Timoshenko and Woinowsky-Krieger, 1959):

$$\sigma_{max} = \frac{P}{h^2} \left[ (1 + \nu) \left[ 0.485 \ln \left( \frac{a}{h} \right) + 0.52 \right] + 0.48 \right]$$

where σ_max was the maximum tensile stress, P was the load measured at fracture, h was the specimen thickness, a was the radius of the knife-edge support, and ν was a Poisson's ratio of 0.25.

Statistical Analysis

Group means were analyzed by one-way ANOVA and Tukey's multiple-comparison test at p < 0.05 (Sigma Stat, version 2.03, SPSS Inc., Chicago, IL, USA). Weibull analysis of the test groups was carried out with WeibullSMITH software (Fulton Findings, Torrance, CA, USA). Weibull m and characteristic strength values were compared for the overlap of their double-sided confidence intervals (95% level) to determine differences.

Secondary Electron Microscopy

Polished and etched (0.1% HF, 60 sec) specimens were gold coated and viewed by scanning electron microscopy (JSM...
Figure 1. Plots showing the: (a) attritor milling regimens for glass A; (b) relationship between milling time and particle size of the attritor-milled glasses A; (c) relationship between the mean leucite crystal size, crystal number, and glass particle size of the experimental glass-ceramics; (d) relationship between the milling time and zirconium, yttrium, and hafnium content in the attritor-milled glasses A; (e) XRD patterns of the attritor-milled glasses; and (f) XRD patterns of the glass-ceramics.
Table 1. The Mean Unit Cell Dimensions and Crystal Strains of the Glass-ceramics

<table>
<thead>
<tr>
<th>Glass-ceramics</th>
<th>Mean a-axis Unit Cell Dimension (SD) [nm]</th>
<th>Mean c-axis Unit Cell Dimension (SD) [nm]</th>
<th>Mean Unit Cell Volume (SD) [nm³]</th>
<th>ε₁</th>
<th>ε₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.31089 (0.00009)</td>
<td>1.37071 (0.00015)</td>
<td>2.35547 (0.0012)</td>
<td>0.33%</td>
<td>-0.35%</td>
</tr>
<tr>
<td>M1A</td>
<td>1.31229 (0.00010)</td>
<td>1.36963 (0.00015)</td>
<td>2.35865 (0.0015)</td>
<td>0.44%</td>
<td>-0.43%</td>
</tr>
<tr>
<td>M2A</td>
<td>1.31172 (0.00009)</td>
<td>1.36916 (0.00013)</td>
<td>2.35579 (0.0011)</td>
<td>0.40%</td>
<td>-0.46%</td>
</tr>
<tr>
<td>IPS Empress Esthetic</td>
<td>1.31069 (0.00006)</td>
<td>1.37170 (0.00009)</td>
<td>2.35645 (0.00032)</td>
<td>0.32%</td>
<td>-0.28%</td>
</tr>
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</table>

ε₁ = crystal strain in the a-axis; ε₂ = crystal strain in the c-axis.

6300F, JEOL Ltd., Tokyo, Japan). Micrographs (x 2200, area = 2210.4 µm²) were used to quantify crystal size, number, and area fraction with a light pen (270SD + INT-40, Trackballs, Camarillo, CA, USA) and image analysis software (Sigma Scan Pro 5.0, Systat Software, Inc., Chicago, IL, USA).

Differential Dilatometry
Glass frit was cut into blocks (16 x 6 x 6 mm³) using a plate saw (Struers Accutom 2, Struers Ltd., Glasgow, Scotland, UK), and glass-ceramic specimens were constructed by either heat extrusion or powder compaction and sintering. The TEC of the specimens were measured by a differential dilatometer (DIL 402PC, Netzsch Instruments, Selb, Germany) at a heating rate of 3°C/min (25 - 1200°C).

RESULTS
Particle Size Analysis Results
The glass particle size (mean Dₐ) vs. milling time is shown in Fig. 1b. A decrease in glass particle size [mean Dₐ (SD)] from 11.37 (0.17) to 3.08 (0.04) µm was identified within the first 60-minute milling period. The particle size of glass M1A was 1.79 (0.05) µm, which was further reduced for M2A to 0.45 (0.01) µm. A correlation (exponential fit) between the glass particle size and mean leucite crystal size (r² = 0.906) and leucite crystal number (r² = 0.985) was found (Figure 1c).

Inductively Coupled Plasma – Mass Spectrometry Results
Quantitative elemental analysis of the attritor-milled glasses with ICP-MS showed a correlation (polynomial fit) between zirconia (r² = 0.99), yttrium (r² = 0.99), and hafnium (r² = 0.99) content and milling time (Figure 1d). Trace amounts of chromium (70 ppm), nickel (20 ppm), and tungsten (22 ppm) were also found in the glass M2A.

Differential Dilatometry Results
Glass M1A showed a TEC value of 8.5 x 10⁻⁴ K⁻¹. The TEC and glass transition temperature (Tg) of the glass-ceramics were: A (19.0 x 10⁻⁴ K⁻¹, 579.1°C), M1A (18.2 x 10⁻⁴ K⁻¹, 589.5°C), and M2A (17.2 x 10⁻⁴ K⁻¹, 589.3°C). A lower TEC value of 16.7 x 10⁻⁴ K⁻¹ and a higher Tg of 616.3°C were found for the IPS Empress Esthetic glass-ceramic.

X-ray Diffraction Results
Experimental glasses were largely amorphous, with some tiny visible crystalline peaks for the 60 min A, 90 min A, 120 min A, and M1A glasses (Figure 1e). These 20 positions matched with the hk1 reflections 112 and 404 for tetragonal leucite. Tetragonal leucite and an amorphous glass phase were identified for all experimental and IPS Empress Esthetic glass-ceramics (Figure 1f). The mean unit cell dimensions and calculated crystal strains are given in Table 1.

Secondary Electron Microscopy Results
Experimental glass-ceramics (Figure 2a, 2b, 2c) showed fine and evenly distributed leucite crystals and minimal matrix microcracking, with a leucite area fraction between 24.9% and 25.4%. The experimental and control glasses show a mean (SD) leucite crystal size and crystal number of: A, 0.99 (0.59) µm², 558; M1A, 0.39 (0.28) µm², 1434; M2A, 0.16 (0.10) µm², 3378; and IPS Empress Esthetic, 1.72 (1.98) µm², 364. The area fraction of Empress glass-ceramic was 31.2%, with microcracking present both within the larger leucite crystals and the glass matrix (Figure 2d).

Biaxial Flexural Strength Results
Glass-ceramic M1A and M2A groups showed significantly higher BFS and characteristic strength (εₙ) values (p < 0.05) compared to those of IPS Empress Esthetic and the glass-ceramic A groups (Table 2). There was no significant difference between the Webull m values for IPS Empress Esthetic and experimental glass-ceramic groups.

DISCUSSION
Attritor milling of the experimental glasses, followed by control sprayed crystallization heat treatments, produced fine-sized 0.16 (10.10) µm² leucite crystals in the same size range as synthesized by sol-gel and hydrothermal techniques (Zhang et al., 2008). The present study allowed for the synthesis and control of a range of glass-ceramics with decreasing leucite crystal size and increasing crystal number, which correlated with the reduction of glass particle size (Figure 1c). Rapid glass particle size reduction was found in the first 60 min of attritor milling (Figure 1b), and major reductions were then achieved only with the use of finer grinding media (McLaughlin, 1999). The resultant fine powder sizes achieved increased heterogeneous nucleation sites.
The increased surface area of the glass powder encouraged a large number of sharp edges and a change in particle shape (Müller et al., 2000), and reduced the inhibiting effects of surface elastic strains (Schmelzer et al., 1993). The dramatic increase in crystalline number from 558 to 3378 after sustained milling supports these assumptions. Glass particle size and heat treatments were previously shown to modify crystallization, with the present nucleation step adopted to increase the number of crystallites (Cattell et al., 2006).

The different milling protocols and longer milling times for the M2A glass led to an increase in zirconium, yttrium, hafnia, and other trace elements, associated with the continuous wear of the YTZ grinding media (Figure 1d). The reduction in mean BFS compared with the M1A material could be due to the local agglomeration of these products or the formation of another species and limits this process. Leucite glass-ceramic powder doped with nano-sized (30-60 nm) zirconia (60 wt%) previously produced a bending strength of 214 MPa (Conrad and Meyer, 2007), in the same range as found for the M2A material. When suitably dispersed, zirconia, yttria (> 3 wt%), and hafnia can act as nucleating agents, influencing the viscosity and crystallization kinetics of fine-scale (40-250 nm) glass-ceramics (Rouf et al., 1978; Zheng et al., 2007; Wandratschek and Pradeau, 2008). Trace elements in the M1A glass, if well-dispersed, could encourage the heterogeneous growth of the leucite crystalline phase (James, 1982). Micro- or nano-immiscibility in these glasses is also likely (Cattell et al., 2005), as is the formation of titanates (Rouf et al., 1978). These phases can induce heterogeneous crystallization of a metastable phase, which at increased temperature breaks down into the stable crystalline phase (Pinekney and Beull, 2008). The experimental glasses had some trace crystalline peaks before crystallization heat treatments (Figure 1e). These fine isostructural sites have the potential to reduce the energy barrier for crystallization and provide low-energy crystallization sites (Zheng et al., 2007).

The mean BFS and $c_1$ of the experimental glass-ceramics were significantly ($p < 0.05$) increased following milling and crystallization heat treatments (Table 2). This increase in
strength was associated with the reduction of leucite crystal size and uniformity of the microstructure. The lack of matrix microcracking at mean leucite crystal sizes of less than 1 μm² also supports previous work (Mackert et al., 2001). The homogeneous and fine-scale crystallization could also influence the local depletion of the glass structure, resulting in more favorable residual glass-crystal interfacial stresses. The glass-ceramic M1A had a-axis and c-axis strains of a similar magnitude (a = 0.44% and c = -0.43%, Table 1), which caused no matrix microcracking and depletion of generated stresses. Changes to the anisotropic stress field and the generation of favorable residual stresses in the glass have been previously linked to strength increases (Denny et al., 1996). Mackert (1988) discussed the presence of microcracks parallel to the c-axis in leucite glass-ceramics, partially decoupling crystallites and reducing the bulk thermal expansion. This was evident for the control group, with a reduced c-axis strain associated with crystal-matrix microcracking and a lower TEC (16.7 x 10⁻⁶ K⁻¹, 100–400°C) and mean BFS. A higher area fraction of the high-expansion tetragonal leucite phase (31.2%) compared with the experimental glass-ceramics (24.9–25.4%) also suggests that strain dissipation may have occurred.

Changes to the lattice parameters for the experimental glass-ceramics with glass particle size reduction may be due to changes in glass diffusivity, mobility (Freiman et al., 1971), and crystallization mechanisms (Tosić et al., 2008). The unit cell dimensions (M1A and M2A, Table 1) are also in the same range (a = 1.212-1.315 nm, c = 1.369-1.374 nm) as reported for solid solutions of tetragonal leucite (Hermansson and Carlsson, 1976). A limited substitution of sodium for potassium is possible, and some geological leucites indicate up to 2.4 sodium atoms per unit cell (16 KAlSi₃O₈ per unit cell) (Deer et al., 2004). The incorporation of lithium and sodium into the leucite crystal lattice can cause reduced TEC and modification to the cubic to tetragonal transformation (Ota et al., 1993). The relationship between the transformation temperature, Tg, and glass properties is important to the maintenance of residual stresses and mechanical properties (Lee et al., 1997).

The present study produced leucite glass-ceramics with higher mean flexural strengths (253.8 MPa) than those reported for current leucite glass-ceramics (120–140 MPa) (Höland et al., 2003), and in the same range (200–300 MPa) as reported for an opaque leucite glass-ceramic (Rout et al., 1978). The original hypothesis can therefore be upheld, because the fine (< 1 μm²) leucite crystal size and uniformity of microstructure in a thermally matched glass produced high mean biaxial flexural strengths. These new fine-grained leucite glass-ceramics also have other advantages in terms of improved translucency, aesthetics, processability, and reduced enamel wear (Metzler et al., 1999), which will be reported in a future study.

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