Residual stresses in a soda-lime–silica glass-ceramic

Valmor R. Mastelaro, Edgar D. Zanotto *

Department of Materials Engineering, Federal University of São Carlos, via Washington Luiz, km 235, Caixa Postal 676, 13.565-905, São Paulo, Brazil

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Abstract

The present study was undertaken to test the validity of existing models for: (i) the residual internal stresses which arise due to thermal and elastic mismatch in duplex systems; and (ii) the critical particle diameter for spontaneous cracking. The specimens studied were bulk nucleated, partially crystallized 17.20Na₂O–32.09CaO–48.12SiO₂–2.59P₂O₅ (mol%) glasses. The residual stress was determined by an X-ray diffraction technique for a particular set of hkl planes. The crystal diameters and volume fractions crystallized were measured by an image analyzer system. The experimental residual stress was in agreement with the calculated value within the measurement errors. On the other hand, the theoretical value of the critical particle diameter, calculated by an energy balance approach, was more than ten times smaller than the experimental value, suggesting that the semi-spherical crack assumed in the model does not hold for our system. A preliminary fitting with a fracture mechanics model was also carried out.

1. Introduction

The mechanical behavior of multi-phase brittle materials may depend heavily on the level of internal micromechanical stresses which arise upon cooling, due to thermal and elastic mismatch between the constituent phases [1]. These stresses have always been of interest from both strengthening and weakening perspectives [2]. Typical examples are glass-ceramics, the microstructures of which comprise one or more crystal phases dispersed in a glassy matrix. In this paper, we review previous research on internal stresses in glass matrix composites and the available models to calculate those stresses. An experimental test of the models using a partially crystallized soda-lime–silica glass is presented for the first time. Additionally, the critical particle diameter for spontaneous cracking is compared with experimental values.

2. Theory

2.1. Residual stresses

In 1957, Eshelby [3] proposed a technique, later complemented by other authors, to calculate the stress field around an anisotropic grain embedded in a matrix. The calculation takes into account the geometry of the inclusion and the (tensorial) properties of the inclusion and of the matrix. Apart from the challenging computations, the main difficulty is that crystal-axis-dependent elastic and thermal prop-
properties are difficult to determine and are seldom available. However, if the inclusion is spherical and isotropic, the radial tension in the matrix, just at the inclusion/matrix boundary, reduces to the equation derived by Selsing [4]:

\[ \sigma_r = P = \Delta \alpha \Delta T / K_e, \]  

(1)

where \( K_e = (1 + \nu_m) / 2E_m + (1 - 2\nu_p) / E_p \), \( E \) and \( \nu \) being the elastic modulus and Poisson ratio, and the subscripts, \( m \) and \( p \), refer to the matrix and particle, respectively. \( \Delta \alpha \) is the thermal expansion mismatch and \( \Delta T \) is the difference between the temperature at which the glass ceases to flow on cooling (\( \approx T_g \)) and the ambient temperature. The circumferential stress, \( \sigma_\theta \), is equal to one-half of \( P \), the hydrostatic pressure on the particle. The stresses decrease with the third power of the distance from the particle/matrix boundary, as illustrated in Fig. 1. At the interface (\( x = R \)), \( \sigma_r = P \).

For a system containing several particles in a matrix, as in real materials, Eq. (1) should still hold if the stress fields around each particle do not overlap. This situation is expected to be valid if the volume percentage of the second phase does not exceed \( \approx 15\% \).

2.2. Critical particle diameter

Residual micromechanical stresses may lead to spontaneous fracture of the matrix, as commonly observed in practice in many materials [5]. At least two models are available to calculate the critical particle diameter, \( D_c \), to induce self-cracking, the energy balance [5] and the fracture mechanics model [6].

2.2.1. The energy balance model

Davidge and Green [5] developed a model that assumes spontaneous cracking of the matrix when the stored elastic energy, \( U_e \), exceeds the energy associated with the creation of two new surfaces, \( U_s \). The elastic energy is the volume integral of the product between the stress and strain fields. Thus, for an isolated particle in a infinite matrix:

\[ U_e = \pi K_e \sigma_r^2 D^2 / 4, \]  

(2)

where \( D \) is the particle diameter and \( \sigma_r \) is the residual stress, given by Eq. (1).

In the derivation of \( U_s \), the authors assume that the fracture surface is a semi-sphere and that the surface energy of the particle, \( \gamma \), is equal to that of the matrix. In this case,

\[ U_s = \pi D^2 \gamma. \]  

(3)

Additionally, it is assumed that the formation of a semi-spherical crack releases only half of the stored deformation energy, \( U_e \), leading to fracture when

\[ U_e / 2 \geq U_s. \]  

(4)

The lower limit of Eq. (4) for the critical diameter, \( D_c \), is

\[ D_c = 8\gamma / K_e \sigma_r^2. \]  

(5)

2.2.2. The fracture mechanics model

The fracture mechanics model, proposed by Ito [6], follows from the methodology suggested by Evans [7]. The fracture surface is assumed to involve the particle, as shown in Fig. 2. This model is much
more detailed than the energy model, and the critical diameter for spontaneous fracture is given by

$$D_c = \left[ 0.3 K_c E_m \sin \omega (2 - \sin \omega) \right]^{-1} \left( K_c / \sigma_t \right)^2,$$

(6)

where $K_c$ is the critical stress intensity factor of the matrix and $\omega$ is the ratio of the semi-spherical crack size and the particle diameter. Itô [6] calculated typical values of that parameter ($\omega \sim 0.3$), using the data of Davidson and Green [5], for two hot-pressed glasses containing 10 vol.% thoria particles.

3. Literature review

Fulrath [8] used model systems produced by vacuum hot compaction to study internal stresses in materials containing oxide glass matrices and one crystalline phase ($\alpha$-Al$_2$O$_3$ or synthetic sapphire). Effects of compaction temperature, time, volume fraction and crystal particle size were presented. His work showed that the development of internal stresses in glass–crystal composites depends on processing time and temperature and appears to be closely related to the interfacial bond formation between the glass and the crystal phases. The higher the internal stresses, the lower the fracture strength of the ceramic bodies for a given particle size. The measured internal strain was dependent on particle size under identical fabrication procedures. This dependence is not consistent with Eq. (1), however; their materials had a high volume fraction of crystals (50%) and, thus, the interaction among the stress fields of the particles could not be neglected.

Davidson and Green [5] measured the strengths of various glasses, having a range of expansion coefficients, containing 10 vol.% thoria spheres, with diameters from 50 to 700 μm. They observed a reduction in strength only for spheres larger than a certain size and noted that the effect due to thermal expansion mismatch is more important than the elastic mismatch. When the expansion coefficient of the spheres was greater than that of the glass, circumferential cracks formed around the spheres, but only when the sphere diameter was greater than a critical value. They also calculated an approximate value for the critical diameter through Eq. (5). The experimental critical particle diameters, $D_c$, were 1.6 to 1.9 times larger than the calculated values. No dependence of the stress magnitudes on particle diameter was found, in accord with Eq. (5).

In his extensive review on “Fracture of Brittle Matrix and Particulate Composites”, Lange [9] made interesting observations about the work of Davidson and Green [5]. According to Lange, Davidson and Green's research was centered on confirming the observation of Binns [2], that cracks only developed around the larger particles, and explaining these results in terms of the total strain energy that develops within and around the particles. He also pointed out that, although the stress magnitudes are independent of particle size, the total stored strain energy depends on the volume of the material under the influence of stress, which, in turn, depends on the particle size. Thus, the larger the particle, the larger the stressed volume, both within the particle and around the particle, and the larger the stored strain energy associated with the particle. Concerning the critical particle size model of Davidson and Green, Lange concluded that, as the calculated values were underestimated, their model can be used only as an approximation of the critical particle size required to form spontaneous cracks. Despite this constraint, their concept indicates that cracks induced by residual thermal stresses can be eliminated by reducing the particle size of the dispersed phase of a given composite.

The strengthening mechanism of brittle matrices has been studied by Borom et al. [10]. They worked with SiO$_2$–Li$_2$O–Al$_2$O$_3$–K$_2$O–B$_2$O$_3$–P$_2$O$_5$ glass-ceramics that had strengths two to three times higher than those of the parent glass. Their samples consisted of 20–95 vol.% of fine grains of a crystalline phase in a glass matrix. They correlated strength with microstructure and attributed the two- to three-fold increase in the strength after heat treatment to the development of a variable field of compressive stress in the glass matrix.

Later, Borom [11] presented a discussion about the various theoretical possibilities for dispersion strengthening. These explanations related strength enhancement in brittle materials either to flaw size limitation by the small interparticle spacing or to increase in the system modulus as a result of the presence of a higher modulus dispersed phase. Based
on the mechanical strength measurements of his previous work [10], Borom concluded that the theoretical explanations mentioned above are inadequate. He confirmed his previous results, saying that the strength improvement in glass-ceramics after crystallization, in excess of that produced by modulus enhancement, results from the creation of compressive stresses in the glass matrix due to the thermo-mechanical mismatch between the crystals and the matrix.

Internal stresses in partially crystallized glasses, based on β-eucryptite and β-spodumene solid solutions, have been measured by Zevin et al. [12] using an X-ray diffraction (XRD) technique. They found that the measured stresses were much smaller than the values calculated by Eq. (1). According to these authors, this discrepancy was due to the formation of a crack network in their glass-ceramics. No information was given concerning the critical particle diameter.

The fracture behavior of glass matrix/glass particle composites has been described by Miyata et al. [13]. They studied two-phase materials consisting of spherical glass particles dispersed in four different soda-lime–silica glass matrices, having thermal expansion coefficients equal to or greater than the expansion coefficient of the glass beads. No microcrazing was observed after cooling for the system with matching thermal expansions of the phases. Microcracks were observed only around particles having a large $\Delta \alpha = (\alpha_{\text{matrix}} - \alpha_{\text{beads}})$ and when the particles were adjacent to each other. The authors used the Davidge and Green model for the critical particle diameter analysis but did not present any results. Only certain considerations about the relationships between the critical particle diameter and the fracture toughness value were presented. They concluded that the use of particle sizes near $D_c$ enables microcrack toughening to be achieved with as small as possible strength reduction.

Levy et al. [14] studied the effect of microstresses on the strength of some two-phase materials. For a glass matrix having quartz crystals varying from 3 to 300 $\mu$m in size, they found that the experimental value of the residual strain decreased as the size of the crystals increased. They explained this decrease by the development of microcracks due to the existence of crystals larger than the critical size. Other than this supposition, they did not present calculations for $D_c$ where, supposedly, the residual stress dropped.

Recently, Khodakovskaya [15] carried out experimental measurements of residual stresses in glass-ceramics and analyzed their relationship to mechanical behavior. This author investigated materials containing 75–95 vol.% of different crystal phases (cordierite, willemite or nepheline), as well as sintered glass-ceramics containing 10–50% of crystal phases (quartz, corundum, rutile, etc.). The values of residual microstresses in the crystals were essentially smaller than would be expected on the basis of Eq. (1). This author suggested that microstress relaxation takes place through microcrack development because the strength of his glass-ceramics fell sharply with increasing stress relaxation.

As demonstrated in this brief summary of previous research, controversy remains concerning internal stresses and critical particle size. In Refs. [8] and [12], the experimental values of internal stresses were dependent on the particle size, but in Ref. [5] they were not. In addition, the experimental values for the internal stresses were smaller than the calculated ones (using the Selings formula) in Refs. [10] and [13]. Concerning the critical particle diameter, $D_c$, only Davidge and Green [5] performed calculations which resulted in underestimated values for $D_c$. Therefore, the aim of the present study is to test the validity of existing models for the residual internal stresses and critical particle diameter in a partially crystallized glass, under conditions in which the models are expected to apply for the first time.

4. Materials and methods

A 17.20Na₂O–32.09CaO–48.12SiO₂–2.59P₂O₅ (mol%) glass was prepared by melting a homogeneous mixture of reagent-grade Na₂CO₃, CaCO₃, SiO₂ and P₂O₅ at 1400°C for 3 h in a Pt crucible. This composition was chosen because it is the basis of a bioactive glass, developed by Professor L.L. Hench in the 1970s, and shows volume nucleation allowing us to produce a series of specimens with controlled microstructures. The melt was then cast between two cold steel plates, with an estimated cooling rate of 400°C/min. To obtain partially crys-
tallized glasses (glass-ceramics), some specimens were submitted to an isothermal treatment at 840°C for periods varying between 28 and 39 min (28 min: sample A; 33 min: sample B; 36 min: sample C and 39 min: sample D). A fully crystallized sample, used for thermal and elastic constant measurements, was obtained by nucleating one specimen at 571°C for 200 h and then heating it at 670°C for 25 min to allow the nucleated crystals to grow (sample E).

4.1. Microstructures and physical properties

The maximum crystal diameters and volume fractions of the crystallized phase, $V_p$, were measured using an image analyzer system. The results are presented in Table 1. The typical errors in these measurements were about 10%.

Fig. 3 shows the thermal expansion data for the glass and totally crystallized samples obtained by thermal analysis (STA 409 Netzch) equipment. To obtain the difference of thermal expansion coefficients, $\Delta \alpha$, of both samples, the curves presented in Fig. 3 were fit in the following way: for the glass curve, a third order polynomial fitting was used in the full temperature range (260–570°C) while, for the glass-ceramic curve, a third order polynomial fitting was used between 260°C and 470°C and a linear polynomial fitting between 470°C and 570°C. As $\Delta \alpha$ is not constant in the temperature range of this work, it was necessary to integrate, as described below:

$$\Delta \alpha \Delta T = \int_{T_1}^{T_2} (\frac{d l_m}{L_m} - \frac{d l_p}{L_p}) \, d T + \int_{T_1}^{T_2} (\frac{d l_m}{L_m} - \frac{d l_p}{L_p}) \, d T$$

where $\Delta P_1 = P_1 - P_1$ and $\Delta P_2 = P_2 - P_2$ are the polynomial functions ($m =$ glass matrix and $p =$ glass-ceramic). From fitting the curves presented in Fig. 3, the polynomial functions found are

$$P_{1m} = 4.16 e^{-5} T - 6.02 e^{-8} T^2 + 5.19 e^{-11} T^3,$$

$$P_{1p} = 7.39 e^{-4} T - 1.77 e^{-7} T^2 + 2.02 e^{-10} T^3,$$

and

$$P_{2m} = 4.16 e^{-5} T - 6.02 e^{-8} T^2 + 5.19 e^{-11} T^3,$$

$$P_{2p} = 2.49 e^{-5} T,$$

where $e^{-n} = 10^{-n}$.

The modulus of elasticity and the Poisson ratios of the glass and fully crystallized glass-ceramic were obtained using a pulse-echo technique. Each specimen was measured three times. Experimental values are presented in Table 2.

4.2. Residual internal stresses

The diffraction method for measuring strains and stresses in crystalline solids has been in use for some time and is well established [8,16,17]. The method relies on using the crystal lattice as an absolute strain gauge [17]. XRD is based on Bragg’s Law (Eq. (7)) which relates the interplanar spacing of atomic

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<td>Sample</td>
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<tr>
<td>A</td>
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<table>
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<td>Physical properties of glass and fully crystallized glass-ceramic</td>
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<td>---------</td>
</tr>
<tr>
<td>Property</td>
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<tr>
<td>$E$ (GPa):</td>
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<td>$\nu$:</td>
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planes, \( d \), to the angle peak position, \( \theta \), of a diffracted beam of monochromatic X-rays [18]:

\[
n \lambda = 2d \sin \theta .
\]  

(7)

The residual strain determined by XRD is based on the displacement of the peaks in the XRD pattern, i.e., on the relative change in the interplanar distance of the crystalline phase under study. Differentiating Bragg's Equation, the following expression is obtained [18]:

\[
\Delta d_{hkl}/d_{hkl} = -0.5 \Delta(2\theta) \cot \theta ,
\]  

(8)

where \( \Delta(2\theta) \) is the displacement of the diffraction peak caused by the strain in the crystal, \( 2\theta \) is the angle between the direction of the primary beam and reflecting plane and \( d_{hkl} \) is the interplanar distance related to the hkl reflecting plane. Comparing this interplanar spacing with that of a stress-free specimen (usually a finely ground, stress relieved, powder) gives the strain normal to the hkl planes used for the measurements. The relative deformation can be assessed from the displacement of the diffracted peaks as follows:

\[
e_{hkl} = \Delta d_{hkl}/d_{hkl},
\]  

(9)

where \( e_{exp} \) is the relative deformation of the crystal normal to the plane, hkl. The experimental residual internal stress can now be determined by Hooke's Law:

\[
\sigma_{exp} = e_{hkl}E ,
\]  

(10)

where \( e_{hkl} \) is the measured deformation and \( E \) is the modulus of elasticity of the crystals, here assumed to be similar to the average value for all [hkl] directions.

X-ray measurements were made using a conventional diffractometer Zeiss model HGZ64C under the following conditions: Cu K\( \alpha \) radiation, fine focus X-ray tube operated at 25 mA and 40 kV and a scintillation counter as detector. Data were collected on the glass-ceramic samples over the range of 48.0–49.0° (two theta) using a 0.02° two theta step interval and a step time sufficient to give a good signal to noise ratio. This angular range corresponds to the interplanar spacing, \( d_{hkl} = 404 \). Only results for the (404) interplanar spacing are quoted due to experimental limitations. In this work, we dealt with quite small volume percentages of crystals (5–12%) and, thus, the diffracted intensities were quite weak. Additionally, we wanted diffraction peaks located at the highest angles to improve the accuracy of the \( 2\theta \) measurements. Under these constraints, the only feasible measurements for our system were at \( 2\theta = 48.8° \), which corresponds to (404). To obtain the interplanar spacing of the stress-free specimen, XRD measurements of the 'fully' crystallized specimen (sample E) were performed in a finely ground powder (free of residual stresses). We assumed that the small percentage of residual glass, that probably remains in the so-called 'fully' crystallized sample, does not affect significantly the results because the large majority of particles, or at least a large number of faces of the powder grains produced by grinding, should not be surrounded by a glass layer. A correction of the diffraction peak position was made by measuring the location of the diffraction peaks of pure silicon powder incorporated into the sample as an internal standard. The results are presented in Table 3 with the internal residual strain and stresses calculated using Eqs. (8) and (10).

If one takes into account the error in the \( 2\theta \) angle measurements (\( \pm 0.02 \)), an average value of 48.72 \( \pm 0.02 \) is found, which corresponds to a mean value of 154 MPa for the experimental residual stress. The estimated error in that value is about 30%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( D_{max} ) (( \mu m ))</th>
<th>( 2\theta ) (( \pm 0.02° ))</th>
<th>( e_{exp} ) ( \times 10^{-3} )</th>
<th>( \sigma_{exp} ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>650</td>
<td>48.74</td>
<td>1.07</td>
<td>102</td>
</tr>
<tr>
<td>B</td>
<td>765</td>
<td>48.70</td>
<td>2.14</td>
<td>205</td>
</tr>
<tr>
<td>C</td>
<td>900</td>
<td>48.74</td>
<td>1.07</td>
<td>102</td>
</tr>
<tr>
<td>D</td>
<td>985</td>
<td>48.72</td>
<td>1.61</td>
<td>154</td>
</tr>
<tr>
<td>E</td>
<td>–</td>
<td>48.80</td>
<td>0.00</td>
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Table 3: Measured X-ray diffraction values and experimental internal strain and stress using Eqs. (8) and (10).

5. Calculation of residual internal stresses, \( \sigma_r \), and critical particle diameter, \( D_c \)

The stress at the particle/matrix interface can be calculated using the Selsing formula, Eq. (1). In this case, we consider a temperature range in which the matrix plasticity is negligible (taken to be from \( T_g \) to
260°C because the thermal expansion mismatch is negligible below 260°C). Using experimental values of the physical parameters $\nu_m = 0.27$, $\nu_p = 0.24$, $E_m = 8.1 \times 10^4$ MPa and $E_p = 9.6 \times 10^4$ MPa in Eq. (1), we found that $\sigma_r = 160$ MPa, in excellent agreement with the average experimental value (154 MPa). This agreement confirmed 'a posteriori' the assumption that the small amount of residual glass in the 'fully' crystallized specimen did not affect the measurements.

The critical particle diameter, $D_c$, can be calculated using the two models described in Section 1: the energy balance model and the fracture mechanics model.

In the energy balance model, the critical diameter can be obtained by Eq. (5). Using the published value of the surface energy of the glass, $\gamma = 3.47$ J/m$^2$, the measured value of the elastic constant, $K_e = 1.327 \times 10^{-5}$ MPa$^{-1}$, and the experimental value of the residual stress, $\sigma_r = 154$ MPa, one finds $D_c = 88 \mu$m, which is much smaller than the crystal sizes, $D_{max}$, shown in Table 1, i.e., no cracking was optically observed for crystals up to 985 $\mu$m. Indeed, a residual stress of about 154 MPa exists in these specimens; hence, no cracking developed.

Since our data are fully consistent, as shown by the previous calculations for $\sigma_r$, the most probable explanation for this large discrepancy is that the crack shape and size (semi-sphere) assumed in the derivation of the energy model [5] does not hold for our glass-ceramic. Another possibility is that an effective (unknown) surface energy for cracking the glass/crystal boundary should be used in the calculations instead of the glass fracture energy, $\gamma$.

In the fracture mechanics model, the critical particle diameter for spontaneous fracture is given by Eq. (6). Due to the fact that $D_c$ depends on $\omega$ (an unknown parameter, a priori), we cannot estimate $D_c$. Additionally, even with $D_{max} = 985 \mu$m (the largest crystal attainable with the constraint of keeping a low volume fraction crystallized), we did not observe any crack in the specimens. However, using known values of $K_c$, $\sigma_r$, $K_e$ and $E_m$ for our sample, we can plot $D_c$ versus $\omega$ and, thus, observe which $\omega$ value corresponds to 985 $\mu$m. Fig. 4 shows the log $D_c$ versus $\omega$ plot for $\omega$ varying from 0.01 to 1.00. Thus, we note that $\omega$ should be smaller than 0.025, for log 980 $\approx$ 3.0. This is clearly an upper bound and is much smaller than the value obtained by Ito [6] for Davidge and Green's hot-pressed composites data ($\omega \sim 0.3$). Thus, if $\omega$ is strongly dependent on the material used, the fracture mechanics model has no predictive power. To generalize the findings of this article, we are presently testing the energy model, as well as the values of $\omega$ for other glass-ceramics in our laboratories.

6. Conclusions

Partially crystallized 17.20Na$_2$O–32.09CaO–48.12SiO$_2$–2.59P$_2$O$_5$ glasses were studied. The experimental residual stress around the crystals, determined by an XRD technique, was in agreement with the calculated value and did not depend on particle diameter, as predicted by theory. On the other hand, the theoretical value of the critical particle diameter for spontaneous cracking, calculated by an energy balance approach, was more than 10 times smaller than the experimental value. A possible explanation for this discrepancy is that semi-spherical crack assumed in the energy model does not hold for our glass-ceramic. Another possibility is that the effective surface energy for cracking the glass/crystal boundary is substantially larger than the glass fracture energy. The mathematical fit to a fracture mechanics model obtained for our glass-ceramic did not match a previous fit obtained with a hot-pressed glass matrix composite. Thus, the fracture mechanics model also appears to fail to predict correctly the critical diameter for spontaneous fracture. In order to
generalize (or not) the present conclusions, these calculations are now being extended to other glass-ceramic systems.

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