RESIDUAL STRESSES IN PARTIALLY CRYSTALLIZED GLASSES

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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. Partially crystallized $1Na_2O$ -2CaO- $3SiO_2$- $6\%P_2O_5$ glasses were studied. The experimental residual stress was in excellent agreement with the calculated value, however, the critical particle diameter, estimated by an energy balance approach, was more than ten times smaller than the experimental value.

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. These stresses have always been of interest from both the strengthening and the weakening perspectives. In this paper, we test the available models to calculate residual stresses as well as the critical crystal diameter for spontaneous cracking, using a partially crystallized soda-lime-silica glass.

2. THEORY

2.1. **Residual Stresses**

In 1957, Elshelby [1] 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 the matrix. Apart from the challenging computations, the main

properties are tricky to determine and are seldom available. However, if the inclusion is spherical and isotropic, then the radial stress in the matrix, just at the inclusion/matrix boundary, reduces to the equation derived by Selsing [2]:

$$\sigma_r = \Delta\alpha \, \Delta T \, / \, K_o \qquad (1)$$

where $K_o=(1+\upsilon_m)/2E_m + (1-2\upsilon_p)/E_p$; E and υ are 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 ΔT is the difference between the temperature where the glass ceases to flow ($\sim T_g$) and the ambient temperature. The tangential stress σ_θ is half of σ_r. These stresses decrease with the third power of the distance from the particle/matrix boundary, and rapidly vanish.

For a system containing several particles in a matrix, as in real materials, Equation (1) should still hold if the stress field around each particle do not overlap. This situation is expected to be valid if the volume fraction of the second phase do not exceed 0.10- 0.15.

The residual micromechanical stresses may lead to spontaneous fracture of the matrix, as commonly observed in practice. In this article we also test the energy balance model to calculate the critical particle diameter (D_c) to induce self-cracking.

2.2. The energy balance model:

Davidge and Green [3] developed a model that assumes spontaneous cracking of the matrix when the stored elastic energy U_s exceeds the energy associated with the creation of two new surfaces, U_s. For an isolated particle in a infinite matrix, the elastic energy is the volume integral of the product between the stress and strain fields. The final result for the critical diameter, D_c, is:

$$D_c = 8 \, \gamma \, / \, K_o \, \sigma_r^2 \qquad (2)$$

where the surface energy of particle and matrix, γ, are assumed to be equal.

3. LITERATURE REVIEW

Fulrath [4] has used model systems produced by vacuum hot compaction to study internal stresses in materials containing oxide glass matrices and one crystalline phase (α-Al_2O_3 or synthetic sapphire). The measured internal strain was dependent on particle size under identical fabrication procedures. This is not consistent with Eq.(1), however, their materials had a high volume fraction of crystals.

Davidge and Green [3] have measured the strengths of various glasses, with a range of expansion coefficients, containing 10 vol% thoria spheres, with diameters from 50 to 700 μm. The experimental critical particle diameters D_c were 1.6-1.9 times larger than the calculated values. In that study no dependence of the stress magnitudes with the particle diameter was found, in accord with Eq.(1).

Internal stresses in partially crystallized glasses, based on β-Eucrypite and β-Spodumene solid solutions, have been measured by Zevin et al. [5] using an X-Ray Diffraction technique. They found that the experimental stresses were much smaller than the values predicted by Eq.(1). According to the 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 have been characterized by Miyata et. al. [6]. They studied two-phase glass specimens consisting of spherical glass particles dispersed in four different soda-lime-silica glass matrices having thermal expansion coefficients equal or greater than those of the glass beads. Microcracks were only observed when the particles were highly adjacent to each other. No calculations were presented.

Levi et al. [7] have 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 μm in size, they found that the experimental value of the residual strain decreased as the size of the crystals increased. This decrease was thought to be due to microcracks caused by crystals larger than the critical size.

Recently, Khodakovskaya [8] carried out experimental measurements of residual stresses in glass-ceramics and analyzed their relationship to the mechanical behavior. He investigated materials containing 75-95 vol% of different crystals (cordierite, willemite, nepheline) as well as sintered glass-ceramics containing 10-50 vol% of crystals (quartz, corundum and rutile). The values of residual microstrains in the crystals were essentially smaller than would be expected on the basis of Eq. (1). The author suggested that microstress relaxation are due to microcracks.

As demonstrated in this brief summary of previous research, much controversy remains concerning internal stresses and critical particle size. 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, in conditions where the theoretical models are expected to apply.

4- EXPERIMENTAL

A 1.07 Na_2O- 2CaO- 3SiO_2- 6% P_2O_5 glass was prepared by melting a homogeneous mixture of reagent-grade Na_2CO_3, $CaCO_3$, SiO_2 and P_2O_5 at 1400°C for 3h in a Pt crucible and then casting the melt between two steel plates. The samples were submitted to an isothermal treatment at 840°C for periods varying between 28 min and 39 min. To obtain a totally crystallized sample, one specimen (B) was nucleated at 571°C for 200 hours and then heated at 670°C for 25 min to allow the nucleated crystals to grow.

The maximum crystal diameter and the volume fraction of crystallized phase (V_P) were measured using an image analyzer system. V_P was between 0.05 and 0.12 for all specimens studied. The thermal expansion curves for the glass and totally crystallized samples, obtained by a Simultaneous Thermal Analysis (STA 409 Netzch) equipment, were fit by polynomial expressions and integrated to obtain the difference in thermal expansion coefficients ($\Delta\alpha$). The Young modulus and Poisson ratios for the glass and totally crystallized sample were obtained using the Pulse-Echo technique.

The residual strain measurement by the X-Ray diffraction method is based on the displacement of the diffraction peaks, i.e, based on the relative change of a interplanar distance of the crystal. Differentiating Bragg's Law, one obtains the following equation [10]:

$$\Delta d_{hkl}/d_{hkl} = - \Delta(2\theta).\cot(2\theta) \qquad (3)$$

where $\Delta(2\theta)$ is the displacement of the diffraction peak caused by the strain of the crystal, 2θ is the diffraction angle and d_{hkl} is the interplanar distance. Comparing this interplanar spacing with that of a stress-free specimen (a finely ground, stress relieved, powder) gives the strain normal to the hkl planes used for the measurements. The relative deformation of the crystal normal to the plane hkl, $\varepsilon_{hkl} = \Delta d/d$ is given by Eq.(3). Then, the residual internal stresses may be determined by Hooke's Law:

$$\sigma_r = \varepsilon_{hkl} . E_c \qquad (4)$$

where E_c is the modulus of elasticity of the crystals in the hkl direction, here assumed to be similar to the average value for all directions.

X-Ray measurements were made using a conventional diffractometer Zeiss model MGZ96. Data were collected over the range 48.0° to 49.0° (two theta) using a 0.02° 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.

5. RESULTS and CONCLUSIONS

The results are presented in Table I with the internal residual strain and stresses calculated using Eqs. (3-4).

Table I Experimental diffraction angles, strain and stress.

Sample	D_{max} (μm)	2θ (± 0.02°)	ε_{exp} (x10^{-3})	σ_r (MPa)
A	650	48.74	1.29	123
B	766	48.70	2.16	207
C	900	48.74	1.29	123
D	985	48.72	1.73	166
E	---	48.80	0.00	000

Some considerations can be made regarding the results presented in table I. If one takes into account the error in the two theta angle measurements (± 0.02), an average value of 48.72 ± 0.02 is found, which corresponds to a mean value 166 MPa for the experimental residual stress.

The critical particle diameter D_c and σ_r can be calculated using the the energy balance model with γ= 3.47 J/m^2, $K_\bullet$= 1.327×10^{-5} MPa^{-1} , E_p= 9.6×10^4 MPa and E_m= 8.1×10^4 MPa, which gives: σ_r =160 MPa (in agreement with the experimental value) and D_c= 80 μm, which is much smaller than the crystal sizes (D_{max}) shown in table I.

Summary

Partially crystallized $1Na_2O$-$2CaO$-$3SiO_2$-6% P_2O_5 glasses were studied. The experimental residual stress was in excellent agreement with the calculated value. On the other hand, the theoretical value of the critical particle diameter, calculated by an energy balance approach, was more than 10 times smaller than the experimental value.

6. REFERENCES

[1] Eshelby, J.D.-Proc. Roy. Soc. London, Ser.A,241(1957)376.

[2] Selsing, J.- J. Am. Ceram. Soc.,44[8](1961)419.

[3] Davidge, R.W and Green, T.J.-J. Mat.Sci.,3[6](1968)629-34.

[4] R. M. Fulrath, Journal of The American Ceramic Society, 42 [7] (1959) 423.

[5] L.A. Zevin, E.A. Levi and Z.G. Bessmertnaya, Neog. Mat., 13 (1977) 1880.

[6] N. Miyata, K. Tanigawa and H. Jinno , in " Fracture Mechanics of Ceramics" vol. 5 ed. by R.C. Bradt, P.P.H. Hasselman and F. Lange (Plenum, New York, 1983) 609.

[7] E.A. Levy, R. Ya. Khoadkovskaya and L.V. Rudenko, Neorg. Mat. vol. 29(3) (1989) 433.

[8] R. Ya. Khoadkovskaya, Bol. Soc. Esp. Ceram. Vid. 31-C vol.5 (1992) 189.

[9] B.D. Cullity, Elements of X-ray Diffraction, 2 ed.; (Addison-Wesley, Reading M.A.(1978) 292.