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Possible Transformation-toughening Mechanism in Glass–C_2S Particulate Composites

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Abstract

The toughness of glass matrix composites containing different amounts of β-C_2S has been measured by an indentation method in order to investigate the strengthening effectiveness for glass of this polymorph of dicalcium silicate. The experimental data confirm this strengthening. Moreover an analysis of the possible toughening mechanisms responsible for the increase of K_{IC} in the composites has been reported. Mechanisms different from transformation toughening may be considered improbable.

Die Zähigkeit von Verbundwerkstoffen aus einer Glasmatrix mit verschiedenen Gehalten von β-C_2S wurde durch die Härteeindruckmethode gemessen um die zähigkeitssteigernde Wirkung dieses Dicalciumsilikat-Polymorphs in Verbindung mit einer Glasmatrix abzuschätzen. Die experimentellen Ergebnisse bestätigen diese Hypothese. Darüber hinaus wird ein möglicher Verstärkungsmechanismus, der für die K_{IC}-Erhöhung des Verbundwerkstoffs verantwortlich ist, beschrieben. Von der Umwandlungsverstärkung abweichende Mechanismen erscheinen unwahrscheinlich.

On a mesuré la ténacité de composites à matrice vitreuse contenant différentes teneurs en β-C_2S par la méthode d'indentation en vue d'étudier l'efficacité du renforcement du verre par cette variété de silicate de dicalcium. Les résultats expérimentaux confirment cette hypothèse. On discute également ici du mécanisme possible par lequel s'effectue l'amélioration du K_{IC} dans ces composites. L'intervention de mécanismes autres que le renforcement par transformation est considéré comme improbable.

1 Introduction

Transformation toughening is one of the research subjects in ceramics which have been studied extensively in recent years. In this field the research was almost completely devoted to the controlled application of the tetragonal/monoclinic transformation in zirconia to toughen a ceramic matrix.

The matrices may be classified into two types. The first type deals with the system where the chemical composition of both the matrix and dispersed phase is similar. This includes magnesia–PSZ (partially stabilized zirconia), yttria–PSZ and calcia–PSZ. In these materials tetragonal particles are coherently precipitated within the cubic-stabilized matrix. In the second type of matrix materials, the composition of the matrix is different from that of dispersed ZrO_2 phase: the metastable zirconia particles are predominantly incoherently dispersed within the matrix.

Although a considerable improvement in the fracture toughness has also been recorded in different second type matrices (Si_3N_4, mullite, Al_2O_3, etc.), in some materials, like glass and epoxy resins, transformation toughening has not been observed. Very recently Low[1] accounted for such results in terms of the yield strength of the matrix being higher than the critical value of the tetragonal zirconia transformation stress.

Several new potential alternative transformation tougheners to zirconia have been identified on the basis of crystallographic considerations and experimental observations.[2] One of the most promising is dicalcium silicate (abbreviated C_2S). As is well known, dicalcium silicate is one of the four major components of Portland cement, the other constituents being tricalcium silicate (C_2S), tricalcium

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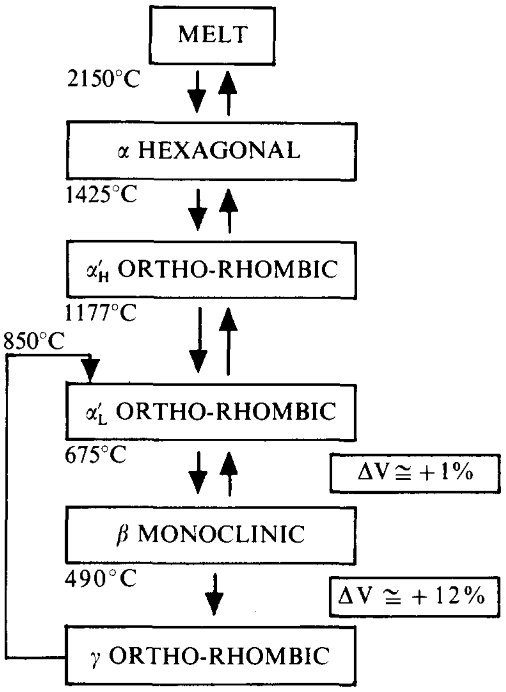

Fig. 1. Schematic stability diagram of C_2S polymorphs.

aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) type phases.

The crystallography and polymorphism of pure C_2S have been extensively studied and reviewed[3-5] and are summarized in Fig. 1. The high-temperature α'-phase is stable between 670°C and 1425°C. The β-phase, which probably has no region of thermodynamic stability at atmospheric pressure, is nevertheless the polymorph into which the α'-phase transforms on cooling to ~670°C and is the metastable low-temperature polymorph. Like unstabilized ZrO_2, C_2S undergoes a large molar volume increase during β-to-γ transformation, which causes fragmentation of the solid body.

This dilatation on cooling, being about 2·26 times greater than that of the martensitic zirconia transformation, has suggested the possibility of a toughening effect in suitable systems incorporating unstabilized β-C_2S. Recently, C_2S particles have been successfully mixed with a calcium zirconate phase to form a composite ceramic.[6] The aim of this work is to try to toughen glass by means of C_2S $\beta \rightarrow \gamma$ martensitic transformation in composites obtained by sintering the two mixed powders.

2 Experimental Procedure

In order to obtain β-C_2S powders, a batch was prepared starting from AR $CaCO_3$ and ignited silica gel (99·99% SiO_2) and adding to the stoichiometric ratio CaO/SiO_2 a little amount of CaO (0·5 wt%).[7] The reagents, after a mechanical mixing, were heated up to 1180°C for 3 h in a platinum crucible and finally cooled and ground to ~325 mesh. Glass powder was prepared by grinding in a ball mill small pieces of commercial soda-lime glass until all the material passed through a ASTM No 200 sieve (74 μm).

The two powders were blended to form mixtures containing nominally 0, 10, 15 and 20% vol. C_2S. The powder mixtures were poured into inox steel dies lined with mica paper, then hot pressed in air. Every mixture was prepressed (4 MPa) at room temperature; the pressure was released and the mold was heated to 530°C, at which time the pressure (6 MPa) was reapplied. The temperature was then increased to 720°C and held for 10 min after ram travel due to compaction ceased. Pressure was released after cooling to 650°C. The composites were annealed at 530°C for 1 h, then cooled slowly to room temperature. The cylindrical pressed blocks each had a diameter of 60 mm and a height of 10 mm. The maximum hot-pressing temperature has been chosen by DTA pattern of the blended powders in order to avoid glass crystallization (Fig. 2).

The bulk density and total porosity were determined by Archimedes' method using ethanol as infiltrating liquid and the phase composition was determined by X-ray diffraction (XRD). On polished-surface samples fracture toughness was determined by the indentation method. Indentation tests were performed using a Vickers diamond pyramid at indenter loads of 20, 30 and 50 N for 0% C_2S glass reference samples and 150 and 300 N for the other ones in order to have appreciable crack lengths. Indent half-diagonal (*a*) and radial cracks extending from the corners (*c*) were measured by optical microscopy about 1 min after removing the load. The crack size increased linearly on a

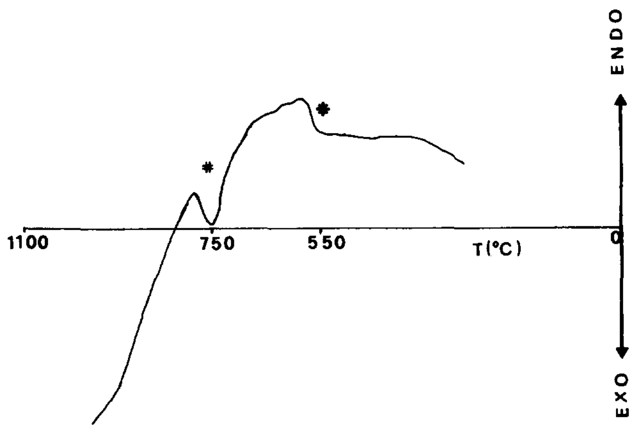

Fig. 2. DTA curve of C_2S and glass powdered mixture. The glass transition (*) and the devitrification (#) temperatures of the glass are reported.

logarithmic scale with increasing load, following substantially the relation

$$P/c^{3/2} = \text{const.} \qquad (1)$$

Evans[8] showed the fracture toughness (K_{IC}) may be expressed for materials with a ratio of $c/a \geq 2{\cdot}5$, as in this case, by

$$K_{IC} = H\sqrt{a}(E/H)^{0{\cdot}4} . 0{\cdot}0667\ (a/c)^{1{\cdot}5} \qquad (2)$$

where H is the hardness and E the Young's modulus. This latter parameter has been measured by the Knoop indentation method according to Marshall *et al.*[9] with indentation loads of 100 and 150 N.

3 Results and Discussion

The CaO doping used here in stabilizing the β-polymorph of C_2S was chosen after preliminary tests made with different dopants such as K_2O, Na_2O and Cr_2O_3 in order to obtain as great a quantity as possible of the β-polymorph. In the powder used here, the β-polymorph is the main constituent; in fact a XRD quantitative analysis made by dilution method on the sample gave a concentration of about 65 mol%.[10] The XRD analysis of the composite samples made immediately after the hot pressing and one month later substantially confirmed this determination.

In Table 1 the characteristics of these composites are shown. The high value of total porosity of sample with 20% volumetric content of C_2S well compares with the decrease of bulk density in calcium zirconate/dicalcium silicate composites with increasing C_2S content as shown by Kriven *et al.*[11] The hardness values are shown in Table 2 together with Young's modulus values. Theoretical E values of the different samples, calculated assuming a linear relationship between E(glass) = 70 GPa and $E(C_2S)$ = 102 GPa[12] are also reported. Toughness values are given in Table 3 showing the same trend as in calcium zirconate/dicalcium silicate composites studied by Moya *et al.*[6]

Taking into account the thermal expansion mismatch—$\alpha_m = 98 \times 10^{-7}$ °C^{-1}, $\alpha_p = 88 \times 10^{-7}$ °C^{-1} (γ-C_2S) and $\alpha_p = 196 \times 10^{-7}$ (β-C_2S)[13]—and the elastic mismatch (E_m = 70 GPa, E_p = 102 GPa) between glass and C_2S that can induce a localized stress field around and within these particles on cooling during fabrication, a line-tension effect may be proposed as the toughening mechanism. In the present case, $\alpha_p > \alpha_m$, therefore the β-C_2S particles are subjected to a tensile stress and the glass matrix to radial tensile and tangential compressive stresses. As the favoured orientation of the crack path should be that which minimizes the total system energy, the fracture path may be influenced by the fracture surface energy Γ_m and Γ_p. When $\alpha_p > \alpha_m$ and $\Gamma_p > \Gamma_m$, the crack is favored to circumvent the particles.

Table 1. Physical properties of the different composites used

C_2S content (vol.%)	*Bulk density (g/cm^3)*	*Total porosity (%)*
0	2·44	2·3
10	2·45	4·6
15	2·55	1·4
20	2·41	8·0

Table 2. Hardness and Young's modulus values of the different composites[a]

C_2S content (vol.%)	*H (GPa)*	*E experimental (GPa)*	*E theoretical (GPa)*
0	5·40 ± 0·05	64 ± 3	70
10	5·55 ± 0·05	64 ± 5	73
15	4·45 ± 0·10	69 ± 5	75
20	3·30 ± 0·10	50 ± 7	76

[a] For comparison Young's modulus values calculated by the mixture rule are also reported.

Table 3. Experimental toughness values compared with theoretical values calculated according to the Lange–Evans model

C_2S content (vol.%)	*K_{IC} (MPa$\sqrt{m}$) experimental*	*K_{IC} (MPa$\sqrt{m}$)*
0	0·70 ± 0·05	—
10	1·79 ± 0·07	1·00
15	2·33 ± 0·10	1·06
20	1·61 ± 0·07	1·12

Moreover, when an external load is applied, localized stress concentrations are also generated around and within particles due to an elastic-constants mismatch between matrix and particles, and they can also alter the orientation of a propagating crack. When $E_p > E_m$, as in this case, the crack will circumvent the particle and therefore the C_2S particles would be considered impenetrable. An increase is then expected in the fracture surface energy, that is related to toughness, with increasing second-phase particles, justifiable with the Lange–Evans theory.[14,15] Lange[14] found that the fracture surface energy is a linear function of the reciprocal of the mean free path between dispersed particles

$$\Gamma = \Gamma_m + \Pi/\lambda \qquad (13)$$

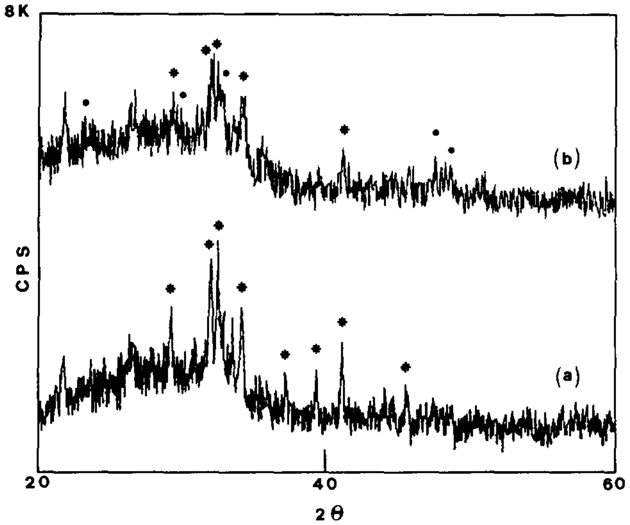

Fig. 3. XRD spectra of glass composite containing 20% of C_2S as made (a) and after prolonged grinding (b). The star symbols refer to β-C_2S and dots to γ-phase.

where Π is the line tension of the crack front and λ the particle spacing $= 2D(1-\Phi)/3\Phi$ where D is the particle size and Φ the volume fraction of the dispersed phase. By means of the formulation for a plane strain condition

$$\Gamma = (1-\nu^2)K_{IC}^2/2E \qquad (4)$$

it is possible to calculate the toughness value for the composites with different C_2S volumetric percentages (see Table 3).

These results clearly indicate the ineffectiveness of this model to explain the experimental data. Therefore a martensitic C_2S transformation may be believed to be responsible for the toughening of the glass matrices. In Fig. 3 two XRD patterns are reported: spectrum (a) refers to 20% C_2S composite as made and spectrum (b) to the same sample after prolonged grinding. The peaks attributable to β-phase are evident in the first spectrum, but they are less pronounced in the second where also some shoulders referred to γ-C_2S appear, confirming the last hypothesis.

4 Conclusions

A noticeable increase in toughness is shown in glass matrix composites reinforced with β-C_2S particles in comparison with glass reference samples. Particularly the 15% C_2S composite increases threefold the glass K_{IC}. It has been demonstrated by means of the Lange–Evans theory that non-transforming particles of C_2S toughen the glass matrix much less than the experimental data show. Moreover the appearance of γ-C_2S peaks and the contemporaneous reduction of β-C_2S reflections in the XRD pattern of a 20% C_2S composite after prolonged milling suggest that the experimental K_{IC} values may be better explained by a transformation-toughening mechanism.

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