

Preparation and characterization of a glass matrix composite containing aluminium titanate particles with improved thermal shock resistance

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Improving the thermal shock resistance of sintered glasses is an important task to broaden their technical and structural applications. In this study, the incorporation of second phase particles with low Young's modulus (E) into glass matrices to form composite materials is shown to be a convenient approach to increase their thermal shock resistance. Novel aluminosilicate glass matrix composites containing aluminium titanate (Al_2TiO_5) particles were fabricated by powder technology and pressureless sintering. By incorporating up to 30 vol.% of aluminium titanate particles a nearly fourfold increase of the thermal shock resistance was achieved. This was determined by measuring the critical temperature difference necessary to cause superficial cracks in cylindrical samples subjected to water-quench tests. The experimental results are shown to confirm qualitatively the theoretical prediction of the model of Hasselman et al. for the thermal shock resistance of low- E /high- E composites.

Herstellung und Charakterisierung von Glasmatrix-Verbundwerkstoffen mit Aluminiumtitanat-Einlagerungen mit verbesserter Temperaturwechselbeständigkeit

Die Erhöhung der Temperaturwechselbeständigkeit von Sintergläsern ist eine wichtige Voraussetzung, um ihr Anwendungspotential im technischen und im Strukturbereich zu erweitern. In diesem Beitrag wird die Entwicklung von Glaskompositen mit erhöhter Temperaturwechselbeständigkeit dargestellt, die auf der Einlagerung einer zweiten Phase mit niedrigem E -Modul (E) in der Glasmatrix basiert. Innovative Verbundwerkstoffe aus einer Alumosilicat-Matrix mit Aluminiumtitanat (Al_2TiO_5)-Teilchen wurden durch Pulvertechnologie und drucklose Sinterung hergestellt. Bei der Einlagerung von 30 vol.% Aluminiumtitanat-Teilchen wurde eine vierfache Erhöhung der Temperaturwechselbeständigkeit erzielt. Diese wurde durch die Messung der kritischen Temperaturdifferenz bestimmt, die durch Abschrecken zylindrischer Proben in Wasser von hohen Temperaturen auf Zimmertemperatur zur Bildung von Mikrorissen auf deren Oberfläche führte. Die experimentellen Ergebnisse bestätigten qualitativ die theoretische Vorhersage des Modells von Hasselman et al. für die Temperaturwechselbeständigkeit dieser Art von Verbundwerkstoffen (niedriger E -/hoher E -Wert).

1. Introduction

Glass and glass-ceramic materials possess a number of attractive properties for several technical and structural applications, including architectural, transportation, telecommunication, aerospace, medicine and electronics [1]. Among the useful properties of these materials are their relative low density, in comparison with the majority of structural metals, their high hardness and compressive strength, high resistance to chemical attack, as well as their optical, electrical and thermal insulating properties. However, the brittleness and flaw sensitivity of glass and glass-ceramics, which result in a high susceptibility to catastrophic failure, are the main disadvantages limiting their broader use in structural applications, particularly those involving severe thermal gradients or thermal shock [1 and 2].

According to their stress-strain diagram glasses do not show a region of plastic deformation, thus they are not able to reduce thermally induced stresses by this mechanism as metals do and tend to fail catastrophi-

cally. One approach to the improvement of the thermo-mechanical properties of glass and glass-ceramics, including thermal shock resistance, is to form a composite material [1 to 7]. Such a composite can be fabricated by incorporating in the glass matrix a second constituent in the form of long or chopped fibres, whiskers, platelets or particles. Although the improvement of the thermo-mechanical behaviour of particle-reinforced glass and glass-ceramic composites may not be as pronounced as that achieved using continuous fibre reinforcement [2, 4 and 7], the use of less expensive powder technology preparation techniques makes particle reinforcement an attractive alternative [3 and 5]. Thus, in a number of previous investigations particle-reinforced glasses with improved fracture strength, toughness and wear resistance over the plain glass matrices have been developed [3, 5, 6, 8 to 11]. Less consideration has been given to the thermal shock resistance of particle-reinforced glasses. The limited previous investigations available in the open literature include borosilicate glass containing antimony particles [12] and SiC particle reinforced calcium magnesium aluminosilicate glass-ceramics [2]. In all cases the addition of a second, particulate phase resulted in the

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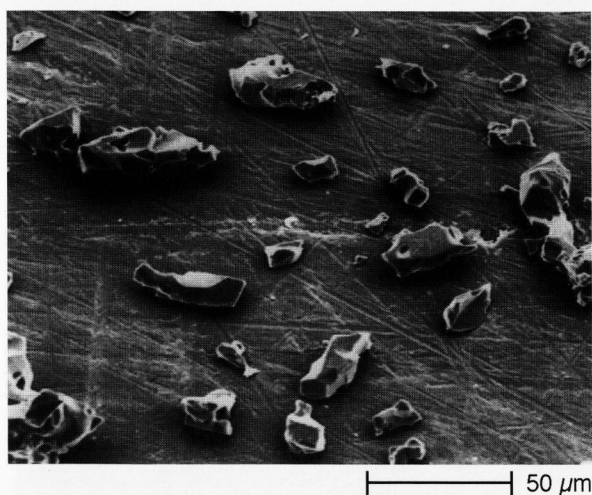


Figure 1. SEM micrograph showing the aluminium titanate particles used as inclusions.

improvement of the thermal shock resistance. In general, thermal shock resistance of brittle materials can be improved by incorporating a dispersion phase of lower elastic modulus and lower thermal expansion coefficient than the matrix, as shown theoretically in the literature [13 and 14], the limiting case being the incorporation of closed porosity [13, 15 and 16].

In the present work a new glass matrix composite system was developed by using aluminium titanate (AT) particles dispersed in an aluminosilicate glass matrix. In a parallel study a similar investigation was conducted using borosilicate glass matrices [17]. Due to the favourable combination of low Young's modulus and low thermal expansion coefficient of AT [18], it is shown that its incorporation in a brittle glass matrix leads to a material with significant improvement of the thermal shock resistance.

2. Experimental

The glass matrix used was a commercial alkali-free aluminosilicate glass (Code 8409, Schott Glass, Mainz (Germany), available in powder form of average particle size 8 μm). The theoretical density of the glass is 2.56 g/cm^3 . The sintering behaviour of this glass powder, which occurs at a temperature of 850 $^{\circ}\text{C}$, has been studied in a previous investigation [19]. The AT (Al_2TiO_5) powder (theoretical density 3.3 g/cm^3) was obtained by sintering reaction of Al_2O_3 and TiO_2 powders for 2 h at 1500 $^{\circ}\text{C}$ and subsequent crushing and milling of the sintered body. The resultant AT powder had a broad particle size distribution with a mean particle size of 50 μm . A SEM micrograph of the AT particles is shown in figure 1. Further properties of the glass and AT used are presented in table 1.

Mixtures containing 0, 5, 10 and 30 vol.% of AT particles were prepared by dry-mixing. This mixing was

Table 1. Properties of the glass matrix and aluminium titanate inclusions

property	glass matrix: aluminosilicate (glas no. 8409 from Schott)	inclusions: aluminium titanate particles [18]
density in g/cm^3	2.56	3.15
Young's modulus in GPa	90	12 to 18
Poisson's ratio	0.24	0.20
thermal expansion coefficient in K^{-1}	4.1×10^{-6}	$1 \text{ to } 1.5 \times 10^{-6}$
flexural strength in MPa	≈ 50	25 to 40

conducted for 24 h in a rotating jar. Cylindrical compacts (15 mm in diameter by 5 mm) were formed by uniaxial compression of the mixed powders in a die at 100 MPa, without using any binder. Relative green densities in the range 0.55 (± 0.02) of the theoretical density of the mixtures were reached. The samples were pressurelessly sintered in an electric furnace at 850 $^{\circ}\text{C}$ for 2 h. Heating and cooling rates of 5 K/min were used. At least 30 samples of each composition were fabricated. The density of sintered samples was determined geometrically. The Young's modulus of samples containing different volume fractions of AT particles was determined by the normal ultrasonic pulse-echo method using the reflection of ultrasonic waves between parallel faces of cylindrical samples. Transverse and longitudinal ultrasonic velocities were measured using an ultrasonic tester interfaced with an oscilloscope. The transducer frequencies were 5 and 15 MHz for transverse and longitudinal waves, respectively. Thermal shock testing involved heating samples in air to the desired temperature (in the range 100 to 500 $^{\circ}\text{C}$) and equilibrating for 30 min. Then the samples were quenched in distilled water at room temperature. Although this procedure was manual, by using tongs, it was simple to perform, and thus adequate reproducibility was assured. The time elapsed between the opening of the furnace and the moment the samples touched the water was approximately 5 s. It was controlled also that the samples entered horizontally into the water and that they remained in the water bath for 5 min. After each thermal shock cycle, the samples were dried in an oven set at 100 $^{\circ}\text{C}$ for 20 min. The samples were carefully inspected visually for the appearance of surface microcracking development using a stereo light microscope.

The appearance of surface cracks was used as the failure criterion to determine the critical temperature difference. Selected samples were polished in order to prepare surfaces for optical and scanning electron microscopy (SEM) examination. Fracture surfaces were also observed by SEM.

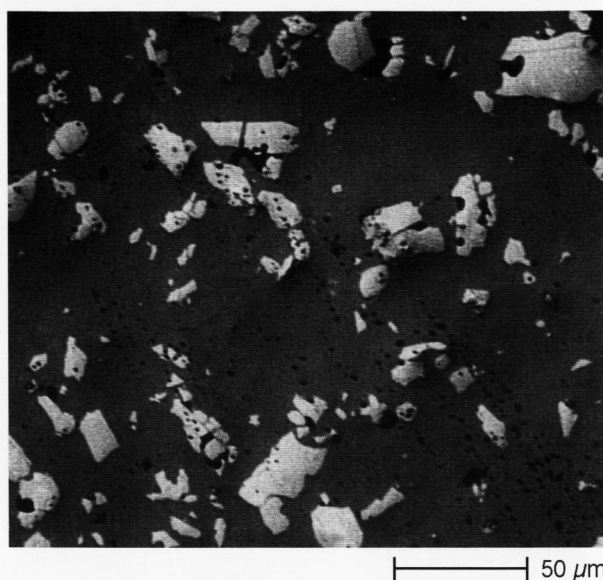


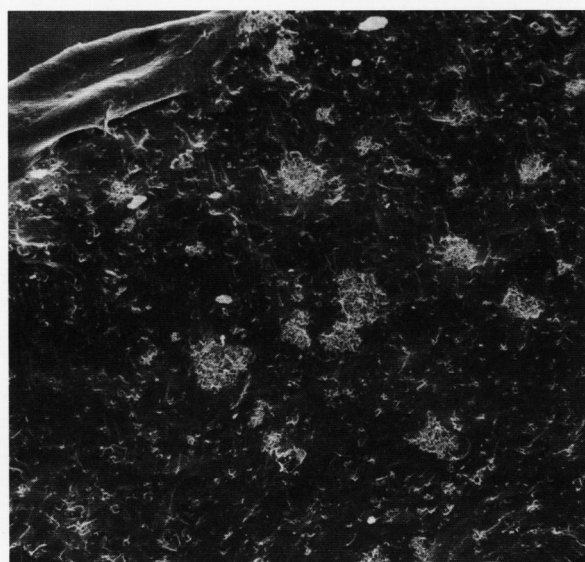
Figure 2. Optical microscopy image of a polished sample containing 30 vol.% AT particles showing the fairly homogeneous distribution of AT particles and very few isolated pores in the glass matrix.

3. Results and discussion

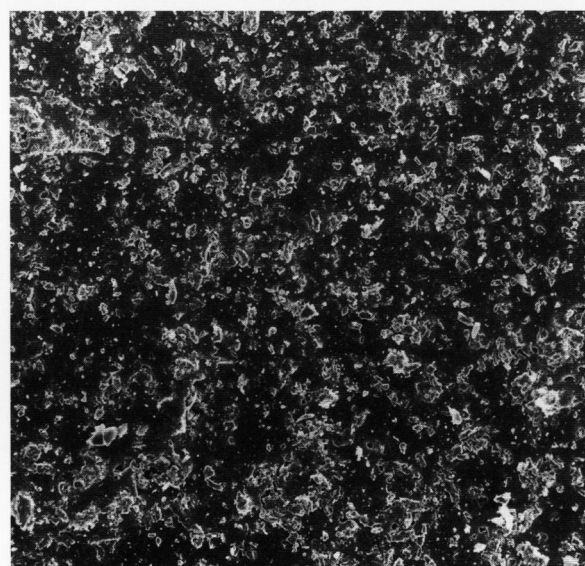
AT is increasingly being used in combination with several ceramic materials, such as alumina, mullite and zirconia [20 to 24], to produce composites with improved thermal shock resistance. The authors are not aware, however, of previous efforts concerning the use of AT in combination with glass.

Figure 2 is a low-magnification optical microscopy image of a sample containing 30 vol.% of AT particles. A homogeneous distribution of the particles can be observed as well as the presence of some isolated pores. The porosity of all samples was <5 vol.%, however, indicating the feasibility of fabricating this kind of glass matrix composites by a simple pressureless sintering technique. Figure 2 also reveals that the particles are well-bonded to the matrix, since they were not pulled out during the polishing procedure.

The fairly homogeneous distribution of particles in the glass matrix also becomes evident by inspection of SEM images of fracture surfaces, as shown in figures 3a and b for specimens containing 10 and 30 vol.% AT particles, respectively. Moreover, under the resolution of SEM, no interfacial reactions or creation of other crystalline phases at the particle-matrix interfaces or in the glass matrix were observed, which was also confirmed by X-ray diffraction analysis of sintered samples. Figure 4 is a SEM micrograph of a fracture surface of a sample containing 10 vol.% AT, showing a thermal-shock induced microcrack. It is seen that the crack propagates with minor deflection through both the matrix (labelled "1") and the AT particle (labelled "2"). Similar observations were made in a parallel study on AT particle reinforced borosilicate glass matrix composites [17]. Due to the sign of the elastic mismatch in these composites



a)



b)

Figures 3a and b. Fracture surfaces of glass matrix composites containing a) 10 vol.% and b) 30 vol.% AT particles.

(see table 1), a tensile tangential stress develops around the inclusions and as a consequence cracks are attracted to the inclusions and tend to propagate through them. These observations are relevant when considering the fracture behaviour of these composites in order to assess the possible active toughening mechanism. The measurement of the indentation fracture toughness and further consideration of the fracture behaviour of these composites are the focus of current work.

Figure 5 shows the results of the dynamic Young's modulus determination. As expected, the Young's modulus shows a monotonic decrease with increasing volume fraction of AT particles. This dependence is in very closed agreement with a prediction based on the

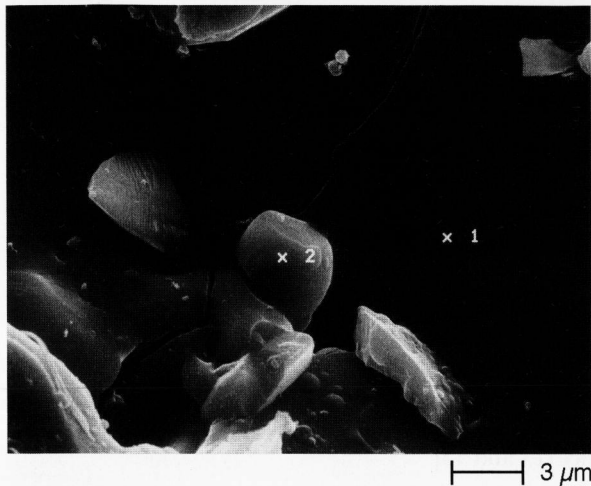


Figure 4. SEM micrograph of a fracture surface of a sample containing 10 vol.% AT, showing a thermal-shock induced microcrack. It is seen that the crack propagates with minor deflection through both the matrix (1) and the AT particle (2).

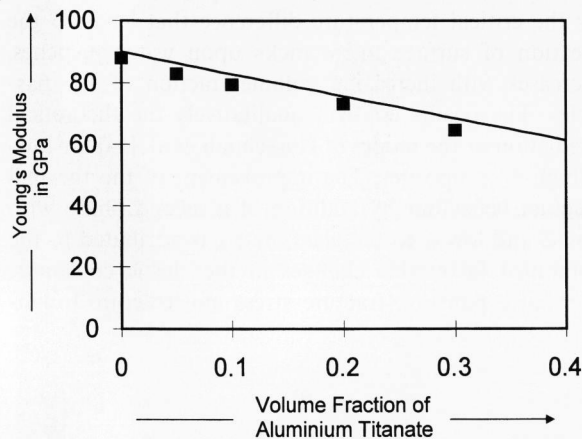


Figure 5. Variation of the Young's modulus of the composites with increasing AT content: (■) experimental data obtained by the ultrasonic technique, (—) prediction of the rule of mixtures.

rule of mixtures, using the Young's modulus of AT and glass no. 8409, as quoted in table 1. The rule-of-mixtures calculation is also shown in figure 5.

The results of the thermal shock tests are summarized in figure 6. Despite the relative large scatter of the data, which is typical for values of ΔT_c gained from water-quench tests [13], a consistent trend can be observed: the average critical temperature difference increases with increasing AT content. As shown by Hasselman et al. [14], the effect of a dispersion phase on the thermal shock resistance of a composite material can be quantified by considering the so-called thermal stress resistance parameters, which are mathematical combinations of several material properties, including fracture strength (σ), Poisson's ratio (ν), Young's modulus (E)

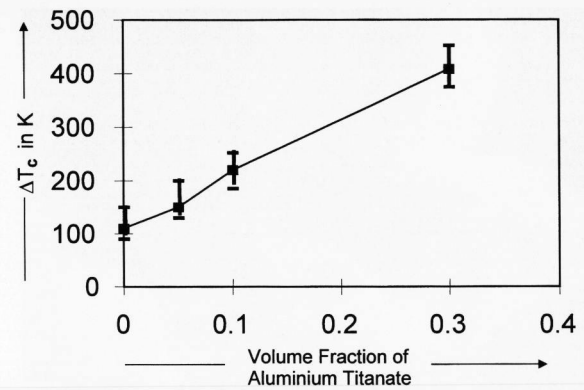


Figure 6. Critical temperature difference (ΔT_c) for the appearance of surface cracks under thermal shock for glass matrix composites containing AT particles.

and coefficient of thermal expansion (α). For example, the thermal stress resistance parameter R can be written as [14]:

$$R = \frac{\sigma(1-\nu)}{\alpha E} \quad (1)$$

A material with high value of R exhibits high resistance to the initiation of thermal stress fracture. Equation (1) is, thus, a fracture strength criterion. The parameter R is proportional to the critical temperature difference (ΔT_c) that a material can withstand without cracking:

$$\Delta T_c = R f(\beta) \quad (2)$$

where $f(\beta)$ is a function of the Biot's modulus and describes the effects of heat transfer since the peak thermal stress occurs at a finite time after the quench initiates [25]. For an infinitely rapid quench, $f(\beta)$ is unity and this can be assumed to be valid also for a very rapid water quench [25]. Since all the material parameters in equation (1) for the glass matrix are available (table 1), it is instructive to estimate the expected value of ΔT_c . For $f(\beta) = 1$, this value is found to be $\Delta T_c = 105$ K, which is in remarkably good agreement with the experimentally determined value (figure 6).

The present experimental results confirm qualitatively the prediction of the theory of Hasselman et al. [14] for the thermal shock resistance of composites, in that the incorporation of a second phase with lower Young's modulus (E) than the matrix (low- E /high- E composites) would lead to an improvement of the thermal shock resistance. Since AT has also a lower thermal expansion coefficient than that of the glass matrix, the thermal shock resistance is further enhanced. Thus, considering equation (1), and neglecting the effect of the AT inclusions on the Poisson's ratio, it becomes clear that the addition of AT particles results in a monotonic increase of the ratio $\sigma/(E\alpha)$ for the volume fraction range investigated. This indicates that the possible reduction of

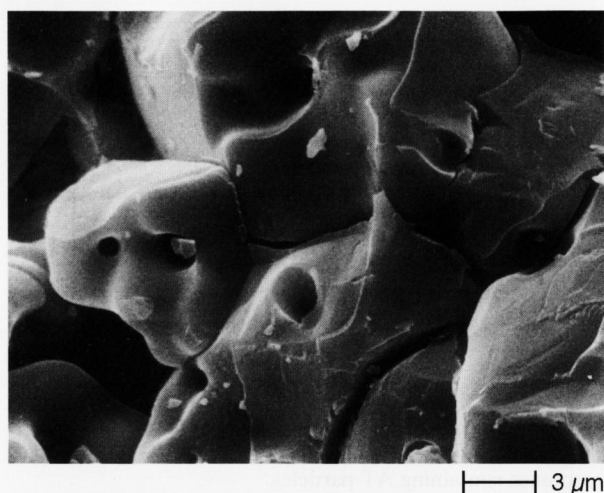


Figure 7. SEM micrograph showing an AT particle in a thermally shocked sample containing 30 vol.% AT particles ($\Delta T = 300$ K). Microcracking of the AT particle can be observed.

the fracture strength σ by incorporation of the low- E inclusions, or by creation of flaws associated with the inclusions, is offset by the significant reduction of E and α with increasing volume fraction of AT particles.

Another thermal shock resistance parameter is given by the index $K_{Ic}/(E\alpha)$, which quantifies the resistance to crack propagation under thermal stress [26]. If the addition of AT particles leads to the increase of the fracture toughness K_{Ic} , as it may be expected by observing the topography of the fracture surfaces (figure 3) and the crack-particle interaction (figure 4), then the present composites will also show a significant increase of the resistance to crack propagation under thermal shock.

The variation of thermal shock resistance, as quantified by ΔT_c , with the volume fraction of inclusions in a composite material can be calculated by replacing microstructure-property correlations in equation (1), as shown elsewhere [13]. This involves utilizing continuum models for the effective properties ν , E and α of the composites [13 and 15], as well as micromechanical approaches for assessing σ and the crack-inclusion interactions. Such a quantitative investigation is however beyond the scope of this experimental study. According to predictions of Lutz et al. [27] on particulate brittle matrix composites, it may be expected that, due to the presence of well-bonded inclusions, strength degradation of the composites for $\Delta T > \Delta T_c$ would be improved compared with the unreinforced glass matrix. Work is in progress to confirm this prediction.

Microcracking of the AT particles, which may occur at temperatures well below ΔT_c due to the very low fracture strength of AT (25 to 40 MPa) and due to its anisotropic thermal expansion behaviour [18], may be another factor contributing to the enhancement of thermal shock resistance. Figure 7 is an SEM image of a microcracked AT particle in a 30 vol.% AT composite after a thermal shock of $\Delta T = 300$ K. This microcracking of

AT particles can contribute to the increase of the thermal shock resistance of the composite due to the favourable combined effect of microcracking on thermal conductivity, elastic properties, coefficient of thermal expansion, and strength, as shown theoretically by Hasselman and Singh [28]. This effect has been known in particulate ceramic composites for over 30 years [29]. It may be speculated that microcracks may provide a means of accommodating some thermal strain and thereby cause a reduction of thermal stress under thermal shock loading. Finally, the presence of some isolated pores in the matrix represents an additional positive contribution to the improvement of the thermal shock resistance, as previous theoretical studies on porous sintered glasses predict [13 and 15].

4. Conclusions

New composite materials consisting of AT particles dispersed in an aluminosilicate glass matrix have been fabricated. The experimental investigation has shown that the thermal shock resistance of the composite, as quantified by the critical temperature difference that leads to the creation of surface microcracks upon water-quenches, increases with increasing volume fraction of AT particles. The results confirm qualitatively the theoretical prediction of the model of Hasselman et al. [14] for low- E /high- E composites. The improvement of the thermal fracture behaviour by addition of a second phase with low E and low α to the glass matrix is attributed to the combined favourable changes in the elastic constants, thermal expansion, fracture stress and fracture toughness.

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