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Theoretical and experimental considerations on the thermal shock resistance of sintered glasses and ceramics using modelled microstructure–property correlations

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The thermal shock resistance of brittle materials such as glass and ceramics is one of their weaknesses. Pores and other incorporated second phases in these materials alter these properties which are decisive for thermal shock behaviour, and may therefore increase this behaviour in a precalculable manner. It has been theoretically demonstrated when and why porosity leads to an improvement in thermal shock resistance. The thermal shock resistance for porous borosilicate sintered glass and porous eutectic calcium titanate ceramic have been calculated and compared to experimental values. The results confirm that low porosities lead to an improvement in thermal shock resistance, that the thermal shock resistance has a maximum at a certain porosity, and that above certain porosities, the presence of pores deteriorates the thermal shock resistance. If porous materials are considered as a special case of composite materials, then relations valid for porous materials can be transferred to composite materials and vice versa ("composite concept"). This has been investigated using the examples of borosilicate sintered glass with incorporated antimony particles and eutectic calcium titanate ceramic with incorporated paladium particles. In the case of the glass–antimony composite material, improvements in thermal shock resistance of about 15% with 10 vol% antimony incorporation, were calculated and confirmed experimentally, while for calcium titanate–palladium composite materials, a 15% improvement in thermal shock resistance was already achieved with about 5 vol% metallic phase.

1. Introduction

The thermal shock behaviour, R_{TS}, of brittle materials such as glass and ceramics, is one of the weak points of these materials. It depends on their rupture strength, R_m, modulus of elasticity, E, and Poisson's ratio, ν, as well as on their thermal expansion coefficient, α, and their thermal conductivity, λ, according to the following equation [1]

$$R_{TS} = \frac{\lambda R_m}{\alpha E}(1-\nu) \quad (1)$$

The background for this equation is the calculation of stresses caused by the temperature gradient, ΔT, between the surface and centre of a specimen being quenched or heated rapidly (Fig. 1). That stress depends on the cited properties and becomes equal to the rupture strength ($\sigma = R_m$), if a certain critical temperature gradient exists ($\Delta T_{crit} = R_{TS}$).

The different material properties enter into the equation with different weights depending on the experimental boundary conditions. A differentiation is therefore made between thermal shock resistances ("thermal stress resistance parameters") of the first, second and higher order [2–13] which either assume only spontaneous elastic behaviour of the material (thermal shock resistances of the first and second order) or take into consideration viscoelastic behaviour (thermal shock resistances of the third and fourth order), as well as plastic deformation, fracture mechanical and fracture statistical approaches (thermal shock resistances of the fifth, sixth and seventh order). The assumption of how rapidily the heat transfer from

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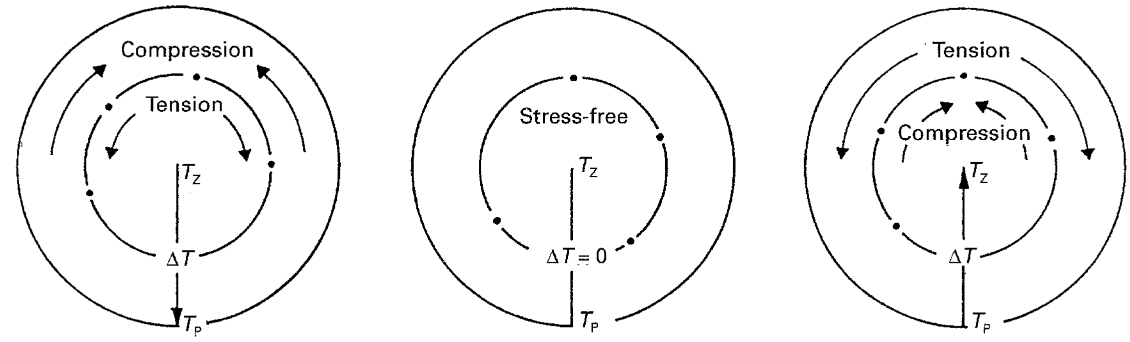

Heating: $T_P > T_Z$
Internal cracks

Isothermal condition: $T_P = T_Z$
No cracks

Cooling: $T_P < T_Z$
External cracks

Figure 1 Stresses development under thermal shock conditions.

the material to the environment takes place under thermal shock conditions is of central significance for the weighting of the individual properties in Equation 1. This, once again, determines the temperature gradient that the material has to tolerate without cracking and which, with a finite heat transfer, corresponds directly to the thermal shock resistance of the second order [1, 14]

$$R_{TS-2} \triangleq \Delta T_{\text{Krit}} = C\frac{\lambda R_m}{\alpha E}(1-\nu) \qquad (2)$$

The proportionality constant, C, is valid for certain specimen geometries and has the dimension mK W^{-1}. As demonstrated by a comparative criticism of the thermal shock resistance of various orders [15], due to the indeterminacy of the actual heat transfer in the experiment and the (associated) neglection of the temperature dependence of the property term in Equation 2, these resistances remain so inexact that for further considerations of the thermal shock resistance of brittle materials, it is sufficient here to restrict the consideration to those of the second order according to Equation 2.

2. The thermal shock behaviour of porous brittle materials

As a rule, ceramic materials are produced by powder technology and thus contain sintering pores. Since the beginning of the century, contradictory statements have been made about their influence on thermal shock resistance so that both an improvement and also a deterioration in thermal shock resistance has been demonstrated by porosity [16–19]. Only the introduction of porosity-dependent property terms in Equation 2 enabled a theoretical representation of the thermal shock resistance as a porosity function, and thus the demonstration that low porosities must lead to an improvement in thermal shock resistance whereas larger porosities lead to a deterioration [18, 19]. The thermal shock resistance of second order for porous materials is obtained from Equation 2 if the individual property terms are substituted as the porosity functions

$$R_{TS-2P} = C\frac{\lambda_P R_{mP}}{\alpha_P E_P}(1-\nu_P) \qquad (3)$$

The experimental determination of these porosity functions for porous glass and porous calcium titanate ceramic and their comparison with theoretical values was the subject of a previous report [15] where, due to a lack of knowledge, the influence of the Poisson's ratio as a porosity function in a first approximation had to be neglected. In the meantime, this influence has been derived and confirmed experimentally [20, 21] and will be reported here.

An extensive analysis of the literature has revealed that only a few contributions have dealt with the porosity dependence of the Poisson's ratio. On the one hand, it has been classified as negligibly small [22], although on the other hand, this has not been confirmed by experimental results, primarily for porous ceramic materials [23]. The theoretical statements were either not compared with experimental values [24–26] or else a comparison revealed that the calculated Poisson's ratios were about 30% higher than the measured values [27]. In order to derive a relationship between the Poisson's ratio and porosity, P, of isotropic, porous materials, the relation known from the elasticity theory is assumed

$$\nu = 0.5 - \frac{E}{6K} \qquad (4)$$

where E is the modulus of elasticity, and K the bulk modulus (cf. e.g. [28]).

The porosity dependence of the modulus of elasticity has already been dealt with and theroretically explored in more depth [29, 30]. The comparison between measured and calculated values has similarly been implemented for porous calcium titanate ceramic and porous borosilicate glass [15]. Fig. 2 shows, as an example, this comparison for normalized values, i.e. relative to the modulus of elasticity of borosilicate glass without pores, for (quasi-)spherical porosity. Corresponding comparisons have, in the meantime, also lead to a satisfactory agreement for other porous materials [31–33]. The materials treated here (borosilicate glass and calcium titanate ceramic) had isometric, i.e. quasispherical, porosity, as reported earlier [15]. Therefore, further discussion will be restricted to this case. However, attention is explicitly drawn to the fact that the available general equations on conductivity, thermal expansion, modulus of

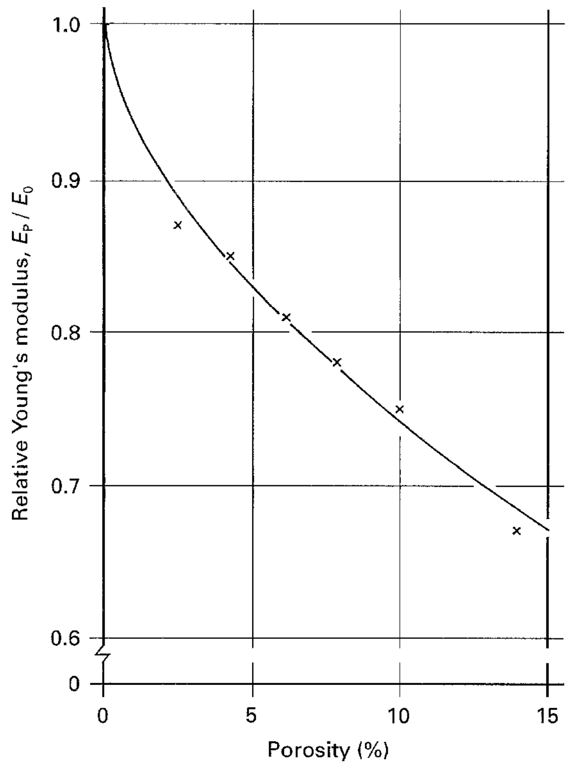

Figure 2 Modulus of elasticity and spherical porosity for porous borosilicate glass: (×) measured data [15], (——) calculated curve, Equation 5.

elasticity or rupture strength permit a treatment of all other pore structures, i.e. forms and orientations such as directional pore channels or flattened pores similar to microcracks [31, 34–37].

The equation valid for the modulus of elasticity in the case of spherical porosity is [30]

$$E_P = E_0(1 - P^{2/3})^{1.21} \qquad (5)$$

where E_0 is the modulus of elasticity of the material without pores. Equation 5 was used to calculate the theoretical curve in Fig. 2. Equations on the porosity dependence are also available for the bulk modulus of porous materials, K_P [34, 35]. Of these equations, two practical relevant cases have a mathematically clear form, i.e. that for spherical porosity and that for cylindrical porosity. The equation for spherical porosity and low volume fraction of porosity has the following form

$$K_{P,1} = K_0 \frac{2(1 - 2\nu_0)(3 - 5P)(1 - P)}{2(3 - 5P)(1 - 2\nu_0) + 3P(1 + \nu_0)} \qquad (6)$$

The subscript 0 always indicates the material without pores. Equation 5 has two zeros ($P = 0.6$; $P = 1$) and is therefore only valid to a limited extent as an adequate approximation ($0 \leqslant P \leqslant 0.5$). A different equation, similarly only with limited validity, has been derived by other authors for higher porosities ($0.5 < P \leqslant 1$) [38, 39]

$$K_{P,2} = K_0 \frac{2}{3} \frac{(1 - 2\nu_0)(1 - P)}{(1 - \nu_0)} \qquad (7)$$

In order to obtain a single equation for the whole porosity range, a "mathematical joint" of both Equations 6 and 7 has been proposed [21], where the following function has been used in order to obtain the endeavoured approximation

$$s = \frac{1}{1 + e^{-100(P - 0.4)}} \qquad (8)$$

On this basis the new approach for the porosity dependence of the bulk modulus can be written as

$$K_P = (1 - s)K_{P,1} + sK_{P,2} \qquad (9)$$

This equation has been compared with experimental data for porous sintered glass and sintered perlite containing a wide range of porosities [21] and sufficient agreement between theory and experiment was found in the frame of an engineering approach.

If the compression and Young's moduli in Equation 4 are replaced by their porosity functions according to Equations 5 and 9 for spherical porosity then the porosity function of the Poisson's ratio of isotropic porous materials with spherical pores is obtained

$$\nu_P = 0.5 - \left\{(1 - P^{2/3})^{1.21} \Big/ 4\left[(1 - s)\frac{(3 - 5P)(1 - P)}{2(3 - 5P)(1 - 2\nu_0) + 3P(1 + \nu_0)} + s\frac{(1 - P)}{3(1 - \nu_0)}\right]\right\} \qquad (10)$$

This equation represents a better solution for the dependence of the Poisson's ratio on porosity than earlier proposed equations [36, 40], which were only valid for a limited range of porosity.

Equation 10 provides the plausible result for the borderline case of a material without pores: $P = 0$; $\nu_P = \nu_0$ (note that for $P = 0$ $s \rightarrow 0$, Equation 8) and thus it fulfils the most necessary borderline case condition.

The low-porosity range of Equation 10 has been experimentally confirmed by comprehensive comparison of calculated and measured values [20, 40] and by comparison with other theories [36]. There is less published experimental work on Poisson's ratio–porosity dependence for the high-porosity range. Therefore, the comparison of Equation 10 with experimental data for this case has been rather limited [21].

Turning again to the thermal shock resistance dependence on porosity, the other property terms required for its determination for the case of spherical porosity according to Equation 3, are already known [19, 30, 31, 36, 41]

$$\lambda_P = \lambda_0(1 - P)^{3/2} \qquad (11)$$

$$\alpha_P = \alpha_0 \qquad (12)$$

$$R_{mP} = R_{m0}(1 - P)^2 \qquad (13)$$

The designations correspond to those in Equation 1, the index P characterizes the porous material and the index 0 the material without pores. Substituting now the properties in Equation 3 by their porosity functions for spherical porosity (Equations 5, 10 and 11–13) and normalizing for the pore-free material, the

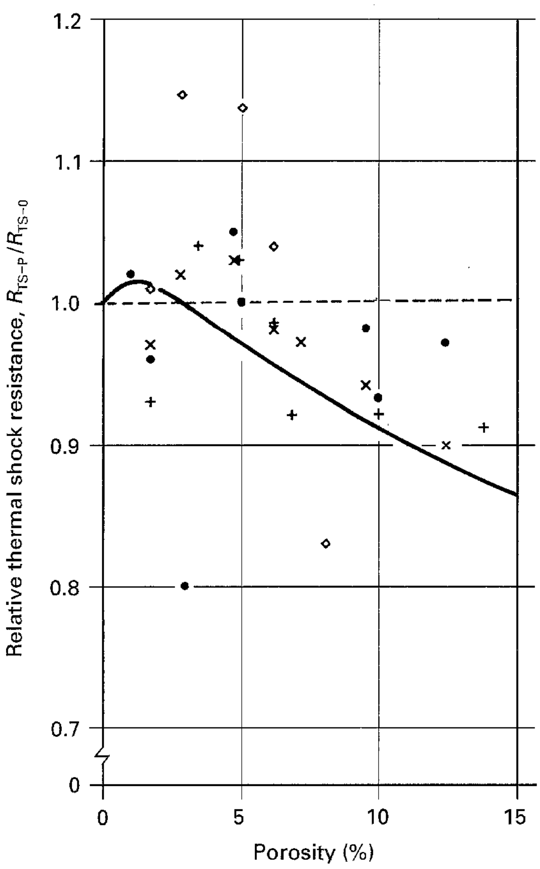

Figure 3 Thermal shock resistance and spherical porosity of borosilicate glass: (●, +, ×, ◇) measured data for different quenching rates [15], (——) theoretical curve, Equation 14.

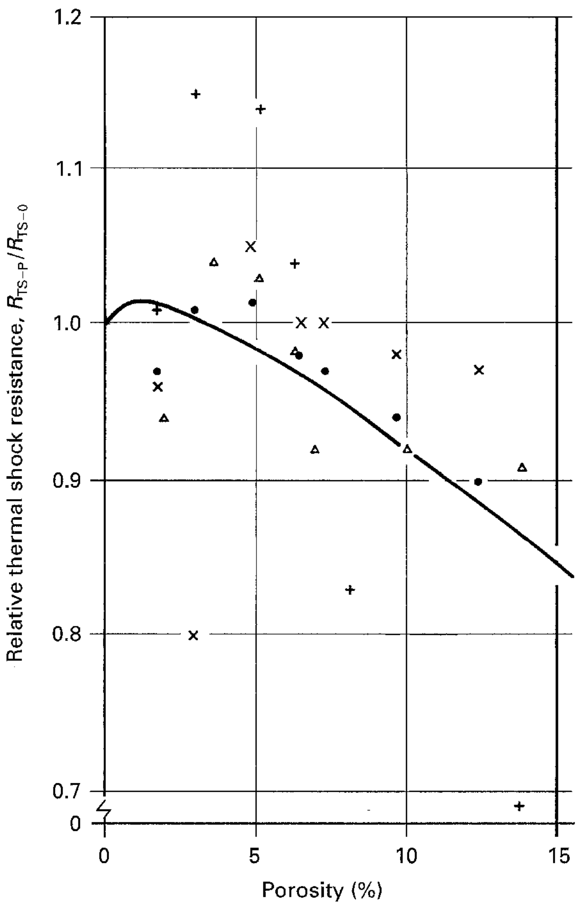

Figure 4 Thermal shock resistance and spherical porosity of eutectic calcium titanate ceramic: (●, +, ×, △) measured data for different quenching rates [15], (——) theoretical curve, Equation 14.

porosity dependence of the relative thermal shock resistance can be obtained

$$\frac{R_{TS-2P}}{R_{TS-20}} = \frac{\lambda_P R_{mP} E_0(1-\nu_P)}{\lambda_0 R_{m0} E_P(1-\nu_0)} \qquad (14)$$

Fig. 3 shows the comparison of experimental and calculated values by means of Equation 14 for the relative thermal shock resistance of borosilicate glass containing quasispherical pores. Fig. 4 shows the same comparison for eutectic calcium titanate ceramic with spherical porosity. The experimental values [15] were normalized with the data for the pore-free material. Despite the considerable scattering of the measured values and although they cannot be related definitely to the theoretical quantities, the course in both cases (calculated curve and experimental results) has the same tendency and may therefore serve as a first confirmation of the approach.

As the theory shows [37], if one considers porosities other than spherical, the following magnitudes depend on the porosity structure, particularly on the shape and orientation of the pores:

(a) the level of the maximum thermal shock resistance achievable by the porosity;

(b) the porosity at which this maximum occurs;

(c) the porosity above which the thermal shock resistance deteriorates.

Thus, for example, according to calculations quasicylindrical pores (prolate spheroids) with a length-to-diameter ratio of about 20 to 1 and randomly oriented through the material, would lead one to expect a 10%–20% increase in thermal shock resistance, whereas values of more than 5% cannot, in principle, be achieved for an increase in thermal shock resistance with "lenticular pores" (oblate spheroids) [37].

Finally, a quantitative assessment of the influence of the Poisson's ratio on the thermal shock resistance as considered here, in contrast to previous studies [15, 19, 42], indicated that in the case of porous eutectic calcium titanate this consideration led to theoretical values in the range of the maximum thermal shock resistance which were only about 2% lower than those without considering the Poisson's ratio effect. Furthermore, with a porosity of more than 30 vol%, the values calculated considering the Poisson's ratio effect were only about 10% above those achieved when a consideration of this influence was neglected in the calculation.

3. The thermal shock resistance of two-phase composite materials

Based on the knowledge of the influence of porosity on the thermal shock resistance of glass and ceramic, an attempt was made to improve the thermal shock resistance by incorporating suitable metallic phases into a borosilicate glass and a eutectic calcium titanate ceramic matrix. In general terms, this objective corresponds to the ductilization of brittle materials under thermal shock conditions by means of the "composite concept". The composite material concept starts from multiphase materials with phases with quite different properties but which adhere to each other as schematically shown in Fig. 5. Basically this concept considers the relationships between properties and microstructure for multiphase materials in general, but uses composites in order to verify theoretical results by experimental values. If the phase properties are similar, then the corresponding functions follow for multiphase materials whose phases belong to the same group of materials (cf. Fig. 6). In contrast, if the phase properties are extremely dissimilar, then the equations for the porous material must follow, i.e. those for the relationship between the porosity, the pore structure and the effective properties of a porous material. If, as in the present case, such equations are already available, then analogous functions should also be available or derivable for the two-phase composite material, leading to its microstructure–property correlations.

Two composite systems will be analysed in this study according to the previous experimental work [15]: a borosilicate glass with quasispherical inclusions of antimony and a eutectic calcium titanate ceramic with quasispherical palladium inclusions. Therefore, for the treatment of interest here concerning the thermal shock resistance of these composites, the corresponding microstructure–property correlation for the properties included in Equation 3, (thermal conductivity, thermal expansion coefficient, rupture strength, Young's modulus of elasticity, and Poisson's ratio) are needed.

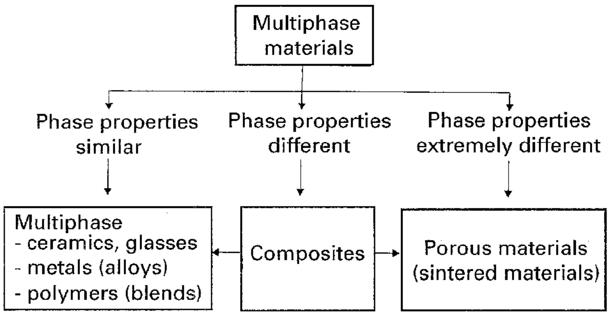

Figure 5 Composite concept and porous material.

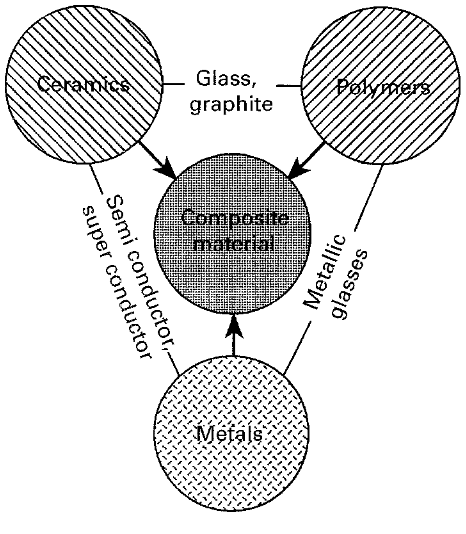

Figure 6 Subdivision of material groups.

After the "state of the art" of the microstructure–property correlations for composite materials, these properties can be given as a function of the corresponding properties of the constituting phases and of the microstructural features for quasispherical shape of the metal phases incorporated in the glass or ceramic matrix phases. The following equations were taken from the literature and verified with respect to their general validity or experimental "reliability" [29–33, 36, 41]

$$E_C = E_M\left[1-\frac{\pi}{A}\left(1-\left\{9\left[1+\frac{1.99}{B}\left(\frac{E_M}{E_D}-1\right)\right]\right\}^{-1} - \left\{3\left[1+\frac{1.68}{B}\left(\frac{E_M}{E_D}-1\right)\right]\right\}^{-1} - \left\{9\left[1+\frac{1.04}{B}\left(\frac{E_M}{E_D}-1\right)\right]\right\}^{-1}\right)\right] \tag{15}$$

$$A = 2.598\, c_D^{-2/3}$$

$$B = 1.612\, c_D^{-1/3}$$

$$(1-c_D) = \frac{\lambda_D-\lambda_C}{\lambda_D-\lambda_M}\left(\frac{\lambda_M}{\lambda_C}\right)^{1/3} \tag{16}$$

$$R_{mC} = R_{mM}\frac{E_C}{E_M} \tag{17}$$

$$\alpha_C = \alpha_M + (\alpha_D-\alpha_M) \times \frac{E_D[E_C(1-2\nu_M)-E_M(1-2\nu_C)]}{E_C[E_D(1-2\nu_M)-E_M(1-2\nu_D)]} \tag{18}$$

where c_D is the volume percentage of the included phase; M, D and C indicate matrix, included phase and composite material.

As in the case of porous material, no relationship has yet been established between the Poisson's ratio of the two-phase isotropic composite material and its microstructure. In order to derive this relationship, once again Equation 4, known from the elasticity theory, is used and accordingly requires the dependence of the effective elasticity modulus, E_C, and the effective compression modulus, K_C, of a two-phase isotropic composite material as a function of the corresponding phase properties and the constitutive microstructure for the quasispherical shape of the included phase.

The modulus of elasticity is given by Equation 15 and the following equation is valid for the bulk modulus of two-phase isotropic composite materials with quasispherical inclusions in lower concentration (<30 vol %) [15, 34]

$$K_C = \left[\frac{3(1-c_D)(1-2\nu_M)}{E_M+4G_C(1-2\nu_M)} + \frac{3c_D(1-2\nu_D)}{E_D+4G_C(1-2\nu_D)}\right]^{-1} - \frac{4}{3}G_C \tag{19}$$

with

$$G_C = \frac{E_M(3-5c_D)}{12(1+\nu_M)} - \frac{E_D(2-5c_D)}{12(1+\nu_D)} + \left\{ \frac{E_D E_M}{6(1+\nu_D)(1+\nu_M)} + \left[\frac{E_M(3-5c_D)}{12(1+\nu_M)} - \frac{E_D(2-5c_D)}{12(1+\nu_D)} \right]^2 \right\}^{1/2} \quad (20)$$

If Equations 15, 19 and 20 are now substituted in Equation 4, then the dependence of the Poisson's ratio of a two-phase isotropic composite material on its phase properties is obtained for spherical shape of the included phase which, according to Equation 4, is as follows in the general form

$$\nu_C = 0.5 - \frac{E_C}{6K_C} \quad (21)$$

The detailed notation of the equation no longer has a clear mathematical form; for this reason a graphical representation is given in Fig. 7 and compared with experimental values from the literature [43]. As the comparison shows, the calculated curve is satisfactorily confirmed by the experimental values.

With Equations 15, 16, 17 and 21 as well as 18, 19 and 20, respectively, all terms necessary to calculate the normalized thermal shock resistance (second order) for two-phase isotropic materials with a quasispherical included phase are available

$$\frac{R_{TSB-C2}}{R_{TSB-CM}} = \frac{\lambda_C \alpha_M R_{mC} E_M (1-\nu_C)}{\lambda_M \alpha_C R_{mM} E_C (1-\nu_M)} \quad (22)$$

Such composite materials, with borosilicate glass matrix phase and quasispherical antimony inclusions, and with eutectic calcium titanate matrix phase and quasispherical palladium inclusions, were fabricated by powder technology and quantitatively characterized by microstructural analysis [15]. The thermal expansion coefficients, thermal conductivities, moduli of elasticity and rupture strengths of composites with different volume fractions of inclusions were measured. All groups of composite materials were porous, the porosity being restricted to the brittle matrix phases [15]. Thus, in this case, two types of inclusions, namely porosity and metallic particles, are present in the composites.

For carrying out the analysis of the data correctly and in order to permit a comparison with theoretical values, the experimental data should be transformed to values corresponding to the non-porous matrix, which was possible by using Equations 5, 6, 10, 11 or 13, for example.

The theoretical values of the different properties for the composite material can then be calculated by means of Equations 15–22 as a function of the volume fraction of the included phase (in this case metal particles). As an example of this procedure, the experimental and theoretical values for the thermal conductivity of porous composite materials are shown in Fig. 8. An excellent agreement is found for both borosilicate glass matrix composites and eutectic calcium titanate ceramic matrix composites.

For the thermal shock resistance of composite materials containing pores, the same procedure was followed. The experimental values given as the critical temperature difference [15] were converted to pore-free matrix values as explained above. The theoretical values of the thermal shock resistance of the two-phase composite materials were determined according to Equation 22. In Figs 9 and 10 the normalized measured data are compared with the normalized calculated thermal shock resistances for the composite materials investigated here, demonstrating sufficient agreement in the frame of an engineering approach and confirming that the precalculated improvement of the thermal shock resistance of glass and ceramics by metal inclusions can be achieved.

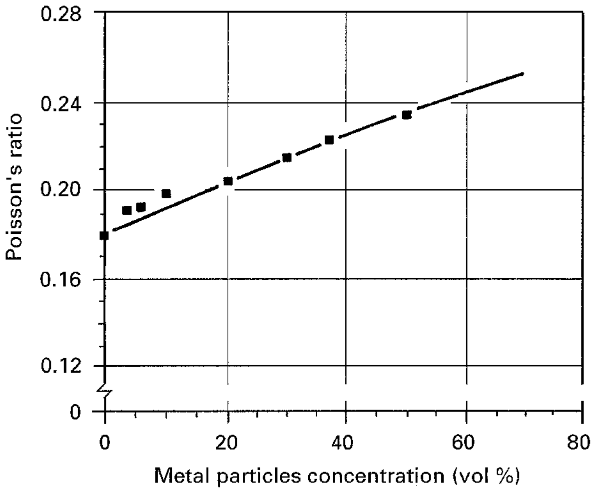

Figure 7 The Poisson's ratio of glass matrix composite materials (calcium aluminium phosphate glass) with quasispherical metal incorporations (cobalt–chromium 788): (■) measured data [43], (——) calculated values.

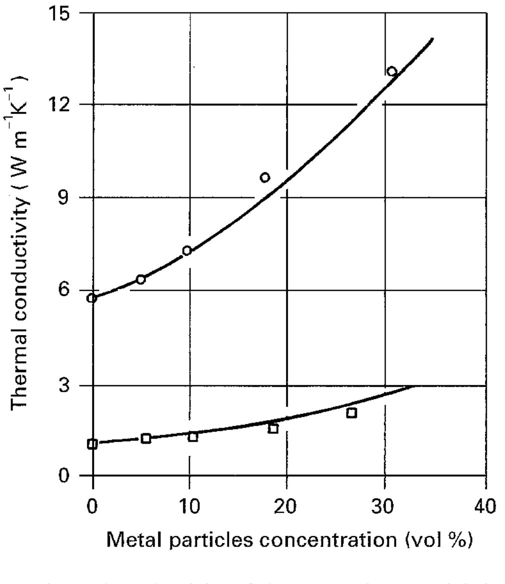

Figure 8 Thermal conductivity of the composite materials investigated, corrected for pore-free matrix measured data [15]: (○) borosilicate glass matrix with antimony inclusions, (□) eutectic calcium titanate matrix with palladium inclusions, (——) theoretical curves, Equation 16.

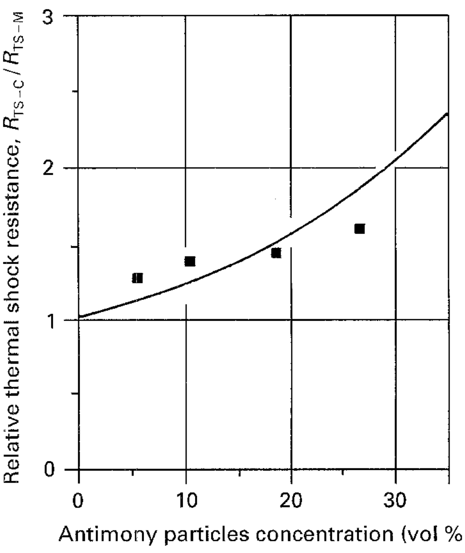

Figure 9 Thermal shock resistance of composite materials with borosilicate glass matrix and quasispherical antimony inclusions: (■) measured data [15], (——) theoretical curve.

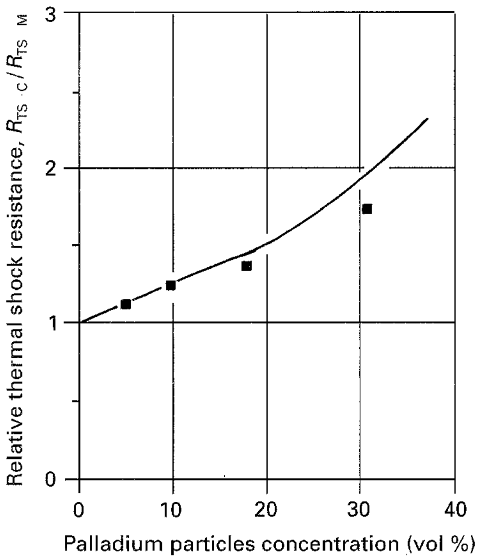

Figure 10 Thermal shock resistance of composite materials with eutectic calcium titanate ceramic matrix and quasispherical palladium inclusions: (■) measured data [15], (—) theoretical curve.

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Sadly, Professor G. Ondracek died tragically during the time this article was being refereed. With his death the international materials research community, which has largely accepted and appreciated his scientific achievements, has lost one of its major figures. Gerhard Ondracek will be sorely missed by all who knew him and had the pleasure of being his colleagues, students and fridends.

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