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Thermal expansion of ceramics in the MgO - CaO system

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The thermal expansion coefficients of refractory ceramics with different compositions in the MgO–CaO system have been measured, and compared with theoretical values for multiphase composites calculated on the basis of the equations of Turner and of Kerner. Good agreement with the predictions of the Turner equation has been found.

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1. Introduction

Knowledge of the thermal expansion behaviour of composite refractory materials is important for both microstructural and macrostructural reasons. The former aspect arises from the fact that expansion differences between the different phases in the composite can lead to the occurrence of cracks or faults in the material when it is temperature cycled; the second aspect lies in the significance of the average value of the coefficient for the composite when considering its structural compatibility with other materials, or when assessing the resistance of the material to thermal shock [1].

The calculation of the average composite value can be based on one of two approaches. The first, that of Turner [2], assumes that the thermal stresses generated by temperature changes are not sufficient to disrupt the body, and that each component in the composite is constrained to change dimensions at the same rate as the whole composite. Further it is assumed that sheer deformation is negligible, i.e. that the generated microstresses are pure hydrostatic tension and compression.

With these assumptions, Turner obtained a general expression for the volume thermal expansion coefficient of the composite

$$\alpha_{\text{comp.}} = \frac{\sum\limits_{\text{phases } i} (\alpha_i K_i F_i/\rho_i)}{\sum\limits_{\text{phases } i} (K_i F_i/\rho_i)} \qquad (1)$$

with α_i the coefficient of volume thermal expansion of phase i, K_i the bulk modulus of phase i, ρ_i the density of phase i, and F_i the weight fraction of phase i in the composite. This equation has been applied with success to plastic composites [2] and to cermets [3].

Another model for the thermal expansion behaviour of composite materials is due to Kerner [4]. For the particular case where the composite can be considered as a random distribution of spherical grains of one phase (A) in a continuous matrix of a second phase (B), this model, which treats in detail the displacements of the matrix around the spherical grains, leads to an expression of the form

$$\alpha_{\text{comp.}} = \alpha_A V_A \alpha_B V_B + (\alpha_B - \alpha_A) V_A \left[\frac{4\mu_B(K_0 - K_A)}{K_0(4\mu_B + 3K_A)}\right] \qquad (2)$$

where α_B, α_A are the coefficients for the matrix and isolated phases, respectively, V_A, V_B are the volume fractions, μ_B is the matrix shear modulus, and K_0 is the composite bulk modulus [4].

It can be seen that in contrast with the Turner equation, this second approach allows a more detailed consideration of the microstructure of the composite in giving attention to the properties of continuous and discontinuous phases.

It is the objective of the present study to apply

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TABLE I Density, modulus and thermal expansion data for MgO and CaO

	$a \times 10^6$ (° C^{-1})	$a \times 10^6$ (° C^{-1})	$K \times 10^{-12}$ (dyn cm^{-2})	$G \times 10^{-12}$ (dyn cm^{-2})	Density (g cm^{-3})
CaO	13.57	13.54	0.218	0.131	3.31
MgO	14.45[7]	14.43	1.550 [8, 9]	0.930	3.58

these equations to an important refractory system [5], that of MgO–CaO, and to vary the composition across this binary eutectic system, so that each of the end-member phases can, in turn, act as the matrix. In addition to its technological importance, therefore, this system is seen as offering a good opportunity to test the relative applicability of the two models.

2. Experimental procedure

2.1. Fabrication

Specimens of CaO–MgO (covering a series of compositions in the range CaO: 0 to 100%, and MgO: 100 to 0%) were prepared using reagent grade calcium hydroxide and magnesium carbonate, or magnesium hydroxide and calcium carbonate as starting materials. These materials (dried at 100° C) were weighed, and mixed in a slurry with distilled water and tungsten carbide balls for 1 h. The resulting mixtures, after drying at 100° C, were calcined in an electric muffle furnace for 1 h in platinum crucibles at 1100° C. The calcined powders were then pressed in 12.7 mm diameter dies at 250 $MN\,m^{-2}$.

To obviate any source of contamination, pellets were placed for firing between pure MgO pellets, the resulting sandwich being set in an alumina muffle. The pellets were pre-fired at 800° C in an electric furnace at a heating rate of 360° $C\,h^{-1}$, and were then fired at 1700° C for $3\frac{1}{2}$ h in a gas furnace.

2.2. Examination of sintered specimens

After sintering, specimens of each composition were examined in terms of density, optical microstructure, and thermal expansion coefficient.

The linear thermal expansion coefficients were measured using a horizontal dilatometer [6], according to the standard test (BSS 1902). Coefficients were measured over the range 20 to 1000°e C at a heating rate of 360° $C\,h^{-1}$. Several cooling contractions were measured to ensure that no hysteresis in the expansion behaviour was occurring.

3. Results

The published values for linear thermal expansion [7], bulk modulus [8, 9], shear modulus (calculated as $\mu = 60\% K$ on the approximation that Poisson's ratio is ≈ 0.25), and densities for both phases, CaO and MgO are shown in Table I. Experimental values of linear thermal expansion coefficients for CaO and MgO stemming from the present study are also listed.

The density values and total porosities of the fired pellets ranged between 2.9 and 3.3 $g\,cm^{-3}$ and 5 to 14% respectively. Typical microstructures for the sintered samples are shown for different compositions in Fig. 1. At low MgO (a) the structure clearly shows a continuous CaO matrix phase; similarly a continuous MgO phase is obtained at high MgO contents (b). The extent of intermediate structures, in which both phases appear as continuous, ranged over some ± 20% of the 50:50 wt % composition (c).

On the basis of the observed microstructures, values for the volume thermal expansion coefficients of samples with different compositions can be calculated using the two equations. These values can in turn be used to calculate coefficients of linear expansion ($\approx \frac{1}{3}\alpha$) which are shown together with the experimentally determined values in Fig. 2. The Kerner equation gives two sets of values depending on assumptions concerning the nature of the matrix phase; the dashed line has been drawn on the basis of the observed microstructures.

4. Discussion

The conclusion from Fig. 2 is that the Turner equation provides a most satisfactory account of the thermal expansion coefficient of mixed-phase composites in the CaO–MgO system. In this connection it may be noted that the system chosen is favourable from the point of view of the assumptions in the equation since the α values of the two end-members are relatively close and the risk of crack formation is correspondingly reduced. The data show the overriding influence of the high-modulus phase (in this case MgO) in that the behaviour of mixtures is dominated by the behaviour of the stiff component so long as that component remains continuous.

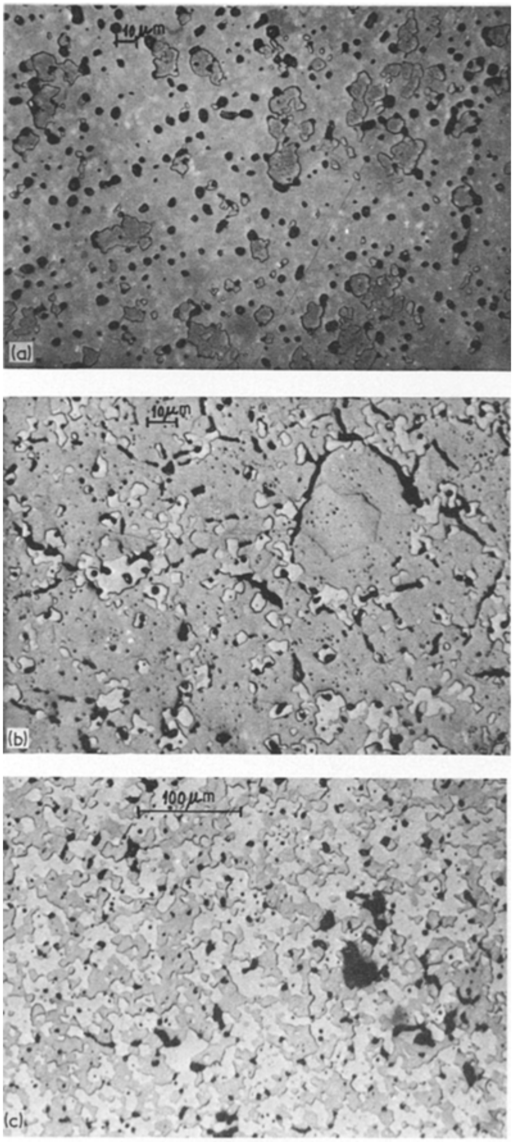

Figure 1 Optical micrographs of ceramics in the CaO–MgO system. (a) 80 wt % CaO with calcia as the continuous phase; (b) 20 wt % CaO with magnesia as the continuous phase; (c) 50 wt % CaO.

The Kerner equation provides less satisfactory agreement over the whole range of compositions, suggesting that the MgO–CaO system is not well represented as particles of one phase isolated in a matrix of another. This is also supported by the fact that there is no suggestion in the data of a "switch-over" from one curve to another as the nature of the continuous "matrix" phase is changed on going from high-MgO compositions to high-CaO compositions.

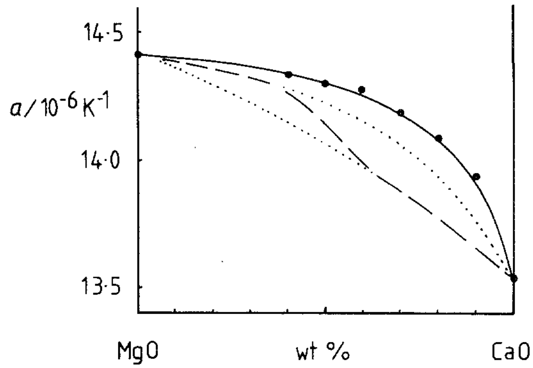

Figure 2 Comparison of experimental and theoretical values for thermal expansion coefficient in the CaO–MgO system. The experimental points fall close to the predictions of the Turner equation (solid line). The two curves from the Kerner equation correspond to a matrix of MgO (high values) or CaO (low values) respectively; the expected "switch-over" between those curves is indicated in the figure.

If the Kerner equation is used in the "packed-grain model" [4], in which the matrix is considered to disappear so that the microstructure consists of grains in contact, values of the expansion coefficient intermediate between the two matrix curves are obtained; this alternative, therefore, also gives an unsatisfactory account of the data.

In summary, the Turner equation provides good values for the coefficients across the CaO–MgO system and appears well suited to these two-phase polycrystalline structures. The Kerner equation is less satisfactory in this instance, and it would be of interest to apply it to microstructures more fairly represented by grains in a matrix, such as, for example, debased alumina compositions or silicate-bonded magnesias. In this respect, the report [10] of its applicability to glass-bonded alumina composites is relevant.

References

1. W. R. BUESSEM, in "High Temperature Technology", edited by L. E. Campbell (Wiley, New York, 1956).
2. P. S. TURNER, *J. Res. Nat. Bur. Stand.* **37** (1946) 239.
3. W. D. KINGERY, *J. Amer. Ceram. Soc.* **40** (1956) 351.
4. E. H. KERNER, *Proc. Phys. Soc. (Lond.)* **B69** (1956) 808.
5. K. K. KAPPMEYER and D. H. HUBBLE, in "High Temperature Oxides", Part 1, edited by A. M. Alper (Academic Press, New York, 1970).
6. M. E. ROSE, R. J. A. SMITH, D. J. HOWLETT and

D. TAYLOR, *Trans. Brit. Ceram. Soc.* **74** (5) (1975) 177.
7. R. J. BEALS and R. L. COOK, *J. Amer. Ceram. Soc.* **40** (1957) 279.
8. O. L. ANDERSON and J. E. NAFE, *J. Geoph. Res.* **66** (1961) 2199.
9. *Idem, ibid* **70** (1963) 3951.
10. R. R. SHAW, Ph. D. Thesis, M.I.T. (1967).

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