

Destabilization of calcia stabilized zirconia

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Calcia stabilized zirconia (CSZ) is destabilized by Al_2O_3 , SiO_2 and TiO_2 at elevated temperatures. The product of destabilization, termed partially destabilized zirconia (PDZ) has been found to possess excellent resistance to thermal shock. The thermomechanical properties of PDZ depend, to a great extent, on the degree of destabilization which is the amount (in weight percent) of free ZrO_2 formed as a consequence of the destabilization reaction. The kinetics of the destabilization reaction has been studied by quantitative X-ray powder diffraction technique, and from the kinetic data, the optimum amount of the destabilizer required to get superior quality PDZ has been estimated.

1. Introduction

Partially stabilized zirconia (PSZ) has been used extensively in many high temperature applications. The unique feature of PSZ ceramic bodies is their ability to withstand severe thermal environments by virtue of their excellent thermal shock resistance [1, 2].

The extent of stabilization in the CaO-ZrO_2 system depends on the amount of the stabilizer and can be determined from the CaO-ZrO_2 binary phase diagram [3]. Any composition which, at the firing temperature, lies in the cubic field is fully stabilized. On the other hand, compositions lying in the two phase (cubic and tetragonal) region will only be partially stabilized in the cubic modification. In other words, PSZ is a mixture of the fully stabilized phase (CSZ) and free zirconia which may be either in the monoclinic form or tetragonal form depending on the temperature. The optimum extent of stabilization for high temperature application under severe thermal flux conditions has been shown to be 70% [2].

Calcia stabilized zirconia (CSZ) can be partially destabilized to produce what is termed partially destabilized zirconia (PDZ) whose phase composition essentially resembles that of PSZ and hence can be expected to possess similar thermomechanical characteristics. PDZ is produced by the reaction of CSZ with oxides such as alumina, silica and titania at high temperatures. The extent of destabilization depends on various factors like the amount and nature of the destabilizer, the reaction (sintering) temperature and time. However, SiO_2 and TiO_2 being acidic in nature tend to react rapidly affecting the quality of the product. Al_2O_3 being an amphoteric oxide reacts rather slowly resulting in PDZ of superior thermomechanical properties. Besides, being refractory in nature Al_2O_3 is the most preferred destabilizer.

2. Sample preparation and characterization

High purity CSZ powder and AR grade alumina of -325 mesh were used as the starting material. Four

different sets of samples, containing 2.95, 4.35, 8.34 and 15.4 wt % alumina were prepared. The above figures correspond, respectively, to one-third, one-half, one and twice the molar equivalent of calcium oxide in CSZ. The powders were mixed in a planetary ball mill using grinding pots and balls made of stabilized zirconia. Thorough mixing of the powder was ensured by addition of acetone, in suitable quantities, during the grinding operation. The powder was then dried and pelletized by uniaxial pressing at a pressure of 1.5 tonnes cm^{-2} into pellets of 1/2 inch (1 in = 2.54 cm) diameter and 2 to 3 mm thick. About 1% polyethylene glycol was added to serve as a binder.

The samples were then heated to different temperatures for different soaking periods in a tubular furnace. The sample temperature was monitored and controlled by a Pt-13% Rh thermocouple positioned in the vicinity (2 to 3 mm above) of the sample. X-ray powder diffraction technique at room temperature and high temperature dilatometry and electron microscopy were employed to study the course of the reaction and characterize the product. The diffraction patterns were recorded using nickel-filtered $\text{CuK}\alpha$ radiation. The study of the kinetics of the reaction was however, limited to the sample coating 8.34 wt % Al_2O_3 . The degree of destabilization in the reacted product was estimated by quantitative X-ray powder diffraction method detailed below.

The degree of destabilization is defined in terms of the weight percent of free zirconia formed as a consequence of destabilization. Quantitative estimate of the degree of destabilization were made from the relative intensities of the diffraction peaks of monoclinic ZrO_2 and CSZ. Standard mixtures containing known amounts of monoclinic ZrO_2 and CSZ were prepared and their powder patterns recorded. A calibration graph relating the intensity ratio of the 11 $\bar{1}$ peak of the monoclinic phase of ZrO_2 and 111 peak of CSZ was drawn. This graph was used to determine the degree of destabilization in the reacted samples.

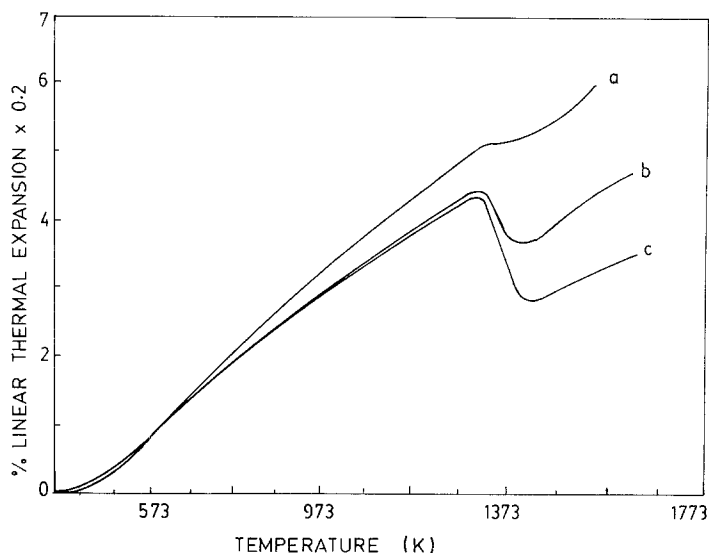


Figure 1 Thermal expansion of PDZ. Wt % of Al_2O_3 in original mix (a) PDZ 4.35 (b) PDZ 8.34 (c) PDZ 15.00.

3. Results and discussion

The room temperature X-ray diffraction patterns of all the samples fired at and above 1473 K revealed the presence of CSZ and monoclinic ZrO_2 , indicating that destabilization has occurred. The monoclinic phase could not be identified in sample fired at or lower than 1373 K. This suggests that the reaction only occurs to any appreciable extent at higher temperatures. The intensities of the ZrO_2 phase depended on the degree of destabilization which depends on a number of factors like the amount of destabilizer, the reaction temperature and time.

The effect of the amount of destabilizer on the degree of destabilization is shown in Table I. It is clearly seen from the Table that for a given reaction temperature, the more the amount of destabilizer the higher is the extent of the reaction. This has also been followed by high temperature dilatometric studies.

Test samples for thermal expansion studies consisted of cylindrical specimens 1/2 inch in diameter and 1 inch long sintered at 1873 K for 8 h. Results are summarized in Fig. 1. The sharp fall in the thermal expansion coefficient around 1300 K is due to the appreciable volume shrinkage associated with the transition from the low temperature monoclinic form of ZrO_2 to the high temperature tetragonal modification [4]. The dependence of the degree of destabilization on the amount of the destabilizer (for a given reaction temperature) is also evident from Fig. 1.

The variation of the degree of destabilization, x , with time t is shown in Fig. 2 for different sintering temperatures in the case of the composition containing 8.34 wt % alumina. The degree of destabilization increases with time at first and then tends to saturate. In other words, the rate of the reaction is found to decrease with the progress of the reaction (time). This

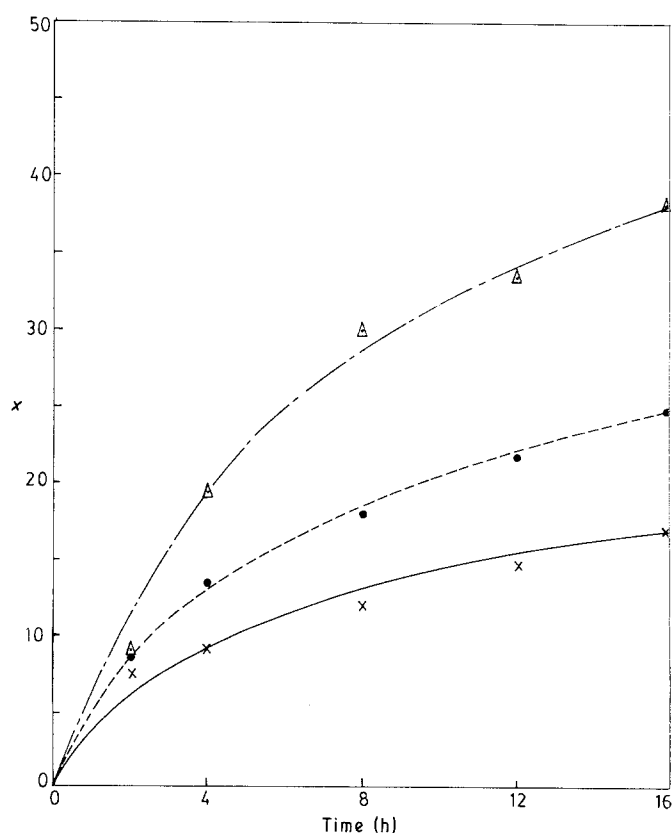


Figure 2 Variation of degree of destabilization (x) with time (h) for different temperatures (— 1473 K, --- 1573 K, - · - · - 1673 K).

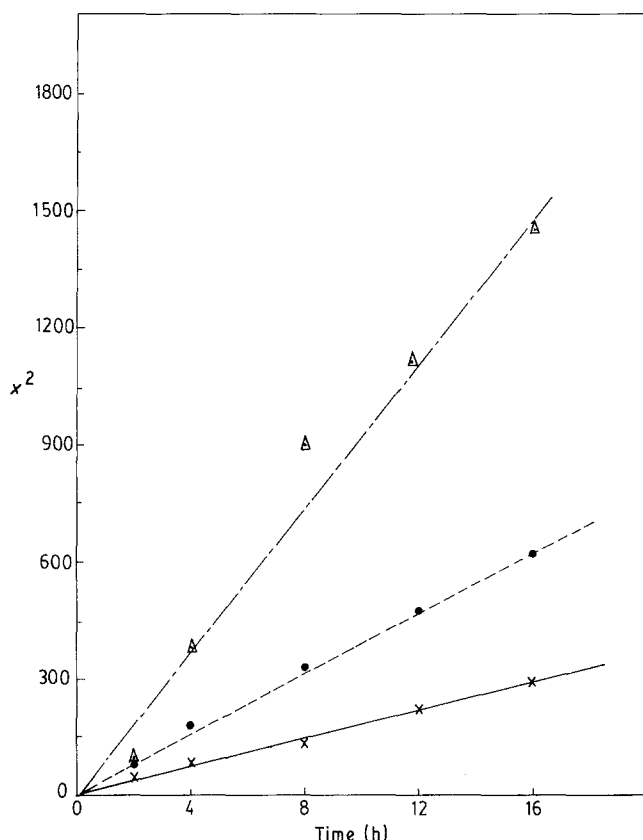


Figure 3 Variation of square of degree of destabilization (x^2) with time (h) for different temperatures (— 1473 K, --- 1573 K, - · - · - 1673 K).

behaviour is characteristic of many a solid state reaction. This is due to the fact that once the product is formed, the reactants have to diffuse through the product layer.

Plots for x^2 against t for different reaction temperatures are shown in Fig. 3. The linear nature of these plots suggests that the reaction obeys the parabolic law [5]. The rate constants for the reaction were calculated from the slope of x^2 against t curve. The variation of the reaction rate constant, K with temperature is depicted in Fig. 4, where $\log K$ is plotted against the reciprocal of the reaction temperature in Kelvin. The curve is linear as required by the Arrhenius Law

$$K = A \exp(-\Delta H/kT) \quad (1)$$

where ΔH is the activation energy of the reaction, k Boltzmann's constant, K the reaction rate constant and T the temperature in Kelvin.

The activation energy calculated from the slope of the $\log K$ against $1/T$ curve gives a value of 45 K cal mole⁻¹. It should be noted here that the rate constant and the activation energy do not, by themselves, characterize a solid state reaction, and therefore, do not have the same significance as in the case of homogeneous reactions [5]. The activation energy and rate constant in the former case represent an overall ther-

mal barrier and its value can vary widely depending on the extent of homogeneity of the reactant mixture, the particle size, area of contact between the reactant particles etc.

The nature of the destabilizer is an important aspect affecting the destabilization reaction and the quality of PDZ produced. Results of reaction of SiO₂ and TiO₂ with CSZ indicate that the extent of the reaction is quite high even for small addition. This is due to the fact that SiO₂ and TiO₂ being acidic oxides, the removal of CaO (strong base) from CSZ proceeds rapidly resulting in crack formation in the product. On the other hand, Al₂O₃, being amphoteric in nature, reacts slowly with CaO, the resulting PDZ having superior resistance to damage by thermal shock.

4. Consequences of destabilization

PDZ has been found to possess excellent resistance to damage by thermal shock [6]. This superior thermal shock resistance of the material is a direct consequence of the destabilization reaction which has a marked influence on the microstructure of the product. The SEM photograph of a typical sample of PDZ sintered at 1873 K is shown in Fig. 5. The sample was polished and etched in 70% orthophosphoric acid before recording the microstructure. The microstructural heterogeneities are evident from the figure. These inhomogeneities in the microstructure arise as a consequence of destabilization reaction which generate free zirconia and calcium aluminate which are dispersed in the CSZ matrix.

The presence of free zirconia and the phase transitions it undergoes during thermal cycling are the principal factors responsible for the improved thermal shock resistance of PDZ. The phase inversion from the monoclinic phase to the tetragonal phase in the

TABLE I Variation of degree of destabilization with composition (x)

| Composition Al ₂ O ₃ (wt %) | Firing temperature | Amount of free ZrO ₂ formed |
|---|--------------------|--|
| 2.940 | 1900 K (3 h) | 11.50 |
| 4.350 | | 24.00 |
| 8.340 | | 34.00 |
| 15.400 | | 48.00 |

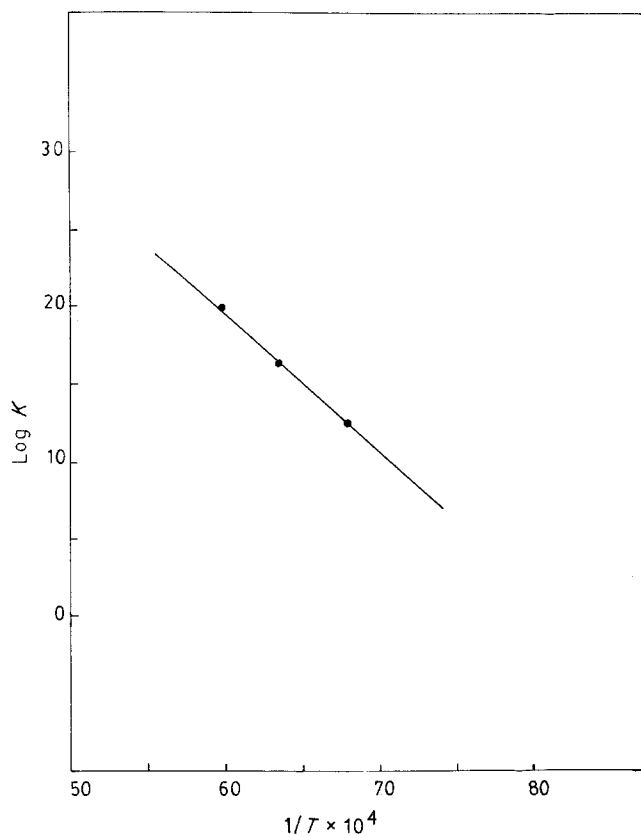


Figure 4 Variation of logarithm of rate constant ($\log K$) with reciprocal temperature ($1/T$).

heating cycle and back to the monoclinic phase in the cooling cycle generate numerous microcracks which act as thermal stress relief centres. During the heating cycle the transformation of the monoclinic phase to the tetragonal phase is accompanied by an appreciable reduction in volume while the bulk material is expanding. During the cooling cycle the tetragonal form reverts to the monoclinic form, with consequent increase in volume in a contracting body. These volume changes introduce a large number of microcracks which propagate only quasistatically [7] enabling the body to maintain its mechanical strength even after continuous thermal cycling.

Apart from the phase inversion of free zirconia, the presence of calcium aluminate in minor amounts, also

contributes to the improved thermal shock behaviour. The appreciable difference in the thermal expansion coefficient of calcium aluminate and zirconia also generates microcracks [6]. Thus the overall crack density is increased which limits excessive crack propagation.

5. Conclusion

The results of the present investigations indicate that oxides of aluminium, titanium and silicon destabilize CSZ to produce partially destabilized zirconia. The degree of destabilization depends on the amount and nature of the destabilizer and the reaction temperature and time.

The phase composition of PDZ is essentially the

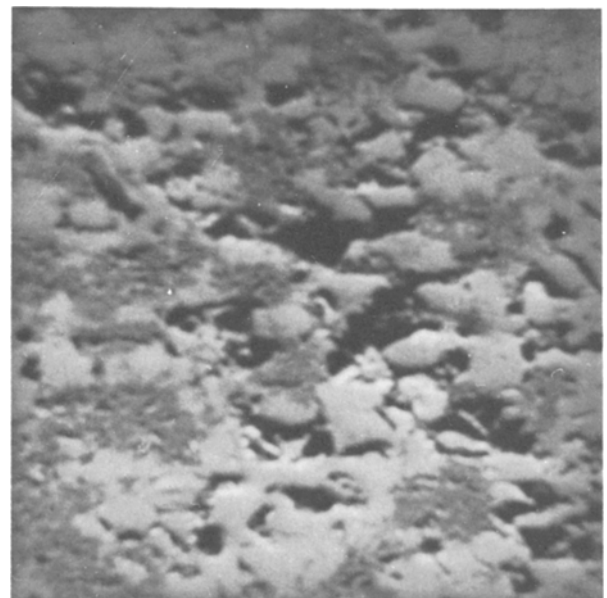


Figure 5 SEM of a typical sintered sample of POZ $\times 200$.

same as that of PSZ. As in the case of PSZ, the presence of free zirconia and the phase transitions it undergoes during thermal cycling are the factors responsible for the excellent thermal shock resistance of the material.

Among the different destabilizers Al_2O_3 is seen to give the best product. Studies on the kinetics of destabilization of CSZ with Al_2O_3 suggest that the degree of destabilization is optimum in the case of composition containing 4.35 and 8.34 wt % of alumina and hence these compositions are the best choice for high temperature applications.

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