phase was suspected.

Nevertheless, the indications are strong that grain boundaries can have a striking effect on the steady-state erosion rate. This result could have practical importance in that an optimum microstructure could be produced which would result in a maximum erosion resistance for a given set of erosion conditions. The effect of grain boundaries on erosion should be studied further.

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Subsolidus Phase Equilibria in the System ZrO_2-Y_2O_3-Al_2O_3

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CUBIC ZrO_2 is presently used as the electrolyte in the automotive exhaust gas sensor which provides the feedback signal for closed-loop control of the air-fuel mixture supplied to the engine.[1–5] The present work was undertaken as part of an effort to optimize the Y_2O_3-stabilized ZrO_2 ceramic electrolyte. Yttria (Y_2O_3) is the preferred stabilizer for sensor applications, despite its high cost, because it produces an electrolyte with both higher conductivity and greater stability.[6–8] Aluminum oxide (Al_2O_3) is added to the body to promote densification and reduce the required firing temperature.[9]

Binary equilibria in the system ZrO_2-Y_2O_3-Al_2O_3 are reasonably well established. However, no information appears to be available for the ternary system. The system Al_2O_3-ZrO_2, the least complex of the binaries, contains only a eutectic at 1870°C between the constituent oxides.[10] The phase diagram for the system Al_2O_3-Y_2O_3 was first proposed by Olds and Otto,[11] but did not include the 1:1 compound $AlYO_3$. Although the existence of $AlYO_3$ has been reported by Roth[12] and by Keith and Roy,[13] the stability limits have not been conclusively established. A 2:1 compound ($2Y_2O_3 \cdot Al_2O_3$) decomposes to yield garnet ($3Y_2O_3 \cdot 5Al_2O_3$) and cubic Y_2O_3 at low temperatures.[14]

A diagram of the system ZrO_2-Y_2O_3, published by Stubican *et al.*,[15] is similar to one reported by Srivastava *et al.*[16] at >1400°C. Decreasing stability limits with decreasing temperature for the cubic ZrO_2 phase and the existence of a cubic allotrope of pure ZrO_2 at high temperatures are significant features of these diagrams.

Specimens for the present study were prepared by mixing appropriate quantities of oxide powders (Table I) to produce batches (≈50 g) of material. The powders were ground in a mortar and pestle as an acetone slurry and calcined for 10 h at 1250°C. The resulting cakes were then crushed and pressed in a hardened steel die using a stearic acid lubricant. Compositions (Table II) were selected to distinguish clearly the valid joins in the system. The subsolidus was determined by exploratory firings at 30°C intervals between 1450° and 1600°C. Ceramographic specimens were then examined by scanning electron microscopy (SEM) for evidence of liquation. Two firing schedules were used: (1) isothermal firing at 1450°±10°C for 500 h and (2) firing for 20 h at 1650° followed by equilibration at 1450°C for 300 h. Pellets were cooled at ≈80°C/min from 1450°C.

The fired pellets were crushed and ground for X-ray analysis in an Al_2O_3 mortar and pestle. (No Al_2O_3 lines could be detected in trial samples prepared without Al_2O_3 additions.) X-ray analysis was conducted using a standard diffractometer,* Cu$K\alpha$ radiation, $^1/_2$° slits, and a graphite monochrometer. Precision lattice parameters for the ZrO_2 solid solutions were obtained using the diffractometer operated at $^1/_2$°/min with silicon as a standard. A Nelson-Riley extrapolation function[17] was used to calculate a_0 values. Sibling samples were prepared for SEM examination using standard ceramographic procedures.

Results of the X-ray analysis are given in Table II. Patterns

*Norelco, North American Philips Corp., New York, N.Y.

Table I. Oxide Powders Used to Prepare Compositions

Oxide	Nominal purity (%)	Particle size (μm)
ZrO_2*	98.6 (Zr + Hf)	2.8
Y_2O_3†	99.99	10
Al_2O_3‡	99+	0.3

*Zircoa A, Zircoa Products, Corning Glass Works, Solon, Ohio. †Code 99.99, Molybdenum Corporation of America, White Plains, N.Y. ‡Linde A, Union Carbide Corp., New York, N.Y.

Table II. X-Ray Results

Composition No.	Composition (mol%) ZrO_2	Y_2O_3	Al_2O_3	Phases identified* C	M	A	Y	YAG	YA	Y_2A	Cubic ZrO_2 lattice parameter, a_0(nm×10)
1	90	5	5	X	X	X					5.12
2	84	8	8	X		X					5.14
3	80	10	10	X		X					5.14
4	76	12	12	X		X		X			5.15
5	73	17	10	X		X		X			
6	65	25	10	X				X			5.17
7	53	32	15	X				X			5.24
8	40	40	20	X				X	X	X	5.24
9	35	10	55	X		X		X			5.15
10	25	50	25	X		X			X	X	5.24
11	20	60	20	X			X			X	5.24
12	15	70	15	X			X			X	
13	0	67	33				X		X	X	

*C = cubic ZrO_2, M = monoclinic ZrO_2 (implies tetragonal ZrO_2 at 1450°C), A = Al_2O_3 (corundum), Y = Y_2O_3 (cubic), YAG = $3Y_2O_3 \cdot 5Al_2O_3$ (garnet), YA = $AlYO_3$, and Y_2A = $2Y_2O_3 \cdot Al_2O_3$.

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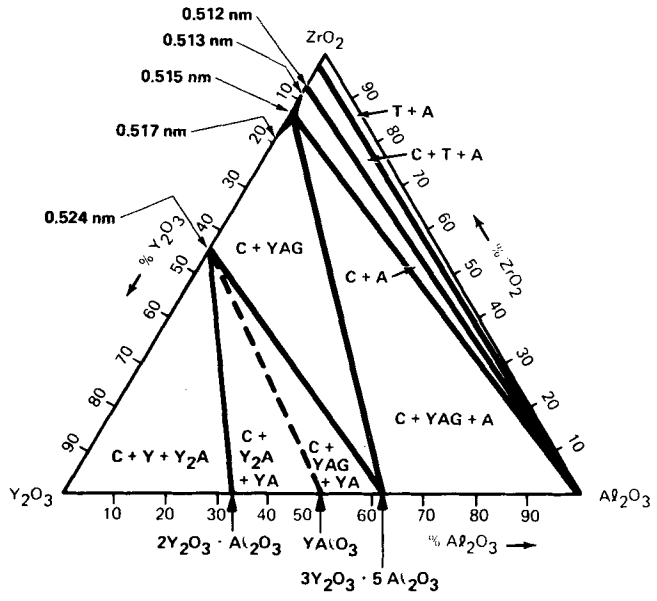

Fig. 1. Subsolidus phase equilibria in the system ZrO_2-Y_2O_3-Al_2O_3.

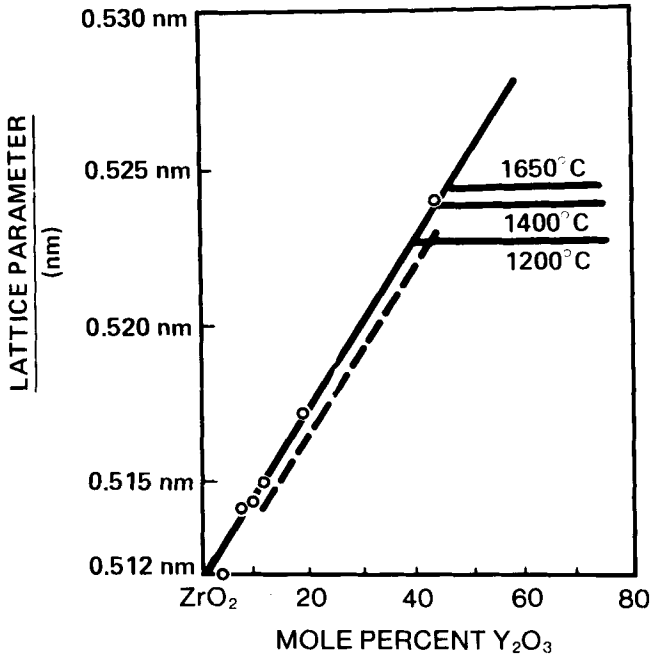

Fig. 2. Solid-solution lattice parameters vs mol% Y_2O_3; solid line from Ref. 15, dashed line from Ref. 8.

obtained from specimens fired isothermally at 1450°C and those fired using the 1650°/1450°C schedule were in agreement. However, patterns from the latter series were used to determine lattice parameters because of better line definition.

The ternary subsolidus phase relations are shown in Fig. 1. Two regions of two-phase equilibria (cubic $ZrO_2+Al_2O_3$ and cubic $ZrO_2+3Y_2O_3 \cdot 5Al_2O_3$) were observed. No change in lattice parameter with composition was noted for Al_2O_3 or $3Y_2O_3 \cdot 5Al_2O_3$. Consequently, it was assumed that solubility of cubic ZrO_2 in either phase was negligible; tie lines could then be drawn from these end-members through the sample compositions to the ZrO_2-Y_2O_3 binary side of the diagram.

The lattice parameters of the cubic solid solutions (Table II) are plotted as a function of the compositions predicted by the tie lines in Fig. 2. The data of Stubican *et al.*[15] and of Strickler and Carlson[8] are included in the figure for comparison. A constant value of the ZrO_2 lattice parameter (0.515 nm) was observed for compositions in the ZrO_2+garnet+corundum three-phase field. On the basis of Fig. 2, the apex of the compatibility triangle was located at ≈12 mol% Y_2O_3.

Microstructural observations by SEM were consistent with the X-ray diffraction data. Nondispersive X-ray analyses of the phases present in both the cubic $ZrO_2+Al_2O_3$ region and the cubic $ZrO_2+Al_2O_3+3Y_2O_3 \cdot 5Al_2O_3$ phase field substantiate ZrO_2 solid solubility below the limits of detection.

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Monolithic Multilayer Electromechanical Transducers for Optical Applications

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LASER-COMMUNICATION and information-processing systems have increased the need for simple electrically controllable micropositioners. Several of these needs have been met by using conventional piezoceramic materials; however, these materials often need very high driving voltages to develop the required displacements. They also lead to zero point drift due to aging and deaging under repeated field cycling.

Integral noble metal electrodes can be used to reduce the high driving voltage requirements in conventional piezoceramics. To explore this possibility, multilayer elements were fabricated from a low-hysteresis commercial PZT by using normal tape casting techniques.[1] The individual units consisted of 10 active layers

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