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Transformation Toughened Ceramics for the Heavy Duty Diesel Engine Technology Program

S. Musikant, E. Feingold,
H. Rauch, and S. Samanta
General Electric Company

October 1984

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SECTION 1

INTRODUCTION AND SUMMARY

The overall objective of this three phase program is to develop a transformation toughened TT structural ceramic with improved high temperature properties, and to scale up the material to a full size component for evaluation of suitability in the Heavy Duty Diesel Engine Technology Program.

In Phase I, a number of ceramics, mainly mullite ($3Al_2O_3.2SiO_2$) and alumina (Al_2O_3), were toughened by additions of 1:1 molar ZrO_2 - HfO_2 solid solution. The best processes to accomplish this were investigated. A small effort on TT SiAlON was initiated but discontinued due to the complexity of that system.

Specimens were fabricated and characterized at room temperature and elevated temperatures for modulus of rupture, fracture toughness (K_{Ic}), expansion coefficient, and thermal diffusivity. Thermal conductivities were calculated from diffusivity, specific heat and density.

As a result of these studies, a decision was made to proceed with Phase II, concentrating on process development of the TT mullite. A strong factor in this decision is the much lower thermal conductivity of the mullite (near that of ZrO_2) and its consequent direct applicability to the "adiabatic" diesel engine. During Phase II, a component will be designed in coordination with a diesel engine development organization (to be selected later in the program). The component selected (such as a piston cap) will be fabricated, for engine testing.

This report covers the development work performed during Phase I.

SECTION 2

TRANSFORMATION TOUGHENING

ZrO_2, HfO_2 and solid solutions of ZrO_2-HfO_2 exist in two phases below 2300°C: low temperature monoclinic and high temperature tetragonal. Transformation toughening by ZrO_2 depends on the metastable retention of the tetragonal phase and the thermal tetragonal monoclinic (t→m) transformation of the ZrO_2 particles with an increase in the volume of the transforming particles under the influence of an advancing macrocrack. This process is represented schematically in Figure 1. Near the t→m equilibrium temperature transformation toughening does not occur because the reaction takes place thermally.

Addition of HfO_2 to the ZrO_2 in the form of a ZrO_2-HfO_2 solid solution is expected to elevate the temperature where the t→m transformation takes place thermally and thus increase the temperature range where transformation toughening is effective.

The three matrixes chosen for study were alumina, mullite and SiAlON, but most of the work accomplished to date has been on the alumina and mullite. The ZrO_2-SiAlON reactions are complex and an early decision was made to drop this candidate.

The temperature of interest for engine applications extends to 2500°F (1371°C), although diesel operation is generally limited to temperatures $<$ 1500°F (814°C). For ZrO_2, the equilibrium temperature for the monoclinic: tetragonal phase transition is about 1000°C (1832°F) during heat up. ZrO_2 and HfO_2 have similar properties and form solid solutions at all compositions. The tetragonal: monoclinic transformation for HfO_2 occurs at 1740°C (3164°F). Figure 2 shows the phase diagram for the ZrO_2-HfO_2 system. A ZrO_2-HfO_2 (1:1 molar) solid solution has a transformation temperature of 1420°C (2588°F). In this program the 1:1 molar ZrO_2-HfO_2 was selected as the toughening agent.

SECTION 3

EXPERIMENTAL PLAN

The experimental plan comprised:

(1) Incorporating a 1:1 molar ZrO_2-HfO_2 ($Zr_{0.5}Hf_{0.5}O_2$) solid solution in the selected matrix materials. The optimum range of additives is 10-20%, based on prior work by others$^{(1)*}$. Bodies are densified by cold pressing and sintering in air at 1620°C.

(2) Determining by x-ray diffraction the fraction of retained tetragonal phase in the sintered bodies.

The fraction of retained tetragonal in the toughening agent is determined by x-ray diffraction$^{(2)}$. The diffracted x-ray intensities (I) from the monoclinic phase $(11\bar{1})_M$ and $(111)_M$ reflections are compared with the $(III)_T$ reflection from the tetragonal phase and the fraction of retained tetragonal phase is calculated by:

$$T/(T+M) = I_{(111)T} / (I_{(111)T} + I_{(111)M} + I_{(11\bar{1})M})$$

where T = fraction of tetragonal phase
M = fraction of monoclinic phase

(3) Characterizing the specimens by scanning electron microscopy and by room temperature fracture toughness using the indentation method of Evans and Charles$^{(3)}$.

(4) Characterizing the materials by four point bending as well as compression tests at room temperature, 700°C (1292°F) and 1200°C (2192°F) to assess the differences between ZrO_2 and $Zr_{0.5}Hf_{0.5}O_2$ additions.

* Numbers in superscript parentheses refer to references listed at end of text

SECTION 4

PROCESSING STUDIES

The major effort during the Phase I study was to develop techniques for incorporation of the HfO_2-ZrO_2 solid solution in the oxide matrixes, while maintaining the sub-micron second phase particle size at the completion of processing. The most successful approach was by preparing a precursor starting with a zirconium oxychloride and hafnium oxychloride solution and, via sol-gel processing, preparing a powder of the correct stoichiometry for incorporation in the oxide matrix. The alternate approach was to use a very fine particle of Zircar** zirconium oxide (unstabilized), 0.1μm average particle size, together with the HfO_2 derived from the hafnium oxychloride sol-gel procedure.

In the former process, the zirconium and hafnium oxychlorides in a 1:1 molar ratio are dissolved together, and a sol-gel process is performed. The gel is washed, dryed, and sintered to yield a 1:1 molar ZrO_2-HfO_2 precursor powder. The process for preparation of this powder is shown schematically in Figure 3.

The x-ray diffraction pattern for a mixture of ZrO_2 and HfO_2 each separately prepared by a similar sol-gel method is shown in Figure 4 (bottom).

The x-ray diffraction pattern for the 1:1 molar ZrO_2-HfO_2 powder is shown in Figure 4 (top). The shift of the monoclinic peaks to the left, and the elimination of the shoulder on the $(111)_M$ and $(11\bar{1})_M$ reflections serve as evidence that a solid solution was achieved.

The selection of matrix powders is critical. The powders need to be pure (so as not to disturb the transformation temperature of the t→m due to additions of unplanned elements), and fine grained since the ability to retain tetragonal phase in the matrix below the transformation temperature depends on the particle size (as well as shape). A number of alumina and mullite matrix precursor powders were investigated. The most satisfactory mullite source was from Baikowski International, Charlotte, NC. This mullite powder is fine grained and of high purity. A suitable alumina matrix precursor was found to the Union Carbide Linde Type A (0.3μm).

The compacts were made by combining the $Zr_{0.5}Hf_{0.5}O_2$ with the mullite or alumina matrix, cold pressing and sintering at 1620°C for 0.5 to 3 hours, or alternatively, by hot pressing at 1620°C. The various alternate processes are indicated in Figure 5.

** Zircar Products, Inc., Florida, New York

4.1 RETAINED TETRAGONAL PHASE

To detect the retained tetragonal phase after sintering, x-ray diffraction patterns of the specimens' surfaces were made. A typical pattern is shown in Figure 6 for 15 v/o ZrO_2 85 v/o Al_2O_3 material. The top pattern shows the presence of tetragonal phase (relative areas under the $(111)_T$ tetragonal peak compared to areas under the $(111)_M$ and $(111)_M$ monoclinic peaks. In this case, the fraction of tetragonal phase which is observed is 0.3 of the total ZrO_2 present or 0.3 x 0.15 = 0.045 of the total specimen.

After mechanically crushing the specimen, another x-ray diffraction pattern was made (bottom) showing that the tetragonal fraction remaining was only 0.08 of the ZrO_2 content. The stresses which had occurred during crushing had triggered most of the tetragonal phase to exhibit the martinsitic t→m transformation.

4.2 MICROSTRUCTURES

Figures 7 and 8 illustrate microstructures of the $Zr_{0.5}Hf_{0.5}O_2$ in alumina and in mullite, prepared by the sintering process. The second phase particle size was observed to be submicron for 3 of the 4 specimens shown. Table I provides a summary of grain size and retained tetragonal for these specimens.

In addition, data obtained from another program for 15 ^{v}/o ZrO_2 in mullite is shown as the last entry in Table I. For this material, 37% of the ZrO_2 second phase was retained tetragonal and the room temperature MOR of the specimen was measured to be 650 MPa with a $K_{Ic} \sim 4$.

SECTION 5

CHARACTERIZATION

5.1 FRACTURE TOUGHNESS

Table II shows room temperature hardness and K_{Ic} of selected specimens from the current study. The relationship between K_{Ic} and the fraction of retained tetragonal is striking. Figure 9 plots this relationship for specimens prepared on this program. Second phase particle size and density are also variables but were not differentiated in the plot. These samples all contained 15 ^{v}/o of the second phase. The second phase particle size and the ^{v}/o incorporated in the matrix can be optimized as a function of the host matrix.

One of the objectives of the study is to achieve an optimum K_{Ic} over the temperature range of interest.

5.2 PREPARATION OF SPECIMENS FOR MOR CHARACTERIZATION

The processes and starting materials which had produced the maximum ^{v}/o of retained tetragonal in the work described earlier were selected as the basis for fabrication of specimens for modulus of rupture (MOR) characterization. However, in lieu of cold pressing and air sintering, a hot pressing technique (using the same time and temperature as for sintering) was employed in an attempt to achieve higher density specimens. The parts were pressed in graphite dies and in flowing argon to produce billets approximately 1.75" diameter x 0.25" thickness.

The samples produced in this manner are described in Table III. The densities ranged from 96.7 to 99.5% of theoretical. However, the retained tetragonal for the 1:1 ZrO_2-HfO_2 solid solution containing specimens was lower than anticipated as summarized in Table IV.

The reasons for the decreased retained tetragonal in the hot pressed specimens are not identified at this writing. However, a reducing atmosphere engendered by the graphite dies may have been a factor.

5.3 MEASUREMENT OF MOR

Specimens were fabricated into flexure bars, 1.5" x 0.100" x 0.040" for four point bending tests. The MOR specimens were machined by an outside vendor. The quality of the bars was degraded due to severe edge chipping. The flex bars were deemed sufficiently poor to obviate any meaningful mechanical strength test. However, a number of bars $1^1/_4$" x $^1/_8$" x $^1/_8$" were also machined which were initially designed for compression testing. The machining was of an acceptable quality and therefore the specimens were diverted to bending tests. These were subjected to three point bending tests at room temperature. MOR and fracture toughness (by indent) were measured.

In addition, specimens of mullite 10 $^v/o$ $Zr_{0.5}Hf_{0.5}O_2$ and alumina 15 $^v/o$ $Zr_{0.5}Hf_{0.5}O_2$ were heat soaked at 1000°C for 100 hours in air and characterized at room temperature. The results of these mechanical tests are presented in Table IV-A. The mullite matrix materials exhibited modestly improved MOR and K_{Ic} for both ZrO_2 and $Zr_{0.5}Hf_{0.5}O_2$ toughening. However, the 100 hr/1000°C heat soak of the mullite -10 $^v/o$ $Zr_{0.5}Hf_{0.5}O_2$ specimen degraded the MOR to about the same level as the untoughened mullite specimens, although the K_{Ic} value was not diminished by the heat soak.

In the case of the alumina matrix specimens the ZrO_2 toughened specimens exhibited enhanced room temperature MOR although the $Zr_{0.5}Hf_{0.5}O_2$ toughened specimens showed lower MOR than the untoughened alumina. The heat soak of this latter sample enhanced the MOR, according to the measurements.

These results are somewhat ambiguous and additional characterization tests will be conducted in Phase II of this program.

5.4 THERMO PHYSICAL MEASUREMENTS

The effect of the t→m transformations on a specimen of mullite - 10 $Zr_{0.5}Hf_{0.5}O_2$ subjected to a dilitation test is shown in Figure 10. This sample had approximately 1.3 $^v/o$ retained tetragonal phase (as a % of the total volume of the specimen) after consolidation. On heating, at about 1000°C the retained tetragonal converts to monoclinic (t→m) as exhibited by the sudden increase in the slope of the heating curve. At about 1400°C the slope becomes negative due to the m→t reaction and the accompanying volume decrease. The coefficients of thermal expansion (CTE) were calculated for the temperature range below any of these transformations and are listed in Table V-B. The CTE's of the mullite materials are about 60% of those measured for the alumina matrix samples. Upon cooling, the t→m reaction is exhibited at about 1000°C.

Diffusivities of the mullite-10 $^v/o$ $Zr_{0.5}Hf_{0.5}O_2$ and of the alumina 15 $^v/o$ $Zr_{0.5}Hf_{0.5}O_2$ were measured by the flash diffusivity technique at three temperatures and the thermal conductivities were calculated from these values and literature values of densities and specific heats. The thermal conductivities and diffusivities are listed in Table V-B.

The thermal conductivity of the mullite matrix specimen is seen to be between 23% and 40% of the comparable alumina matrix specimen over the temperature range investigated.

5.5 COMPARISON OF MICROSTRUCTURES - HOT PRESSED VS SINTERED BILLETS

Figures 11 and 12 show respectively microstructures of sintered and hot pressed billets. In general, for the particular specimen examined, the hot pressed billets exhibit a more uniform particle size of second phase which are well distributed. A few large second phase grains are seen in the hot pressed specimens but not as many as appear in the sintered structures. These large grains will be minimized in the Phase II program. Typically, for the mullites, the grain size of the second phase particle in the specimens appear to be predominantly in the range of 0.5 to 1.5 µm. Figure 12A and 12B, before and after a 100 hour 1000°C heat soak, show no grain growth of the second phase. However, after thermal etching, subsequent examination showed grain growth of the mullite matrix.

Comparison of Figures 12A and 12 C indicates that the mullite-10 $^{v}/o$ $Zr_{0.5}Hf_{0.5}O_2$ and the mullite 10 $^{v}/o$ ZrO_2 have very similar microstructures.

SECTION 6

PLANNED WORK IN PHASE II

The objective of this three phase program is to develop a transformation toughened structural ceramic with improved high temperature properties and scale up the processes to fabricate full size components for diesel engine testing and evaluation.

During the first year Phase I of this study, the feasibility of using ZrO_2-HfO_2 solid solution as a toughening agent in mullite ($3 Al_2O_3 . 2 SiO_2$) and alumina (Al_2O_3) has been demonstrated. Specimens of mullite and alumina containing 10-20v/o of ZrO_2-HfO_2 (1:1 molar) solid solution were fabricated by sintering or hot pressing at 1590-1620°C, characterized and tested for physical, mechanical and thermal properties. Significant toughening of both matrix materials was exhibited.

Based on the need for a low thermal conductivity and high thermal shock resistant ceramic in advanced diesel engines, transformation toughened (TT) mullite has been chosen as the candidate material. The second year Phase II efforts will concentrate on the optimization of processes and scale up for transformation toughened mullite. The materials will be characterized in sufficient detail to provide the component designer/user the data base necessary for design.

In addition, during Phase II, a component will be designed in coordination with a diesel engine development organization (to be selected). Also, processes will be scaled up and optimized to provide a technology base, which will lead to the third year Phase III effort to fabricate full scale components for diesel engine testing.

The Phase II second year effort consists of four tasks plus a reporting task. The four technical tasks are described below:

TASK 1 PROCESS OPTIMIZATION

Process variable will be investigated to achieve high strength transformation toughened mullite. The variables to be investigated are:

1. Powder preparation method for mullite matrix material.
2. Powder preparation method for the toughening agent precursor $Zr_{0.5}Hf_{0.5}O_2$.
3. Composition, namely volume % of the second phase additive or toughening agent $Zr_{0.5}Hf_{0.5}O_2$.

4. Powder milling, blending and cold pressing (including isostatic pressing procedures.

5. Near net shape consolidation by sintering and/or HIP ing.

The resulting specimens will be characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Flexural strength or modulus of rupture, compressive strength and fracture toughness of the materials will be determined at room temperature as well as elevated temperatures. The characterizations will be repeated for specimens subjected to a thermal soak in air at 1000°C for 100 hours.

TASK 2 PROCESS SCALE UP

The best process developed in Task 1 will be scaled up to a size consistent with a diesel engine component. A typical size to be considered for scale up is a piston cap approximately 5 1/2" O.D. X 1/2" thick.

Billets will be fabricated to the scaled up dimensions and test specimens will be cut from these billets for detailed characterization (Task 3).

TASK 3 CHARACTERIZATION

The scaled up billets will be characterized as follows:

1. Microstructure by SEM

2. Modulus of rupture at RT, 500°C, 1000°C, and 1200°C.

3. Compressive strength at RT, 500°C, 1000°C, and 1200°C.

4. Fracture toughness at RT by indentation technique and fracture toughness at RT, 500°C, 1000°C, and 1200°C by Single Edge Notched Beam (SENB) method.

5. Coefficient of thermal expansion RT to 1200°C.

6. Thermal conductivity at 110°C, 700°C and 1250°C.

TASK 4 DESIGN SUPPORT

During the design phase of the diesel engine component for test and evaluation, materials properties and technical data will be provided on a consulting basis to the diesel engine organization performing the design task as directed by NASA.

During the third year of the program, Phase III (government option) will be directed at fabricating a number of full scale components from the best material developed during Phase II.

SECTION 7

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3 "Fracture Toughness Determinations by Indentation", A.G. Evans, E.A. Charles, J. Am. Ceramic Society, V59, No. 7-8, (1976), pp. 371-372

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TABLE I GRAIN SIZE OF 2ND PHASE PARTICLES BY SEM

COMPOSITION		DENSITY % THEORETICAL	2ND PHASE APPROX. GRAIN SIZE μM	RETAINED TETRAGONAL (BY XRD)	
MATRIX	2ND PHASE			AS % OF 2ND PHASE	AS % OF TOTAL VOLUME
MULLITE (# 081883A-1)	15 $^{V}/O$ ZrO_2	97.3	0.3	15	3.0
MULLITE (# 081983A-2)	15 $^{V}/O$ $Zr_{0.5}Hf_{0.5}O_2$	$\sim$95	1.3	16	2.4
ALUMINA (# 081883B-1)	15 $^{V}/O$ $Zr_{0.5}Hf_{0.5}O_2$	94.1	0.6	18	2.7
ALUMINA (# 081883C-1)	15 $^{V}/O$ $Zr_{0.5}Hf_{0.5}O_2$	94.9	0.4	39	5.9
MULLITE PROCHAZKA GE-CRD MOR = 650 MPa	15 $^{V}/O$ ZrO_2	$>$98		37	5.6

TABLE II HARDNESS AND K_{1C} OF SELECTED SPECIMENS

MATERIAL	DENSITY % THEORETICAL	CONDITION	DPH (GPa)	K_{IC} (MPa $\sqrt{m}$)	RETAINED TETRAGONAL FRACTION OF TOTAL ZrO_2 + HfO_2
MULLITE (THIS STUDY)	~ 98	AS POLISHED AND ANNEALED AT 1620C/20 MIN.	10.2	1.83	-
MULLITE - 15 $^{V}/O$ ZH*	98	AS POLISHED AND ANNEALED AT 1620C/20 MIN.	10.2	2.61	0.22
MULLITE - 15 $^{V}/O$ ZH*	97	AS POLISHED AND ANNEALED AT 1620C/20 MIN.	11.6	2.17	0.11
Al_2O_3 (TYPICAL)				3.5	-
Al_2O_3 - 15 $^{V}/O$ ZH*	95	AS POLISHED AND ANNEALED AT 1620C/20 MIN.	15.1	4.58	0.36
MULLITE - 15 $^{V}/O$ ZrO_2		AS POLISHED AND ANNEALED AT 1620C/20 MIN.	10.6	3.55	0.55
Al_2O_3 - 15 $^{V}/O$ ZrO_2		AS POLISHED AND ANNEALED AT 1620C/20 MIN.	11.0	6.24	0.41

* ZH = $Zr_{0.5}Hf_{0.5}O_2$

TABLE III DESCRIPTION OF HOT PRESSED SPECIMENS

Specimen ID	Composition $^V/o$				Processing/Hot Pressing	Density of Hot-Pressed	Comments
	ZrO_2	HfO_2	Mullite	Al_2O_3	Conditions	Billets (% Theoretical)	
TTHP841 (5 billets)	5 (2)	5 (2)	90 (1)		Planetary ball milled 15 mins., hot pressed at 1610C/30 mins., 6200 PSI	99.0	.13 fraction tetragonal Phase retained
TTHP842 (2 billets)			100 (1)		" "	98.7	---
TTHP843 (2 billets)				100 (4)	Planetary ball milled 15 mins., hot pressed at 1590C/30 mins., 6200 PSI	98.3	---
TTHP844 (2 billets)	10 (3)		90 (1)		Planetary ball milled 15 mins., hot pressed at 1610C/30 mins., 6200 PSI	99.5	.56 fraction tetragonal Phase retained
TTHP845 (5 billets)	7.5 (2)	7.5 (2)		85 (4)	Planetary ball milled 15 mins., hot pressed at 1590C/30 mins., 6200 PSI	97.6	.10 fraction tetragonal Phase retained
TTHP846 (2 billets)	15 (3)			85 (4)	" "	96.7	.39 fraction tetragonal Phase retained

Note: All billets were hot-pressed in the form of 1.75" diameter x 0.25" thickness (approx.) discs.

(1) Baikowski Mullite, Planetary ball milled-wet 1-1/2 hrs., dried and further ball milled 15 minutes.
(2) ZrO_2-HfO_2 (1:1 molar) from Sol-gel oxychlorides, calcined 750C/2 hrs., wet ball milled 1 hour, dried and then ball milled 15 minutes.
(3) Zircar Zyp ZrO_2, unstabilized, 0.1μm
(4) Linde Type A 0.3μm Al_2O_3

TABLE IV

RETAINED TETRAGONAL PHASE IN SINTERED AND HOT PRESSED BILLETS

Composition			Fraction of Retained Tetragonal	
v/o ZrO_2	v/o $Zr_{0.5}Hf_{0.5}O_2$	Matrix	Hot Press *	Sinter**
	10	Mullite	0.13	0.32
	15	Alumina	0.10	0.31
10		Mullite	0.56	0.72
15		Mullite		0.55
15		Alumina	0.39	0.75

---

* Hot Pressed 1610°C/ 1hour 1 3/4" dia x 1/4"th. disc.

** Sintered 1610°C/1/2 hour 1" long x 1/4" x 1/4" bar

TABLE V-A MECHANICAL CHARACTERIZATION DATA FOR MULLITE AND ALUMINA SPECIMENS

BILLET DESCRIPTION	BILLET NO	FRACTION RETAINED TETRAGONAL PHASE	V/O RETAINED TETRAGONAL PHASE	AS FABRICATED ROOM TEMP		AFTER HEAT SOAK 100 HR/1000C ROOM TEMP		AS FABRICATED ROOM TEMP		AFTER HEAT SOAK 100 HR/1000C ROOM TEMP	
				E GPa	MOR MPa	E GPa	MOR MPa	K_{IC} $MPa\sqrt{m}$	DPH GPa	K_{IC} $MPa\sqrt{m}$	DPH GPa
MULLITE	TTHP842	N/A	N/A	212	290			1.88	12.4		
MULLITE + 10 $V/_0$ ZrO_2	TTHP844	.56	5.6	209	365*			2.75	11.7		
MULLITE + 10 $V/_0(Zr_{0.5}Hf_{0.5}O_2)$	TTHP841	.13	1.3	199	340	225	274	2.22	11.7	2.30	10.5
ALUMINA	TTHP843	N/A	N/A	363	327*			1.98	17.7		
ALUMINA + 15 $V/_0$ ZrO_2	TTHP846	.39	5.9		424						
ALUMINA + 15 $V/_0(Zr_{0.5}Hf_{0.5}O_2)$	TTHP845	.10	1.5		275		393				

NOTES

K_{IC} BY INDENT METHOD

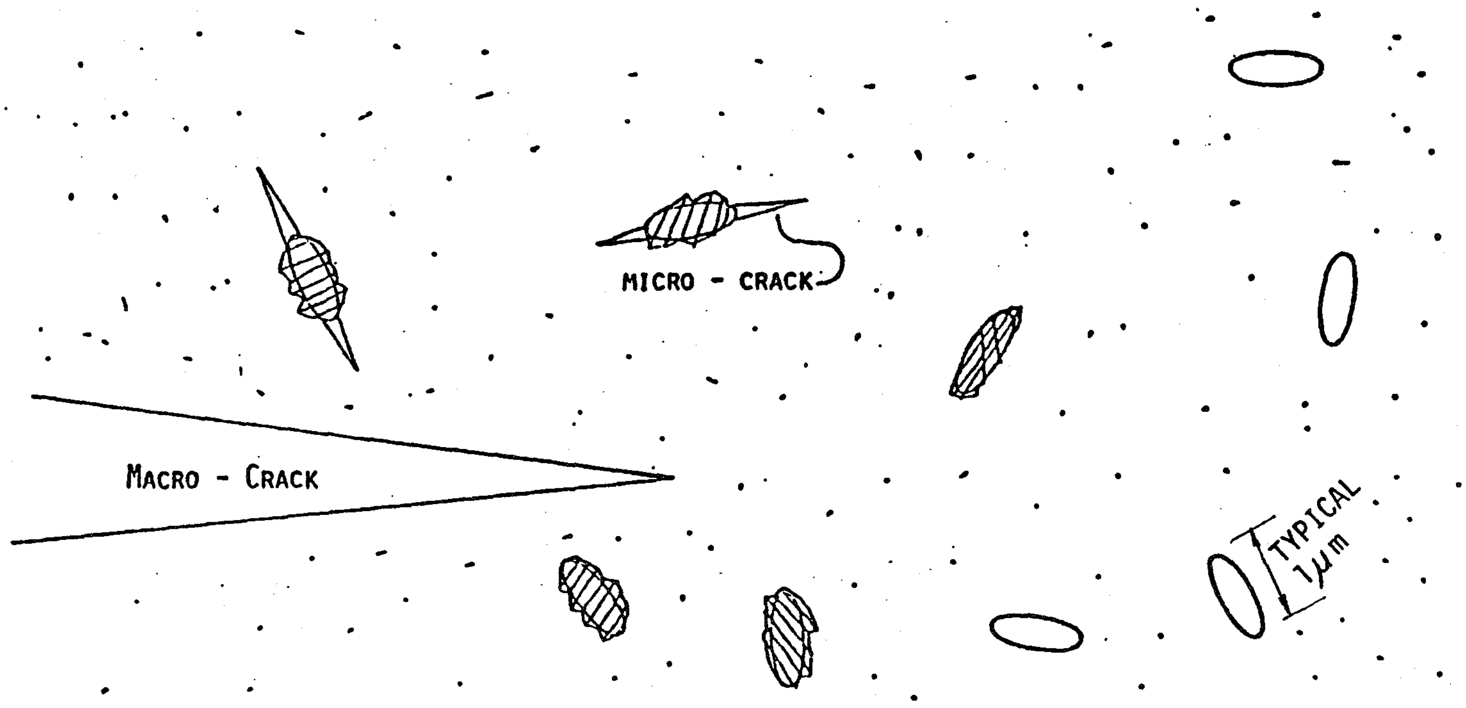
MOR AND E BY 3 POINT BEND TEST 1.0"SPAN, SPEC SIZE 1.25" X 1.25" x 1.25"

FRACTION RETAINED TETRAGONAL PHASE BY X RAY DIFFRACTION

ALL VALUES OF MECHANICAL PROPERTIES ARE AVERAGE OF THREE SPECIMENS EXCEPT WHERE INDICATED BY * IN WHICH CASE ARE THE AVERAGE OF TWO SPECIMENS

TABLE V-B THERMOPHYSICAL CHARACTERIZATION DATA FOR MULLITE AND ALUMINA SPECIMENS

BILLET DESCRIPTION	BILLET NO	FRACTION RETAINED TETRAGONAL PHASE	V/O RETAINED TETRAGONAL PHASE	THERMAL CONDUCTIVITY - CAL/SEC°C CM (THERMAL DIFFUSIVITY - CM^2/SEC)			LINEAR COEFFICIENT OF EXPANSION $°C^{-1} \times 10^6$
				110°C	700°C	1250°C	
MULLITE	TTHP342	N/A	N/A				5.0
MULLITE + 10 $V/_0$ ZrO_2	TTHP844	.56	5.6				5.8
MULLITE + 10 $V/_0(Zr_{0.5}Hf_{0.5}O_2)$	TTHP841	.13	2.0	0.0085 (0.0127)	0.0065 (0.0078)	0.0050 (0.0069)	5.0
ALUMINA	TTHP843	N/A	N/A				8.1
ALUMINA + 15 $V/_0$ ZrO_2	TTHP846	.39	5.9				8.0
ALUMINA + 15 $V/_0(Zr_{0.5}Hf_{0.5}O_2)$	TTHP845	.10	1.5	0.0362 (0.0417)	0.0136 (0.0120)	0.0126 (0.0101)	7.8



ZrO_2 TRANSFORMS IN STRESS FIELD OF CRACK TIP, TETRAGONAL → MONOCLINIC, + Δ V

COMPLEX STRESS AND STRAIN FIELD IMPEDES CRACK PROPAGATION

<u>CANDIDATE MATRIXES</u>	Al_2O_3	<u>TOUGHENER</u>	ZrO_2/HfO_2
	$3\ Al_2O_3 \cdot 2\ SiO_2$ (MULLITE)		SOLID SOLUTION
	SiALON		

FIGURE 1 SCHEMATIC - TRANSFORMATION TOUGHENING

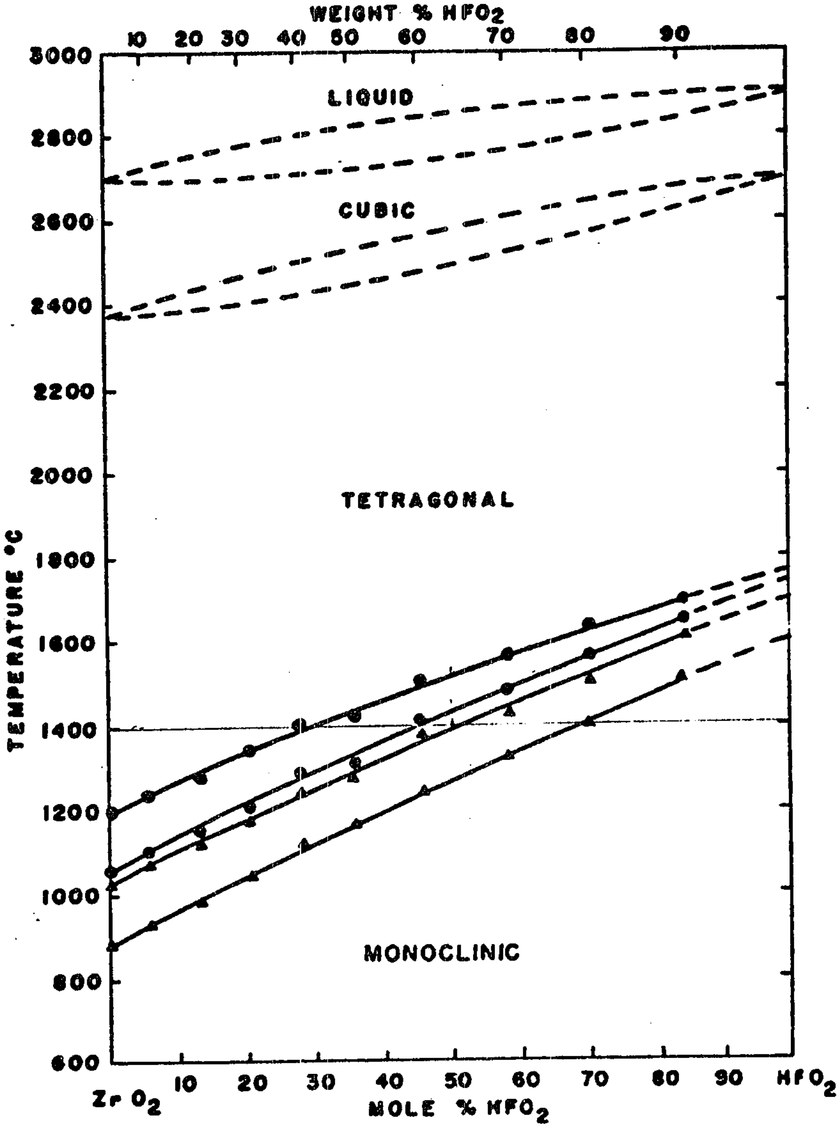


FIGURE 2 THE ZIRCONIA-HAFNIA SYSTEM (AFTER RUH ET AL.)

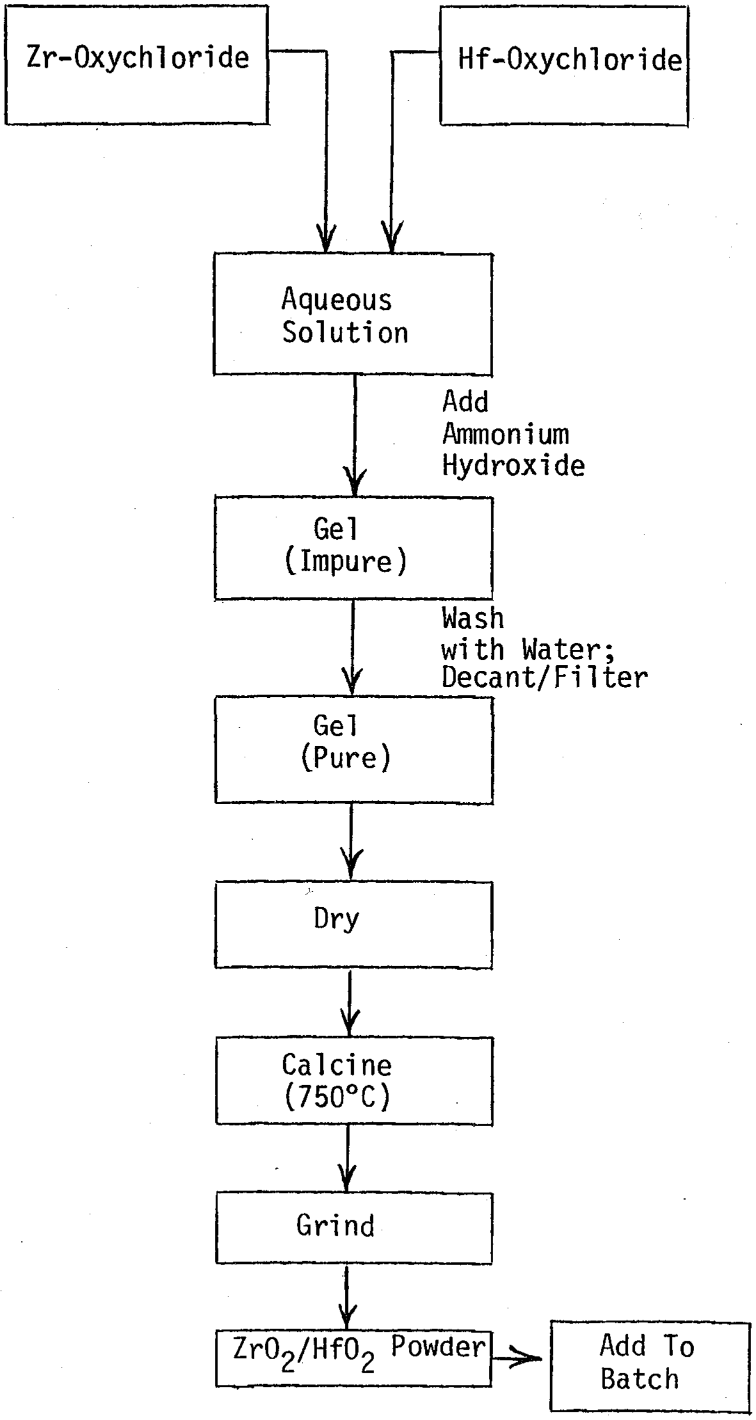
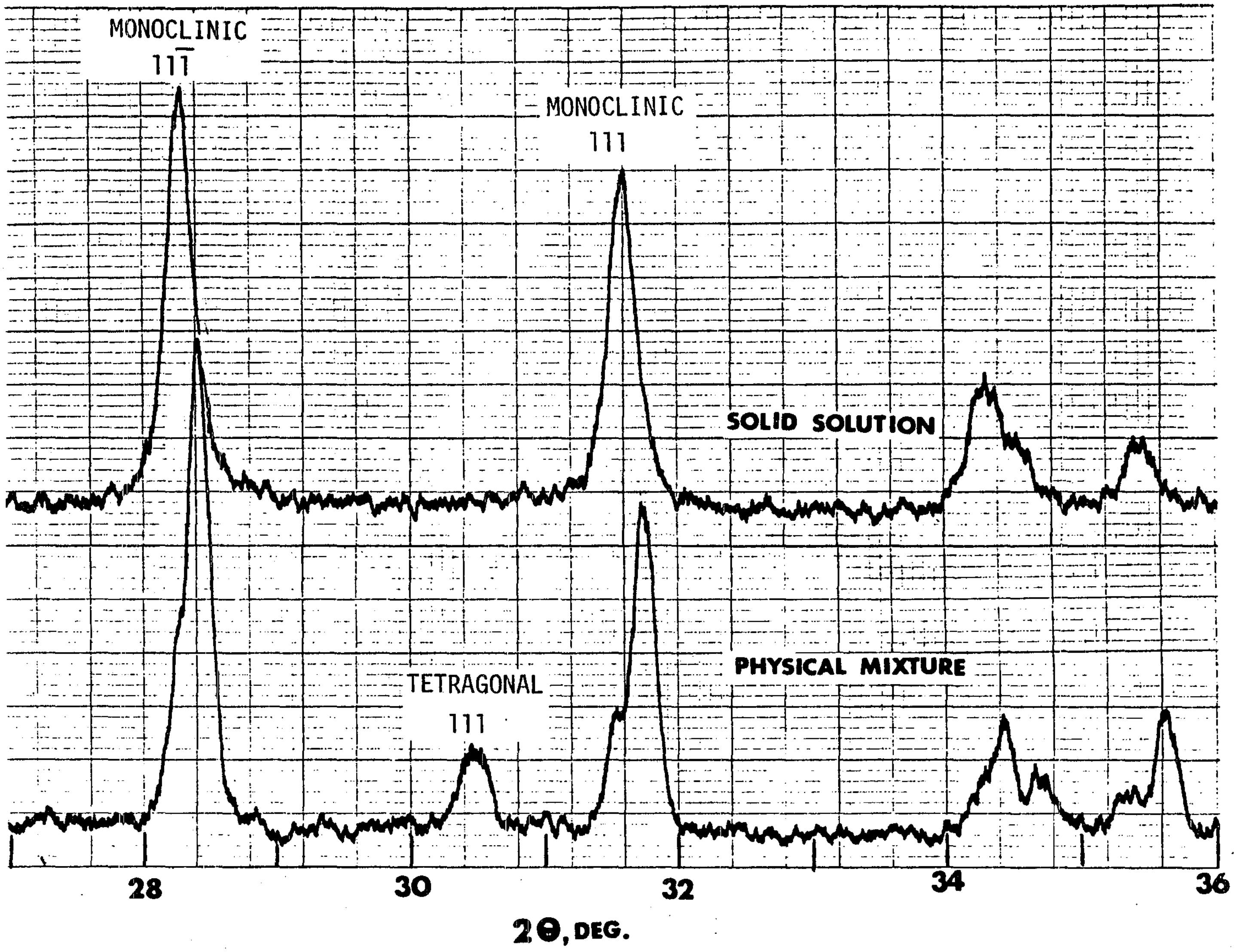


FIGURE 3 PREPARATION OF $(ZrO_2 + HfO_2)$ POWDER BY SOL-GEL METHOD



TOP: ZIRCONIA OXYCHLORIDE + HAFNIA OXYCHLORIDE } SOL-GEL, SINTER 1650/3 H

BOTTOM: ZIRCONIA OXYCHLORIDE, SOL-GEL, SINTER 1650/3 H + HAFNIA OXYCHLORIDE, SOL-GEL, SINTER 1650/3 H

FIGURE 4 X-RAY DIFFRACTION PATTERNS HfO_2/ZrO_2

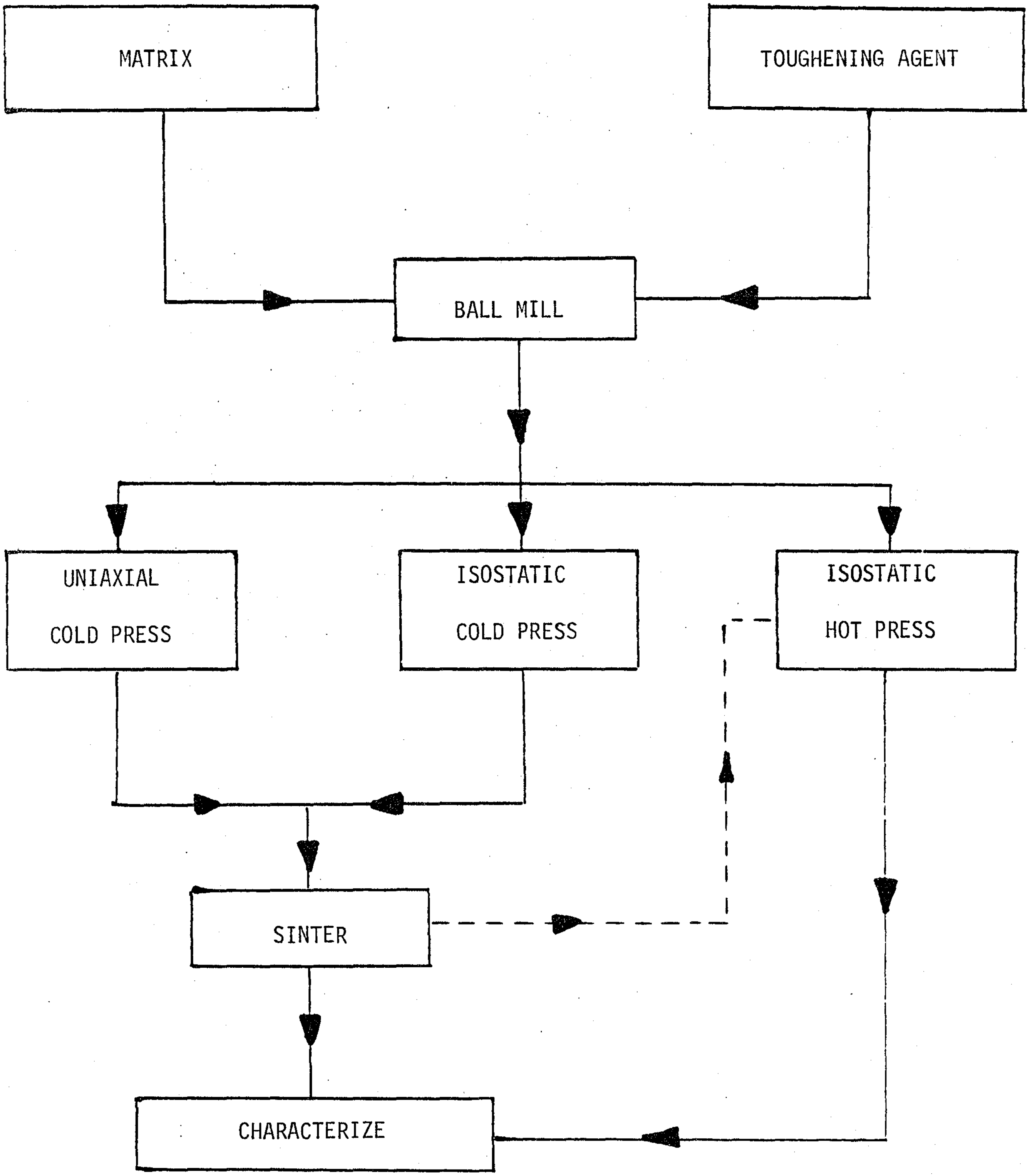
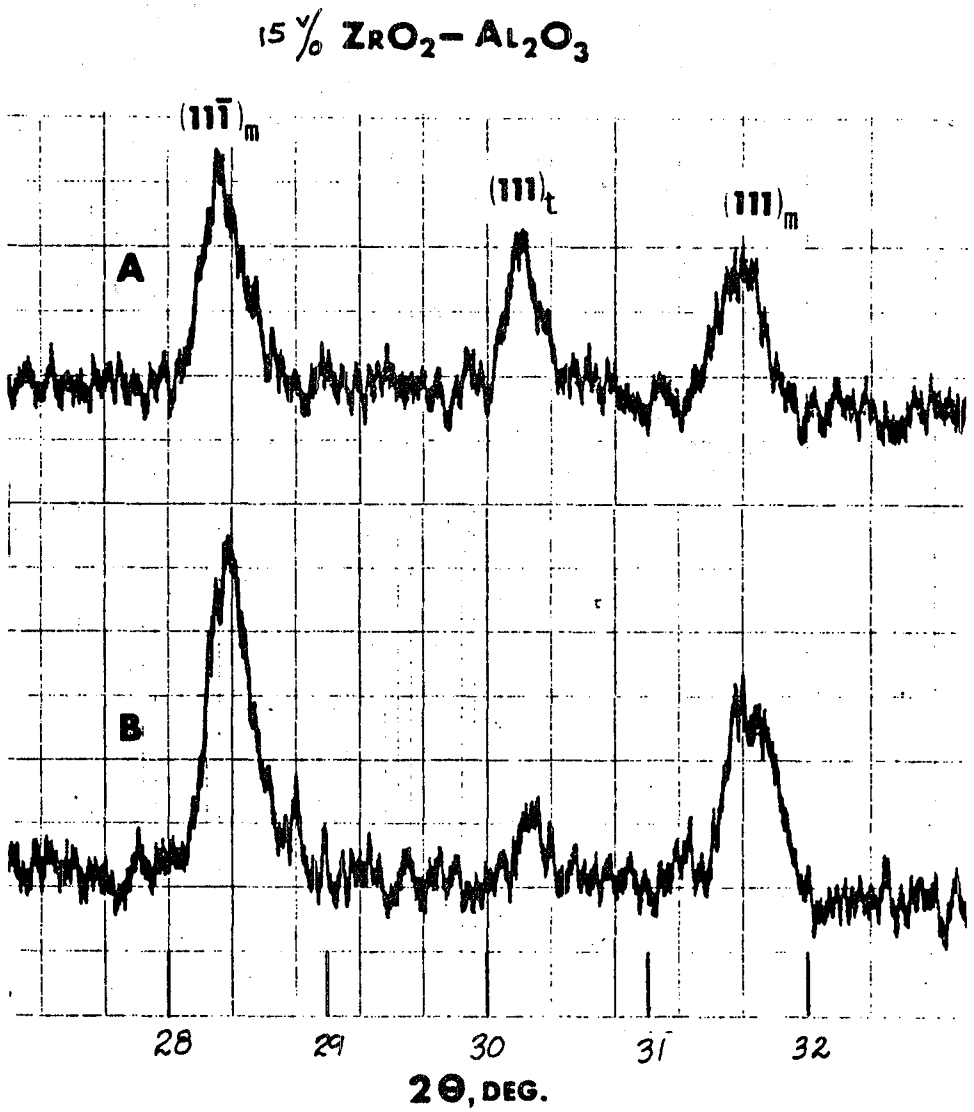


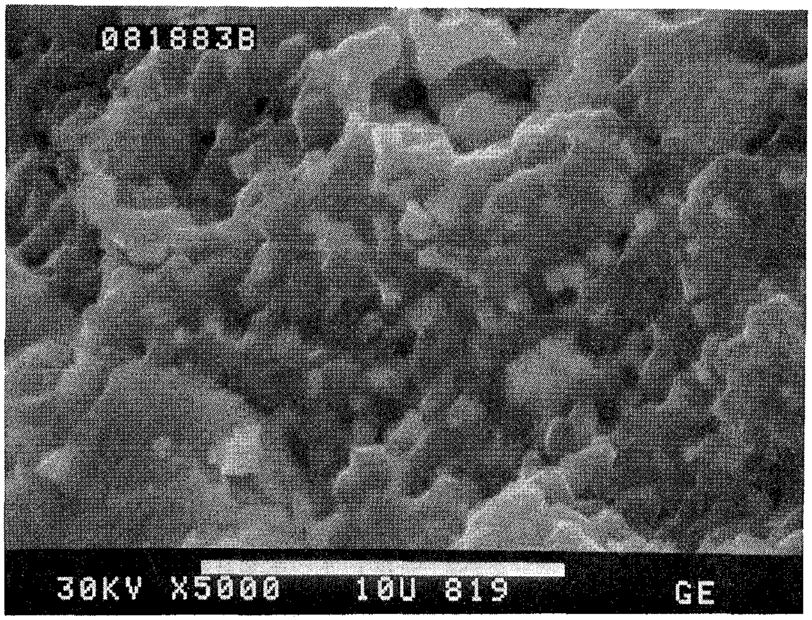
FIGURE 5 PROCESSING ROUTES



TOP: SHOWS PRESENCE OF TETRAGONAL PHASE AFTER SINTERING (0.30 FRACTION OF ZrO_2)

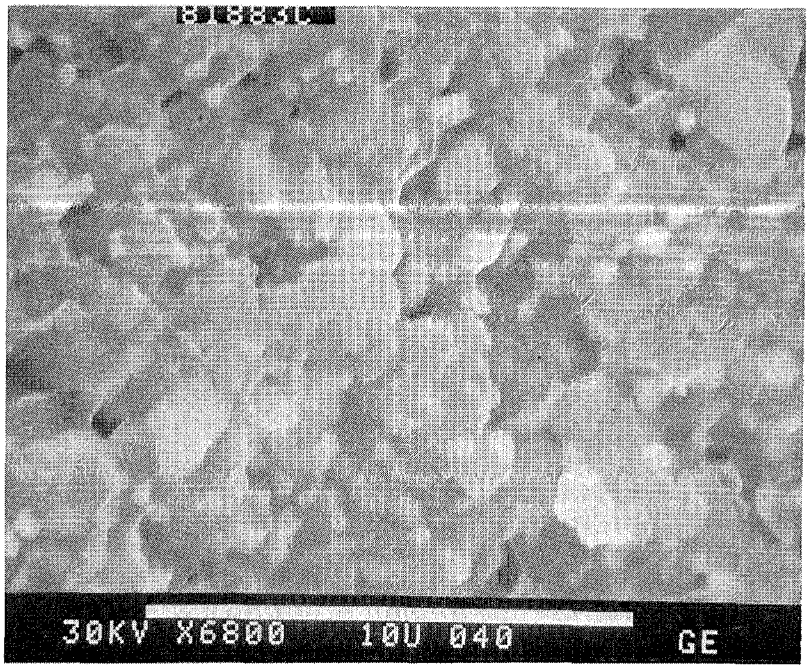
BOTTOM: SHOWS REDUCED TETRAGONAL PHASE AFTER MECHANICAL CRUSHING (0.08 FRACTION OF ZrO_2)

FIGURE 6 X-RAY DIFFRACTION PATTERNS - Al_2O_3 15 V/O ZrO_2



Spec. # 081883B-1

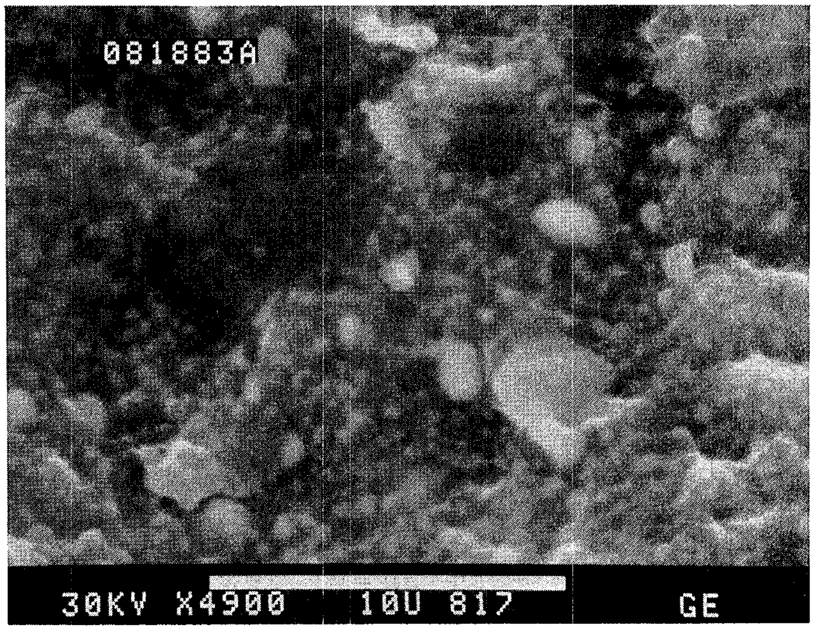
15 $^{V}/o$ (ZrO_2 - HfO_2) - Al_2O_3 Matrix



Spec. # 081883C-1

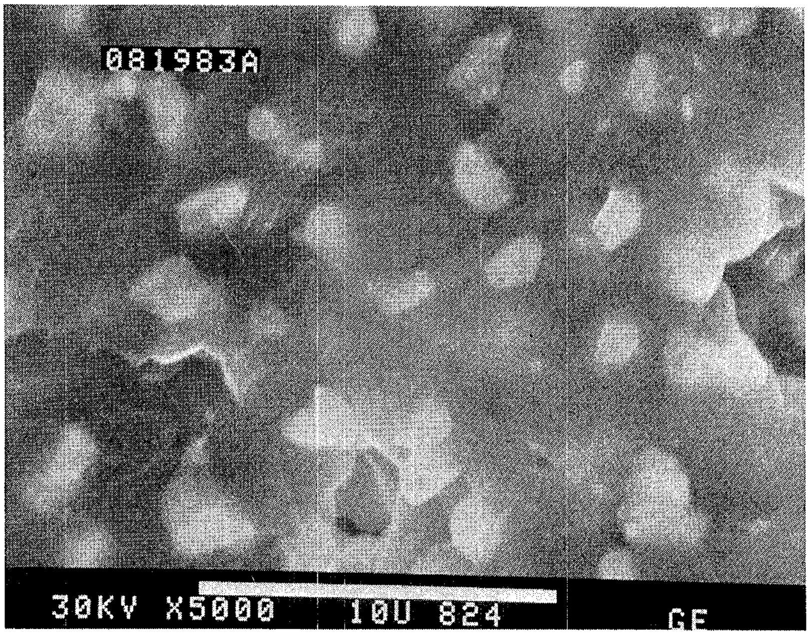
15 $^{V}/o$ (ZrO_2 - HfO_2) - Al_2O_3 Matrix

Figure 7: SEM ZrO_2 - HfO_2 - Al_2O_3 Specimens



Spec. # 081883A-1

15 V/o (ZrO_2 - HfO_2) - Mullite Matrix



Spec. # 081983A-2

15 V/o (ZrO_2 - HfO_2) - Mullite Matrix

Figure 8 : SEM ZrO_2 - HfO_2 - Mullite Specimens

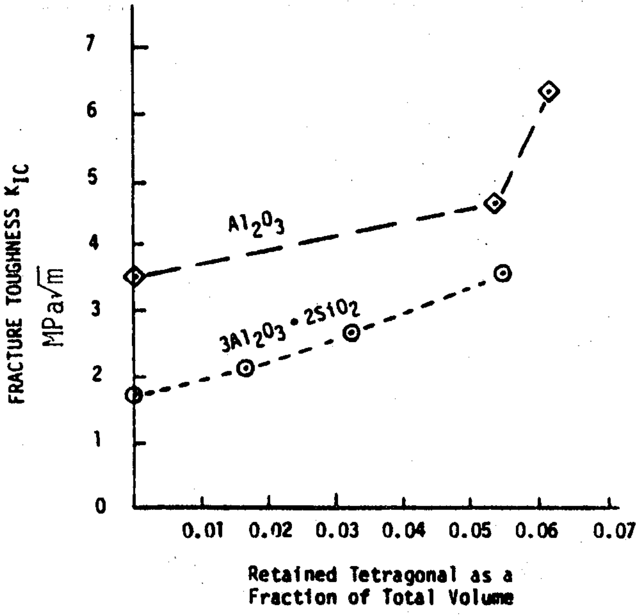


FIGURE 9 FRACTURE TOUGHNESS VS FRACTION OF RETAINED TETRAGONAL PHASE IN ALUMINA AND MULLITE

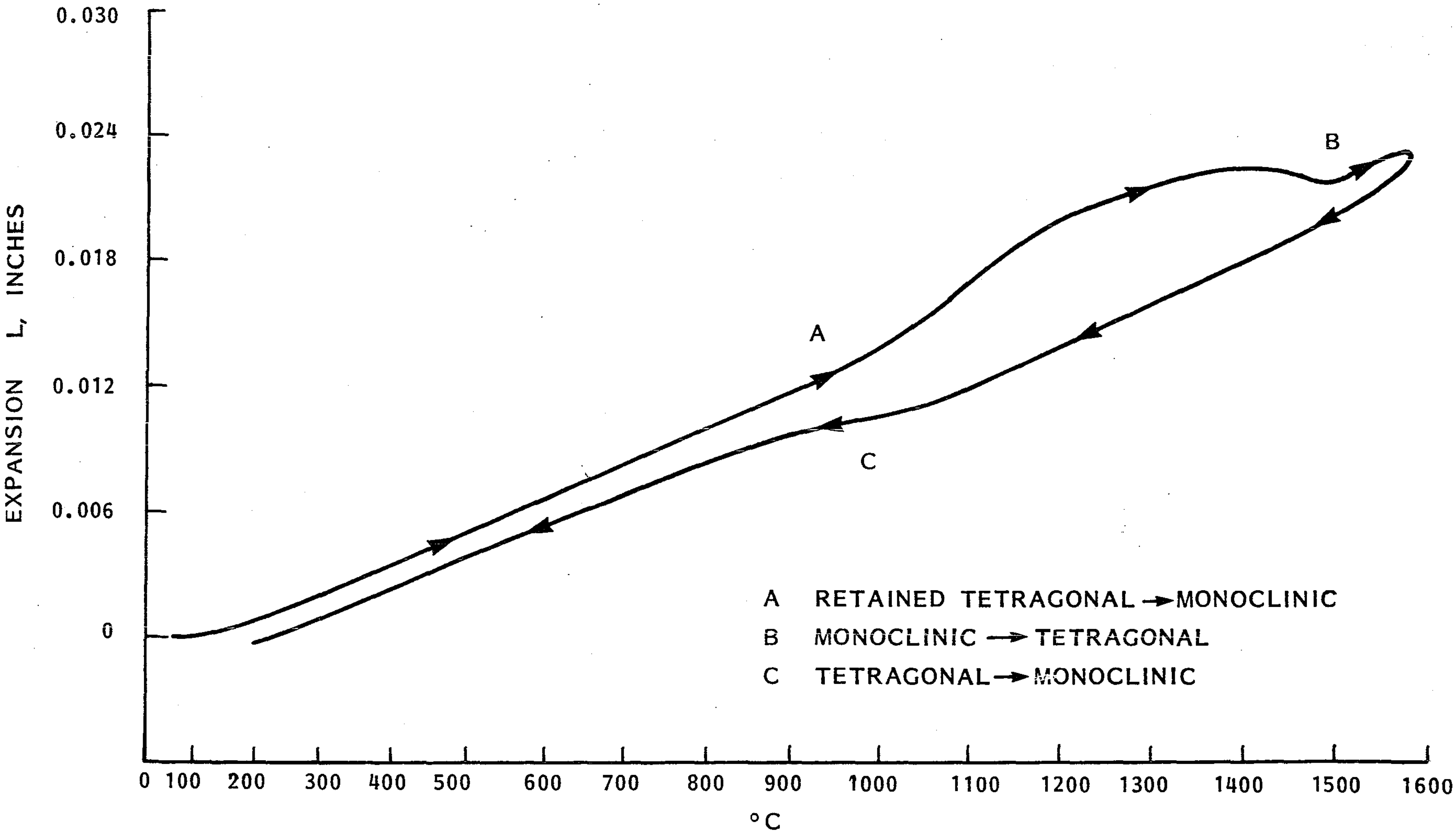


FIGURE 10 THERMAL EXPANSION BEHAVIOR OF MULLITE - 10 V/O $Zr_{0.5}Hf_{0.5}O_2$

SPECIMEN BAR 2" X 1/4" X 1/4"

SINTERED 1610C 30 MIN

(FABRICATED FROM SAME POWDER BATCH AS SPECIMEN NO. TTHP841, TABLE III

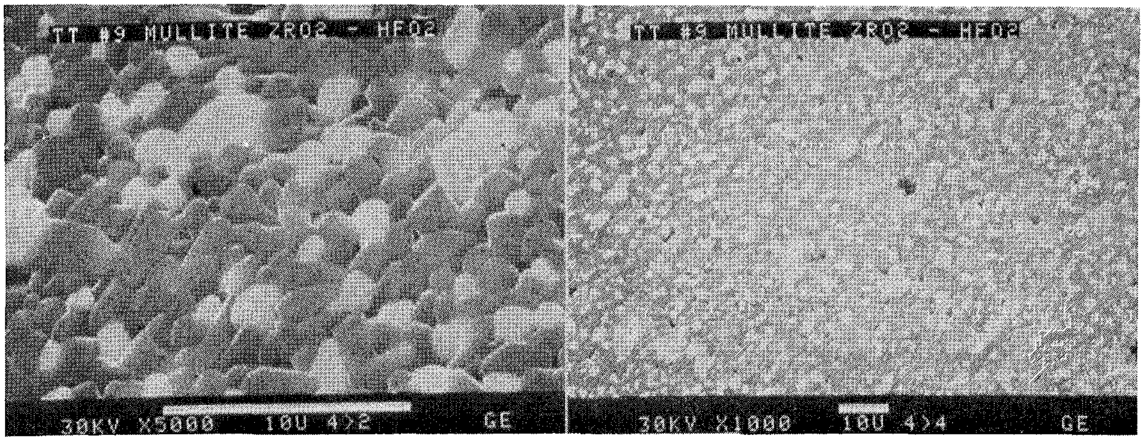


FIGURE 11 A MULLITE 15 v/o 1:1 ZrO$_2$/HfO$_2$
AS PROCESSED (SINTERED)
SPECIMEN TT 102183 M

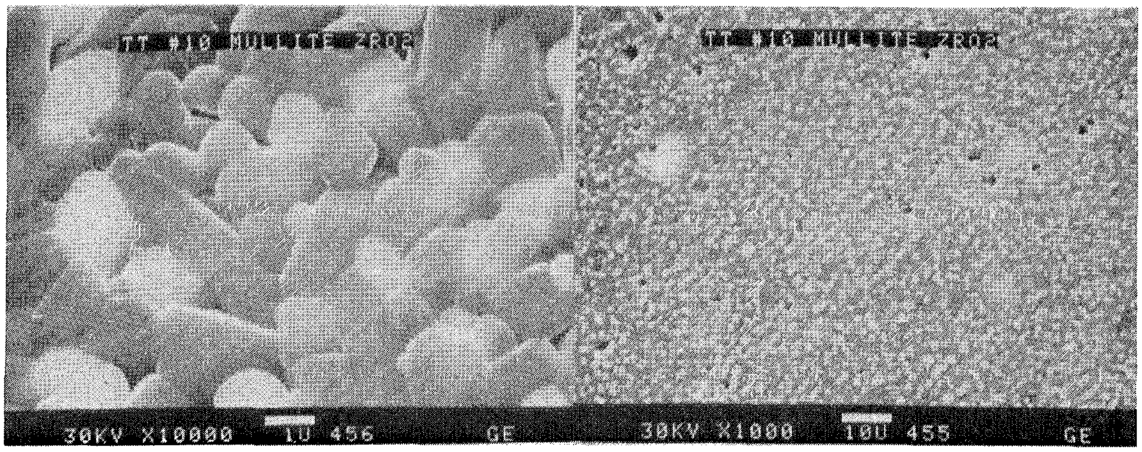


FIGURE 11 B MULLITE 15 v/o ZrO$_2$
AS PROCESSED (SINTERED)
SPECIMEN TT 100483 M

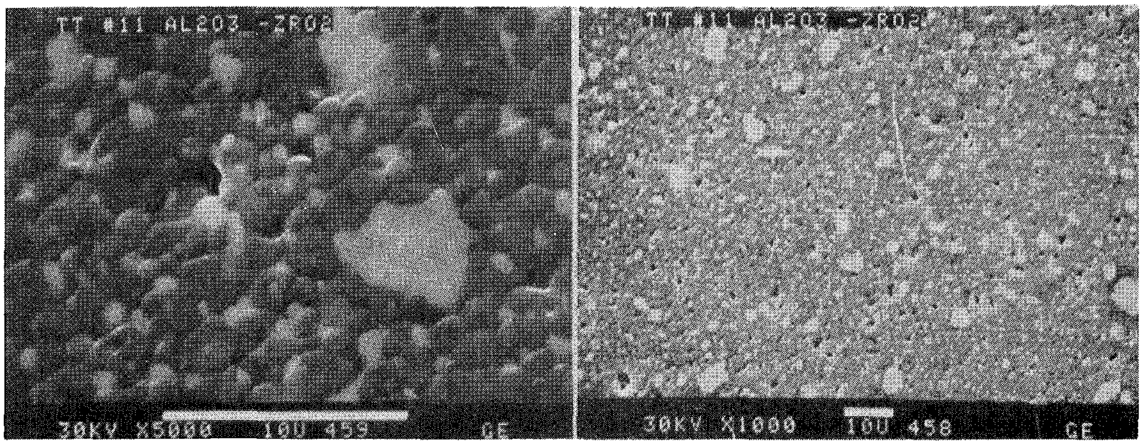


FIGURE 11 C ALUMINA 15 v/o ZrO$_2$
AS PROCESSED (SINTERED)
SPECIMEN TT 100583 A

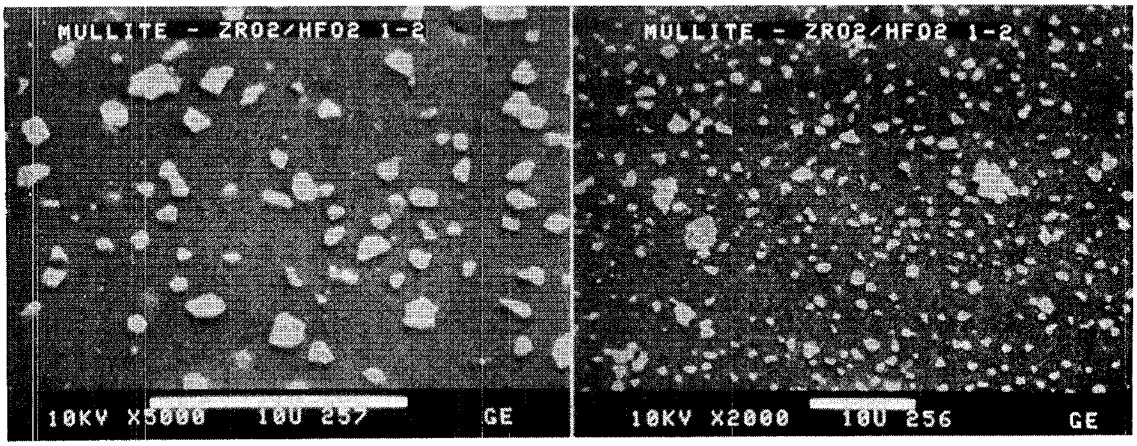


FIGURE 12 A MULLITE 10 v/o 1:1 ZrO_2/HfO_2
AS PROCESSED (HOT PRESSED)
BILLET NO. TT HP841

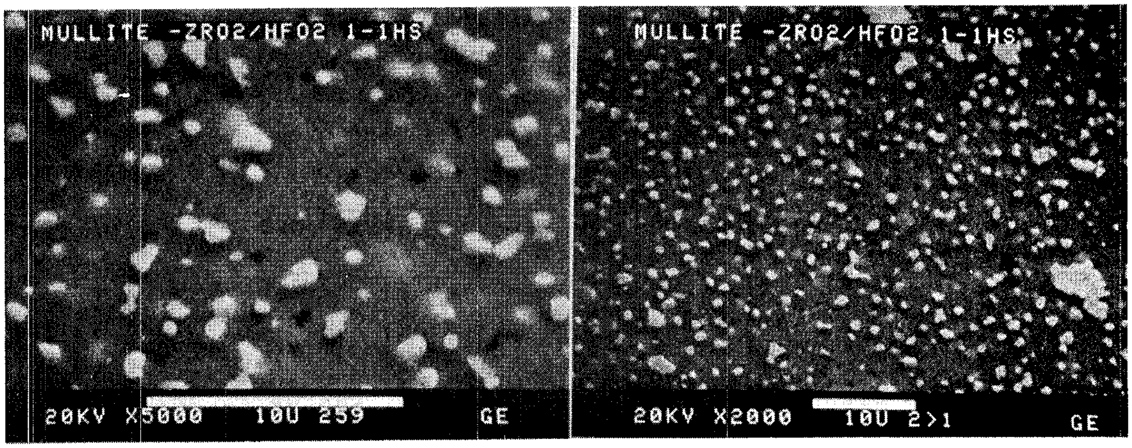


FIGURE 12 B MULLITE 10 v/o 1:1 ZrO_2/HfO_2 (HOT PRESSED)
AFTER 100 HR. SOAK AT 1000°C IN AIR
BILLET NO. TT HP841

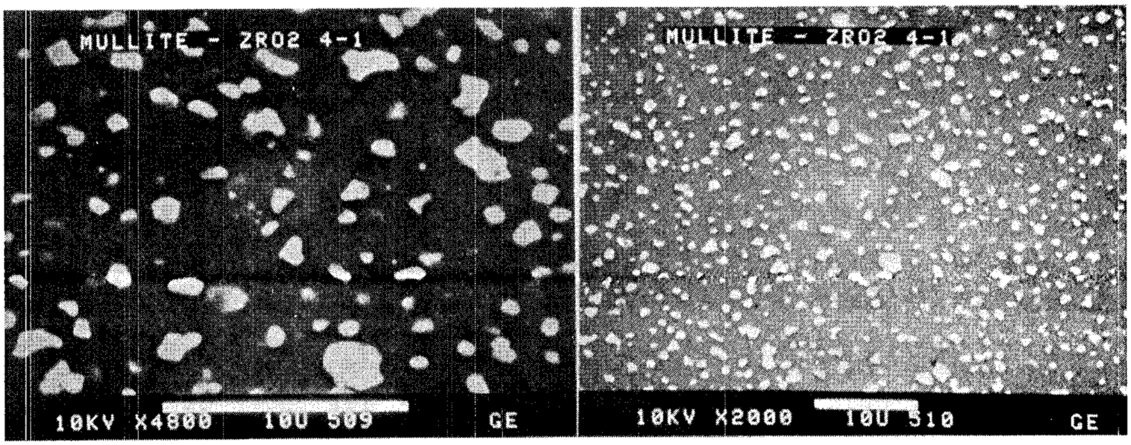


FIGURE 12 C MULLITE 10 v/o ZrO_2
AS PROCESSED (HOT PRESSED)
BILLET NO. TT HP844

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16. Abstract
The objective of this program is to develop an advanced high temperature oxide structural ceramic for application to the heavy duty diesel engine. The approach is to employ transformation toughening by additions of $Zr_{0.5}Hf_{0.5}O_2$ solid solution to the oxide ceramics, mullite ($3Al_2O_3S2SiO_2$) and alumina (Al_2O_3). The study is planned for three phases, each 12 months in duration. This report covers Phase I. During this period, processing techniques were developed to incorporate the $Zr_{0.5}Hf_{0.5}O_2$ solid solution in the matrices while retaining the necessary metastable tetragonal phase. Modulus of rupture and of elasticity, coefficient of thermal expansion, fracture toughness by indent technique and thermal diffusivity of representative specimens were measured. In Phase II, the process will be improved to provide higher mechanical strength and to define the techniques for scale up to component size. In Phase III, full scale component prototypes will be fabricated.

17. Key Words (Suggested by Author(s))
Heavy duty diesel engine; Ceramic materials; Adiabatic diesel; Ceramic components; Mullite; Alumina; Transformation toughening; Zirconia; Hafnia

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