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SUBSOLIDUS EQUILIBRIA AND METASTABLE PHASE DEVELOPMENT IN THE SYSTEM $ZrO_2-Al_2O_3-SiO_2$

by

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1975

Approved by

Charles A Sorrell Advisor

______________ Chairman

ABSTRACT

Subsolidus equilibria in the low silica portion of the system ZrO_2-Al_2O_3-SiO_2 were studied by X-ray diffraction of quenched samples fired at 1300°, 1400°, and 1480°C. Samples prepared as powders from combinations of α-Al_2O_3, $Al(OH)_3$, silicic acid, ZrO_2, and kaolinite reacted very slowly at 1300° and 1400°C and the trends toward equilibria are not apparent. A mixture of zircon and $Al(OH)_3$ reacted slowly at 1480°C to form mullite and ZrO_2, indicating that the latter phases are the stable assemblage rather than zircon and alumina. A gel prepared from aluminum nitrate, zirconyl nitrate, and colloidal silica reacted at 1480°C to form alumina, zirconia, zircon, and mullite; with continued firing, however, the zirconia and mullite developed further at the expense of aluminia and zircon. A tetragonal, pseudocubic, metastable phase developed in the calcined gel and was quite persistent, even at 1480°C.

Hypothetical ternary liquidus surfaces have been proposed on the basis of available binary data from the literature.

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I. INTRODUCTION

Phase equilibria data for the system ZrO_2-Al_2O_3-SiO_2 are important for interpretation of equilibrium or non-equilibrium crystallization in both sintered and fused ZAS refractories and of their behavior in service. Available subsolidus compatibility data are contradictory, however, and the only published phase diagram is not consistent with reported liquidus temperatures in the binary systems. This work was done to determine which of the two alternative subsolidus configurations is correct, to define non-equilibrium assemblages developed during solid state reaction which could explain the disagreement in the literature, and to suggest revisions of the liquidus surface consistent with subsolidus and binary equilibrium relationships.

II. REVIEW OF THE LITERATURE

The only melt equilibria data for the system ZrO_2-Al_2O_3-SiO_2 were obtained by Budnikov and Litvakovskii[1] and are restricted to the high alumina portion. As seen in Figure 1, the essential feature is the ternary eutectic at the intersection of the primary crystallization fields of ZrO_2, Al_2O_3, and mullite at $\sim 1800^{\circ}C$. The eutectic composition is at 53 wt % Al_2O_3, 30 wt % ZrO_2, and 17 wt % SiO_2, with compositional uncertainty estimated at $\pm$ 2.5 wt %. Mullite is shown as a congruently melting compound; the systems Al_2O_3-ZrO_2 and ZrO_2-SiO_2 are shown as simple eutectic systems. No primary crystallization field is shown for zircon, $ZrSiO_4$, and the only subsolidus join is between mullite and ZrO_2, indicating that zircon dissociates in the solid state to ZrO_2 and SiO_2. In the portion investigated, the isotherms are at considerable variance with available binary liquidus data and the inferred isotherms, shown as dashed lines, in the remainder of the system are totally unrealistic.

The binary system ZrO_2-SiO_2 has been the subject of many studies, with disagreement as to the extent of solid solutions in ZrO_2, the existence of liquid immiscibility, and the incongruent melting or solid state dissociation of zircon.

Geller and Lang[2] (Figure 2) showed zircon as an incongruently melting compound, with a peritectic at $1775^{\circ} \pm 10^{\circ}C$, $\sim 82\%$ SiO_2 , no liquid immiscibility, and $\sim 8\%$ SiO_2 in

Figure 1. The liquidus surface of the system ZrO_2-Al_2O_3-SiO_2 according to Budnikov and Litvakavskii.[1] Dashed lines are inferred isotherms.

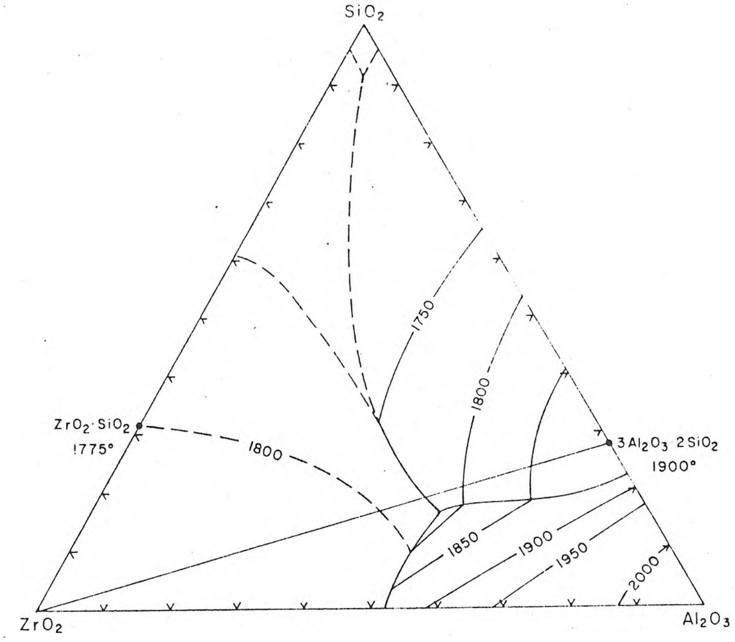

SiO2
ZrO2·SiO2
1775°
3Al2O3·2SiO2
1900°
1750
1800
1800
1850
1900
1950
2000
ZrO2
Al2O3

Figure 2. The system ZrO_2-SiO_2 according to Geller and Lang.[2] Dashed lines are inferred solubility limits.

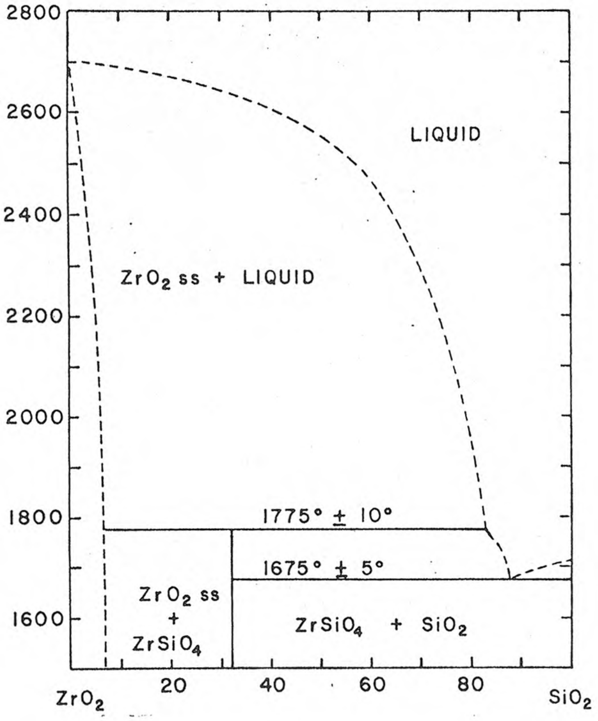
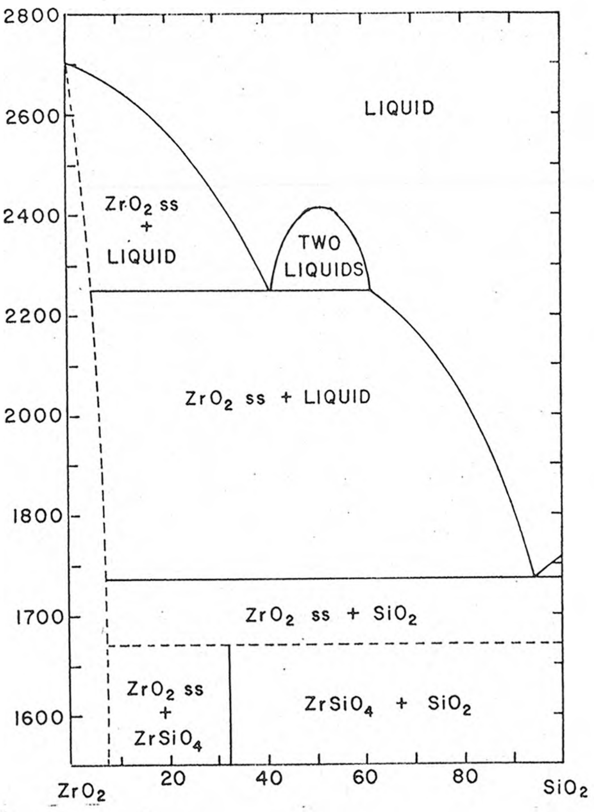

2800
2600
2400
2200
2000
1800
1600
LIQUID
ZrO2 ss + LIQUID
1775° ± 10°
1675° ± 5°
ZrO2 ss + ZrSiO4
ZrSiO4 + SiO2
ZrO2
20
40
60
80
SiO2

Figure 3. The system ZrO_2-SiO_2 according to Toropov and Galakhov.[3] Dashed line is inferred solid solubility limit.


2800
2600
2400
2200
2000
1800
1700
1600
LIQUID
ZrO$_2$ ss + LIQUID
TWO LIQUIDS
ZrO$_2$ ss + LIQUID
ZrO$_2$ ss + SiO$_2$
ZrO$_2$ ss + ZrSiO$_4$
ZrSiO$_4$ + SiO$_2$
ZrO$_2$
20
40
60
80
SiO$_2$

solid solution with ZrO_2. The binary eutectic was placed at 1675° ± 5°C; ∿88% SiO_2.

Toropov and Galakhov[3] (Figure 4) indicated that zircon dissociates in the solid state at ∿1670°C and that the eutectic between ZrO_2 and SiO_2 is at 1775°C; ∿94% SiO_2. They further indicated a liquid immiscibility field between 41% and 61% SiO_2 with a base at 2250°C and a consolute at 2430°C.

Butterman and Foster[4] (Figure 4) provided a thorough summary of available data and proposed a diagram which indicates solid state dissociation of zircon at 1676°C, a binary eutectic at ∿95% SiO_2; 1687°C, liquid immiscibility in accordance with Toropov and Galakhov, and no solid solution.

The system ZrO_2-Al_2O_3 has received little attention. Alper[5] (Figure 5) melted 16 samples in an induction furnace, using an argon atmosphere and setters having the same compositions as the samples. A eutectic is placed at ∿40 wt. % ZrO_2; ∿1880°C. Limited solid solution in both components is inferred. Though the solubility of ZrO_2 solid solution in the liquid is inferred, the negative curvature is marked, with addition of 20% Al_2O_3 lowering the liquidus by ∿500°C.

The system Al_2O_3-SiO_2 has long been problematical, particularly with regard to the compositional range and melting characteristics of mullite, $3Al_2O_3 \cdot 2SiO_2$. Aramaki and Roy[6] (Figure 6) reported mullite to melt congruently at ∿1850°C and placed the eutectics at ∿94 wt. % SiO_2;

Figure 4. The system ZrO_2-SiO_2 according to Butterman and Foster.[4]

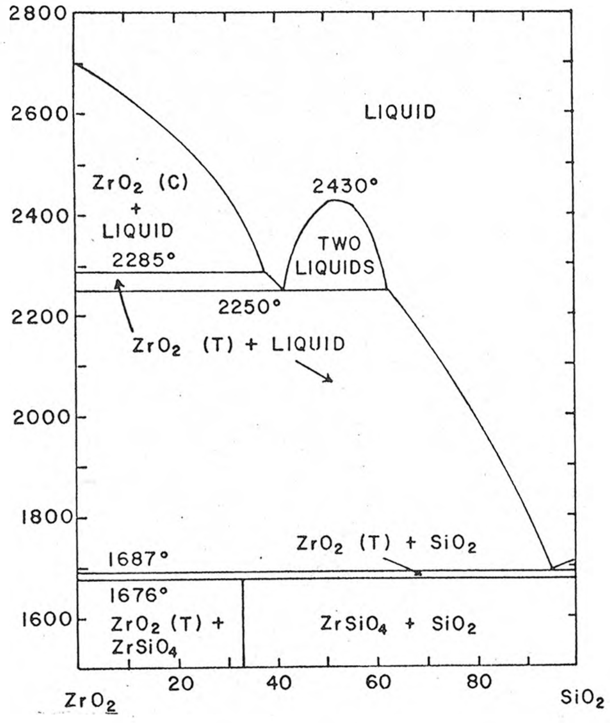

2800
2600
2400
2200
2000
1800
1600
LIQUID
ZrO2 (C) + LIQUID
2430°
TWO LIQUIDS
2285°
2250°
ZrO2 (T) + LIQUID
ZrO2 (T) + SiO2
1687°
1676°
ZrO2 (T) + ZrSiO4
ZrSiO4 + SiO2
20
40
60
80
ZrO2
SiO2

Figure 5. The system ZrO_2-Al_2O_3 according to Alper.[5] Dashed lines are inferred solubility limits.

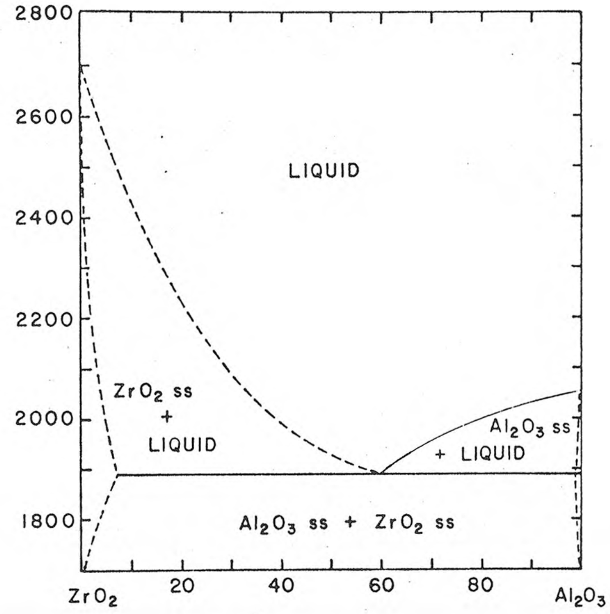
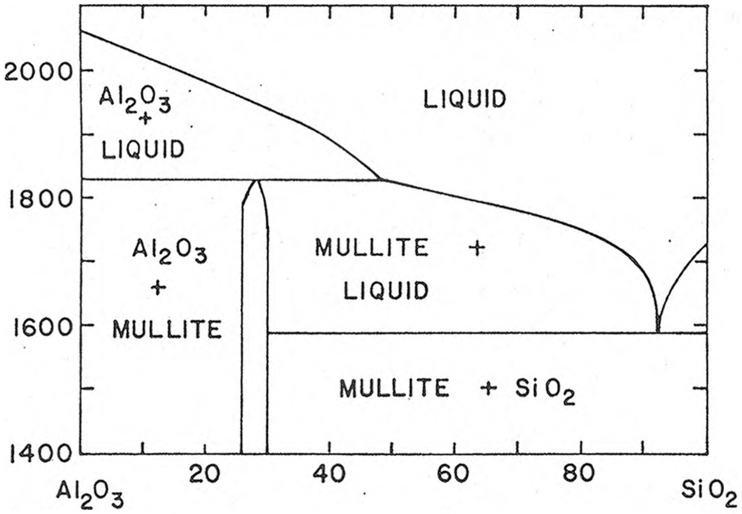

2800
2600
2400
2200
2000
1800
LIQUID
ZrO_2 ss + LIQUID
Al_2O_3 ss + LIQUID
Al_2O_3 ss + ZrO_2 ss
ZrO_2
20
40
60
80
Al_2O_3

Figure 6. The system Al_2O_3-SiO_2 according to Aramaki and Roy,[6] showing mullite as a congruently melting compound.


2000
1800
1600
1400
Al_2O_3
20
40
60
80
SiO_2
Al_2O_3 + LIQUID
LIQUID
Al_2O_3 + MULLITE
MULLITE + LIQUID
MULLITE + SiO_2

∿1590°C and ∿22 wt. % SiO_2; ∿1840°C. Their diagram was used as the standard by Osborn and Muan in preparation of the large scale phase diagrams published by the American Ceramic Society.

A considerably more detailed study of stable and metastable equilibria in the system Al_2O_3-SiO_2 has recently been reported by Aksay and Pask,[7] who showed (Figure 7) that mullite melts incongruently at 1828°±10°C, with the peritectic at ∿48 wt. % SiO_2. The eutectic was located at ∿9 wt. % SiO_2; 1587°±10°C. Metastable equilibrium curves for the system, showing the effects of superheating and supercooling, indicate, in general, the reasons for discrepancies among previous results.

If it is assumed that zircon dissociates in the solid state, as shown by Toropov and Galakhov[3] and by Butterman and Foster,[4] subsolidus compatibility immediately below the high-silica eutectic temperature must necessarily be as shown by Budnikov and Litvakovskii,[1] with a join between mullite and ZrO_2 (Figure 1). Below the dissociation temperature of zircon, however, there are two possible subsolidus compatibility configurations, as shown in Figure 8. In addition to the mullite - ZrO_2 join, which must be valid above the dissociation temperature of zircon, a join between mullite and zircon could be developed as a consequence of reaction between ZrO_2 and SiO_2, which takes place on cooling. The other possibility is that the stable join is between zircon and Al_2O_3, in which case an exchange reaction would necessarily occur on cooling below the stability temperature

Figure 7. The system Al_2O_3-SiO_2 according to Aksay and Pask,[7] showing mullite as an incongruently melting compound.

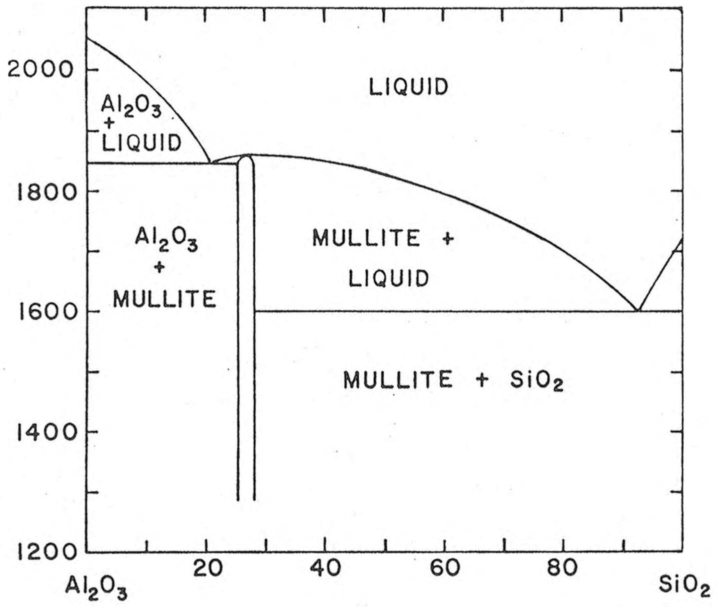
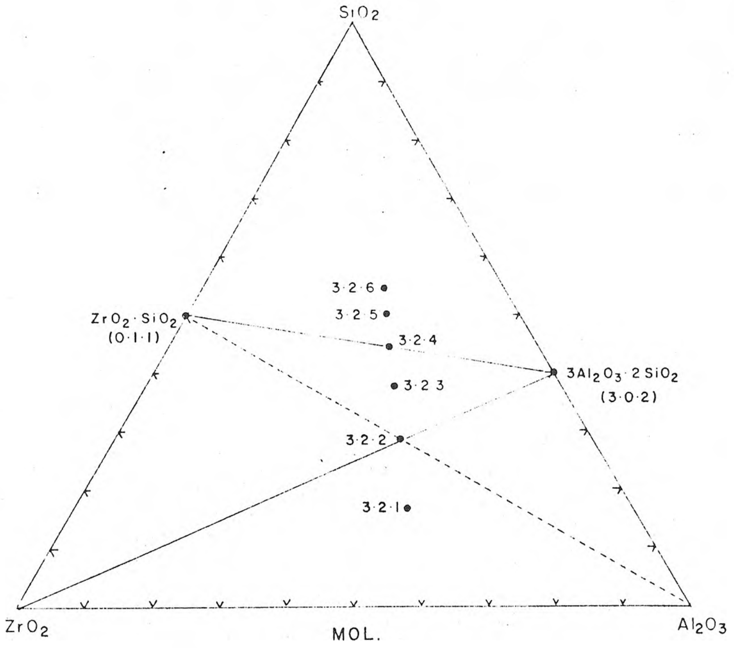

2000
1800
1600
1400
1200
LIQUID
Al2O3 + LIQUID
Al2O3 + MULLITE
MULLITE + LIQUID
MULLITE + SiO2
20
40
60
80
Al2O3
SiO2

Figure 8. Compositions prepared for study of subsolidus equilibria. Numbers represent the molar quantities of Al_2O_3, ZrO_2, and SiO_2, e.g. 3·2·2 contains $3Al_2O_3 \cdot 2ZrO_2 \cdot 2SiO_2$.


SiO2
ZrO2·SiO2
(0·1·1)
3·2·6
3·2·5
3·2·4
3·2·3
3·2·2
3·2·1
3Al2O3·2SiO2
(3·0·2)
ZrO2
MOL.
Al2O3

of zircon, as shown by:

$$3Al_2O_3 \cdot 2SiO_2 + 2ZrO_2 \rightarrow 3Al_2O_3 + 2ZrSiO_4.$$

Three subsolidus compatibility studies have been made, with contradictory results. Herold and Smothers[8] fired mixtures of A-1 Alcoa alumina, c.p. ZrO_2, and calcined c.p. silicic acid for 2-4 h at 1300°-1400°C and obtained diffractometer data indicating zircon-mullite and zircon-alumina compatibility. The reported compatibility triangles are, therefore, $ZrSiO_4-3Al_2O_3 \cdot 2SiO_2-SiO_2$, $ZrSiO_4-3Al_2O_3 \cdot 2SiO_2-Al_2O_3$, and $ZrSiO_4-Al_2O_3-ZrO_2$.

Fowler[9] heated mixtures of the oxides corresponding to 10% intervals along the three possible compatibility joins at 1650°C and reported unequivocally that the stable joins are mullite-zircon and mullite-ZrO_2. Fowler also reported partial fusion of samples with compositions near the "binary eutectic" between alumina and zircon, at about 20% alumina. Glass formation was associated with considerable decomposition of the zircon present.

Kordyuk and Gul'ko used natural zircon, synthetic mullite, c.p. Al_2O_3, and c.p. ZrO_2 to show that the reaction

$$3Al_2O_3 + 2ZrSiO_4 \rightarrow 2ZrO_2 + 3Al_2O_3 \cdot 2SiO_2$$

takes place at subsolidus temperatures, "beginning" at 1397°C and "proceeding intensively" at 1447°C. The reverse reaction was not observed. The compatibility triangles $ZrSiO_4-3Al_2O_3 \cdot 2SiO_2-SiO_2$, $ZrSiO_4-3Al_2O_3 \cdot 2SiO_2-ZrO_2$, and $3Al_2O_3 \cdot 2SiO_2-Al_2O_3-ZrO_2$ are thus considered valid by Kordyuk and Gul'ko and by Fowler.

One other study is of some interest in connection with equilibria in the system. Rea[11] made pyrometric cone equivalent studies on mixtures of $ZrSiO_4$, Al_2O_3, and SiO_2 using a gas-fired P.C.E. furnace. On the basis of the cone fusion diagram, Rea assumed a ternary eutectic near 70% SiO_2, 15% ZrO_2, and 15% Al_2O_3 at cone 27 (1600°C) and a binary eutectic between Al_2O_3 and $ZrSiO_4$ near 20% Al_2O_3 at cone 31 (1680°C).

First consideration of available information on subsolidus equilibria suggests that the correct joins are mullite-zircon and mullite-ZrO_2. A more critical study, however, leads to many questions which cast doubt on that conclusion. Herold and Smothers fired samples at relatively low temperatures, 1300° to 1400°C, for very short times, 2 to 4 h. Comparison of these factors with those employed by other investigators raises serious doubts as to attainment of equilibrium. Fowler heated samples at 1650°C, very near the upper stability limit of zircon (1676°C, according to Toropov and Galakhov) and reported partial fusion and dissociation of zircon. Kordyuk and Gul'ko identified the crystalline phases by optical microscopy and utilized a natural zircon containing 1.2 wt. % impurities. The most serious question, applicable to all three studies, arises because none presented kinetics data; only Herold and Smothers reported firing times. For these reasons, and other, the experimental effort described herein was undertaken.

III. EXPERIMENTAL PROCEDURE

For investigation of subsolidus compatibility relationships, samples were fired for various time periods at various temperatures, air quenched, and examined by X-ray diffractometry. The following types of samples were prepared:

1. Mixtures of α-Al_2O_3, ZrO_2, and silicic acid powders.
2. Mixtures of $Al(OH)_3$, ZrO_2, and silicic acid powders.
3. Mixtures of kaolinite, ZrO_2, and $Al(OH)_3$ powders.
4. Mixtures of $Al(OH)_3$, ZrO_2, and silicic acid fused with an oxyacetylene torch.
5. Mixtures of kaolinite, ZrO_2, and $Al(OH)_3$ fused with an oxyacetylene torch.
6. Mixture of $ZrSiO_4$ and $Al(OH)_3$ powders.
7. A gel with the composition $3Al_2O_3 \cdot 2ZrO_2 \cdot 2SiO_2$, prepared from solutions of aluminum nitrate, zirconyl nitrate, and colloidal SiO_2.

A. Materials

All materials used were Fisher reagent grade with the exceptions of kaolinite, a Florida air-floated china clay with small amounts of included quartz and muscovite, and colloidal SiO_2, which was Matheson, Coleman, and Bell practical grade. The materials, with ideal formulas, nominal oxide contents, and measured oxide contents are listed in Table I. Oxide contents were determined by calcining ∿5 g samples in platinum crucibles for 4 h at 800°C in a muffle furnace, and measuring weight loss to the nearest 0.1 mg.

TABLE I

MATERIALS

NAME	FORMULA	WT. % OXIDE, IDEAL	WT. % OXIDE, MEAS.
Zirconia	ZrO_2	100.00	99.73
Corundum	Al_2O_3	100.00	99.55
Zircon	$ZrSiO_4$	100.00	100.00
Kaolinite	$Al_2Si_2O_5(OH)_4$	86.05	87.12
Silicic Acid	$H_2SiO_4 \cdot nH_2O$	—	82.08
Gibbsite	$Al(OH)_3$	65.36	66.08
Colloidal Silica	SiO_2+H_2O	30.00	30.77
Zirconyl Nitrate	$ZrO(NO_3)_2 \cdot nH_2O$	—	32.38
Aluminum Nitrate	$Al(NO_3)_3 \cdot nH_2O$	—	7.62

B. Sample Preparation

The sample compositions prepared, using the combinations of materials listed above, are shown in Figure 8 and summarized in Table II. The numerical notation used is to indicate the oxide contents in the order: $Al_2O_3 \cdot ZrO_2 \cdot SiO_2$. For example, 3·2·2 corresponds to 3 moles of Al_2O_3, 2 moles of ZrO_2, and 2 moles of SiO_2. The sample compositions were selected to represent the 3 possible subsolidus compatibility triangles, the possible joins, and the compositions of mullite and zircon. The composition 3·2·2 is particularly important because it lies on the intersection of the two joins in question, the mullite-zirconia join and the zircon-alumina join. The dry powder mixes were prepared in 100 g batches, with each ingredient measured to the nearest 0.1 g on a triple beam balance. The mixes were blended by shaking in plastic containers and then milled with mortar and pestle for approximately 10 minutes.

Approximately 10 g of each of the powders was placed on a graphite block and fused with an oxyacetylene torch at a temperature above 2000°C, as determined by melting Al_2O_3. After the sample had aggregated into a globular shape, the torch flame was applied to it for approximately 10 minutes longer to assure that fusion had occurred in all portions. The resulting globule was, in all cases, an opaque white material which had obviously crystallized to some extent on cooling. The globules were then crushed and ground with an agate mortar and pestle for X-ray examination.

TABLE II

SAMPLE COMPOSITIONS

MIX	MOLE %			WEIGHT %		
	Al_2O_3	ZrO_2	SiO_2	Al_2O_3	ZrO_2	SiO_2
3·0·2	60.00	0	40.00	71.80	0	28.21
0·1·1	0	50.00	50.00	0	67.22	32.78
3·2·1	50.00	33.33	16.67	49.948	40.24	9.81
3·2·2	42.86	28.57	28.57	45.485	36.65	17.87
3·2·3	37.50	25.00	37.50	41.755	33.64	24.61
3·2·4	33.33	22.22	44.45	38.590	31.09	30.32
3·2·5	30.00	20.00	50.00	35.871	28.90	35.23
3·2·6	27.27	18.18	54.55	33.51	27.00	39.49

A gel with the 3•2•2 composition was prepared by mixing dry zirconyl chloride with a 7.62% aluminum nitrate solution, which was then heated to dissolve the zirconyl chloride, and added to a 30% colloidal silica suspension. The gel thus formed was boiled to dryness, the water and nitric acid components were driven out by heating at 500°C, and the dry powder was then calcined at 800°C to remove all residual volatile components.

Samples were fired in platinum crucibles in a SiC resistance furnace at temperatures between 1300° and 1480°C for various periods, air-quenched and examined by X-ray diffractometry. The gel samples were also heated at 800°, 900°, and 1000°C in an Inconel resistance furnace for various periods.

C. Analytical Procedures

Qualitative phase identification was accomplished with a General Electric XRD-5 recording diffractometer, using CuKα radiation at 50 kV, 16 ma, with a scanning rate of 1° 2θ/minute or a General Electric XRD-700 recording diffractometer, using CuKα radiation at 50 kV, 16 ma, with a scanning rate of 1° 2θ/minute. More detailed quantitative data were obtained with the XRD-700, using CuKα radiation at 50 kV, 20 ma, with a scanning rate of 0.2° 2θ minutes. No attempt was made to obtain quantitative phase analyses; rather, intensity changes of diagnostic peaks are presented.

X-ray powder data for the phases observed, cristobalite,[12] corundum,[13] ZrO_2,[14] zircon,[15] and mullite,[16] were, in all cases, in excellent agreement with published data.

IV. RESULTS

A. Reactions in Powders

Powder mixes, corresponding to the points shown in Figure 8, were prepared with combinations of ZrO_2, α-Al_2O_3, $Al(OH)_3$, kaolinite, and silicic acid, fired in platinum crucibles at 1300° and 1400°C for various times, air quenched, and examined by X-ray diffraction. The phases identified are listed in Table III and qualitative changes with time are indicated by measured line heights. It is immediately obvious that attainment of equilibrium at 1300° and 1400°C in powders, regardless of the reactivity of the materials, requires impractically lengthy firing periods and no conclusions can be drawn regarding the final equilibrium assemblages in the 3·2·2 mixes.

B. Reactions in Fused Samples

As an alternative method of sample preparation, intended to provide more uniform mixing of reactants, the 3·2·n samples (n = 1 to 6), formulated with kaolinite, ZrO_2, and $Al(OH)_3$, were fused with an oxyacetylene torch. The fused samples were then ground, fired in platinum crucibles at 1300°C, air quenched, and examined by X-ray diffraction. The results are shown in Table IV. In all compositions, phase development was quite rapid during the first 24 hour firing period but then continued very slowly so that, as in the case of the powder samples, it is not possible to determine the correct phase assemblages.

TABLE III

PHASE DEVELOPMENT IN FIRED POWDERS

Zircon Composition - ZrO_2 + Silicic Acid
1° 2Θ/min., Peak heights in inches; XRD-5

Temperature	Hours	Zircon	Zirconia
1300°C	4	0	7.0
1300°	9	0	7.0
1300°	16	0	6.4
1400°	24	.8	5.6
1400°	48	1.5	4.9
1400°	72	1.7	4.6
1400°	96	2.5	4.5
1400°	144	2.6	4.5

Mullite Composition - $Al(OH)_3$ + Silicic Acid
1° 2Θ/min., Peak heights in inches; XRD-5

Temperature	Hours	Cristobalite	Alumina	Mullite
1300°C	1	2.0	4.4	0
1300°	4	.8	4.0	0
1300°	9	3.2	3.8	0
1300°	16	5.2	4.0	0
1300°	25	4.8	4.0	0
1300°	36	5.2	4.0	0
1300°	49	5.8	4.2	0
1400°	24	5.4	4.0	0

Mullite Composition - Al_2O_3 + Silicic Acid

1° 2Θ/min., Peak heights in inches; XRD-5

Temperature	Hours	Cristobalite	Alumina	Mullite
1300°C	1	1.8	4.2	0
1300°	4	1.6	4.2	0
1300°	9	3.8	4.4	0
1300°	16	5.2	4.2	0
1300°	25	4.8	4.2	0
1300°	36	5.0	4.4	0
1300°	49	5.0	4.0	0
1400°	24	4.8	3.5	0
1400°	48	5.4	3.4	0.4
1400°	72	3.5	2.5	1.2
1400°	96	4.2	2.6	0
1400°	144	3.5	2.2	0

3·2·2 Composition - Al_2O_3 + ZrO_2 + Silicic Acid

1° 2Θ/min., Peak heights in inches; XRD-5

Firing Temperature	Hours	Zircon	Zirconia	Mullite	Alumina
1300°C	4	0	4.4	0	2.0
1300°	9	0	5.0	0	1.4
1300°	16	.6	3.8	0	2.0
1400°	24	1.3	3.5	0	1.8
1400°	48	1.6	3.6	0	1.7
1400°	72	1.8	3.2	0	1.8
1400°	96	2.5	3.8	0	1.7
1400°	120	2.6	3.1	0	2.1
1400°	192	3.5	3.1	0	1.6

3·2·2 Composition - Kaolinite + $Al(OH)_3$ + Silicic Acid

1° 2Θ/min., Peak heights in inches; XRD-5

Temperature	Hours	Zircon	Zirconia	Mullite	Alumina
1400°C	24	3.6	2.0	1.0	.9
1400°	48	3.8	2.3	1.1	.9
1400°	120	4.3	2.2	1.1	1.3
1400°	288	4.0	2.0	.9	.9
1400°	360	3.2	2.4	0	1.5

TABLE IV
PHASE DEVELOPMENT IN FUSED SAMPLES
3·2·n Compositions - Kaolinite + ZrO_2 + $Al(OH)_3$ - 1300°C
2° 2θ/min.; Peak heights in inches; XRD - 700

Mix	Hours	Metastable	Zirconia	Zircon	Mullite	Alumina	Cristobalite
3·2·6	24	1.0	6.6	1.5	1.9	0	3.5
3·2·5	24	3.7	4.4	.6	2.7	0	3.4
3·2·4	24	.7	7.2	0	3.0	0	0
3·2·4	48	.4	2.8	9.1	3.3	0	1.0
3·2·3	24	.6	6.7	.4	3.0	0	1.0
3·2·3	24	2.9	6.2	.5	3.4	0	1.6
3·2·3	48	1.0	4.9	4.9	3.3	0	.5
3·2·2	24	.8	7.5	0	3.1	0	0
3·2·2	48	1.5	5.5	1.4	2.7	0	0
3·2·2	72	1.8	5.8	3.0	3.1	0	0
3·2·2	140	2.5	5.6	3.9	3.6	0	0
3·2·1	24	.5	8.1	0	.9	1.9	0
3·2·1	48	.9	6.2	2.2	.9	1.5	0
3·2·1	72	.9	5.9	3.7	1.1	1.6	0
3·2·1	140	.8	4.9	6.3	.7	1.9	.7

In each of the patterns a diffraction line, not identified with any of the reported phases in the system, was noted at 30.2° 2Θ. The origin of the line could not be determined from the patterns of the fused samples; it was subsequently found to be the major line of a metastable phase as described later in connection with crystallization of a 3·2·2 gel. Measured variations in the height of the line are listed in Table IV.

C. Reactions in Zircon-Gibbsite Mix

Both Fowler[9] and Kordyuk and Gul'ko[10] reported that mixtures of zircon and alumina undergo an exchange reaction to produce the equilibrium assemblage of mullite and zirconia. As stated previously, however, those reports leave several important questions unanswered. A mixture of zircon and $Al(OH)_3$, corresponding to $3\ Al_2O_3 \cdot 2\ ZrO_2 \cdot 2\ SiO_2$, at the intersection of the subsolidus joins in question, was prepared, therefore, and fired at 1480°C in an effort to determine the validity of the conclusions of Kordyuk and Gul'ko. The results are shown in Table V. Because Kordyuk and Gul'ko did not state firing times at 1447°C, it is not possible to compare results, but it is obvious that the exchange reaction does occur very slowly.

Two features of the X-ray powder data are worth noting. Very small quantities of the metastable phase, previously observed in fused samples, were noted in the patterns and the powder pattern of zircon exhibited anomalies, in the

TABLE V

PHASE DEVELOPMENT IN ZIRCON-GIBBSITE POWDER

3·2·2 Composition - $ZrSiO_4$* + $Al(OH)_3$ - 1480°C

0.2° 2Θ/min; Peak areas in square inches; XRD-700

Time, hrs.	Al_2O_3 (102)	Mullite (120) (210)	ZrO_2 $(11\bar{1})$	Metastable (111)	Al_2O_3/ZrO_2 Ratio
21	0.82	0.03	0.28	0.08	2.93
43	.80	.09	.37	.06	2.16
62	.71	.14	.43	.13	1.65
85	.67	.17	.44	.10	1.52
106	.65	.23	.50	.07	0.77

*$ZrSiO_4$ intensities omitted because of random variations noted during dissociation.

form of random variations in relative intensities and line shape, during the reaction.

D. Reactions in 3·2·2 Gel

To obtain maximum reactivity, a gel having the 3·2·2 composition was prepared from aluminum nitrate, zirconyl nitrate, and colloidal silica. After calcination at 500° and 800°C, X-ray diffraction analysis revealed a previously unreported phase and a small quantity of γ-Al_2O_3. The powder data for the new phase have been indexed on a tetragonal, pseudocubic, unit cell, as shown in Table VI. X-ray line broadening measurements on the (111) line indicate very small crystallite sizes, with the mean diameter 0.009 µm in samples calcined at 800°C, 0.011 gm in samples calcined at 900°C, and 0.035 µm in samples calcined at 1000°C.

Samples of the 3·2·2 gel were fired at 1480°C for various times, air quenched, and examined by X-ray diffraction. The results are shown in Table VII. The metastable phase was quite persistent, even at high temperatures, but did decrease with time. All four of the phases in the low silica portion of the system, zircon, mullite, alumina, and zirconia, developed rapidly; continued firing resulted in very slow changes. The trend toward equilibrium is evident: the gradual increase in the intensity the zirconia line and the corresponding decrease of the alumina line indicate the final equilibrium assemblage to be mullite and zirconia.

TABLE VI

X-RAY POWDER DATA FOR METASTABLE PHASE

CuKα Radiation; 50 kV, 20 ma.; XRD-700; 0.2° 2θ/min.
Intensities measured by counting squares

Tetragonal (Pseudocubic)
$a = 5.085 \pm 0.001$ A°
$c = 5.194 \mp 0.001$ A° at 22°C.

d_{hkl}	I	hkl	$\sin^2\theta$obs.	$\sin^2\theta$calc.
2.957	100.0	111	.06795	.06798
2.597	8.3	002	.08809	.08808
2.543	11.5	200	.09193	.09192
1.818	36.2	202	.17981	.18000
1.798	23.0	220	.18378	.18384
1.561	13.3	113	.24390	.24414
1.537	27.0	311	.25166	.25182
1.479	5.3	222	.27184	.27192
1.299	1.4	004	.35215	.35232
1.272	4.7	400	.36756	.36768
1.178	10.3	313	.42791	.42798
1.168	5.1	331	.43560	.43566
1.157	3.4	204	.44409	.44424
1.140	4.6	402	.45720	.45576
		420		.45960

TABLE VII

PHASE DEVELOPMENT IN 3·2·2 GEL

3·2·2 Composition-Al nitrate+Zr nitrate+colloidal SiO_2; 1480°C
0.2° 2Θ/min; Peak areas in square inches; XRD-700

Time, Hrs.	Al_2O_3 (102)	Mullite (120) (210)	Zircon (200)	ZrO_2 (11T)	Metastable* (111)	Zircon/ZrO_2 Ratio
3	0.22	1.40	1.28	1.27	2.94	1.01
24	.21	1.54	1.09	1.98	1.67	.55
44	.15	1.39	.93	1.95	1.80	.48
65	.16	1.58	.91	2.16	1.77	.42

* Mean Diameter = 0.14 μm

V. DISCUSSION AND CONCLUSIONS

A. Subsolidus Equilibria

It has been shown that the correct subsolidus compatibility triangles in the system ZrO_2-Al_2O_3-SiO_2 are: silica-zircon-mullite, zircon-mullite-zirconia, and mullite-zirconia-alumina. This is in agreement with the work of Fowler[9] and Kordyuk and Gul'ko,[10] though the extent to which the reaction proceeds as a function of time seems to be quite different. Fowler, of course, heated samples at a much higher temperature, 1650°C, for an unspecified period but Kordyuk and Gul'ko reported "intensive" reaction at 1447°C. Fowler used natural zircon, referred to as "high-grade," and Kordyuk and Gul'ko used natural zircon consisting of 98.8% $ZrSiO_4$; the possibility exists, therefore, that the reaction between zircon and alumina was enhanced by the presence of impurities. The phase assemblages reported by Herold and Smothers[8] for samples fired 2 to 4 hours at 1300° to 1400°C, indicating stable coexistence of zircon and alumina, are puzzling. Unless significant impurities were present in their raw material--e.g. Na_2O, which is known to impede mullite formation--their results can only be attributed to inadequately sensitive X-ray diffraction equipment.

Budnikov and Litvakovskii[1] indicated only two subsolidus compatibility triangles: silica-mullite-zirconia and mullite-zirconia-alumina. This is in accordance with the reported subsolidus dissociation of zircon and the absence of a primary crystallization field for zircon in the phase diagram.

The kinetics of the approach to equilibrium indicate that equilibrium is nearly unattainable in practice and that sintering of ZAS bodies formulated from pure materials is not feasible. A fourth component will, of course, affect the reaction and sintering characteristics and a systematic study of additives should be useful.

B. Structure of the Metastable Phase

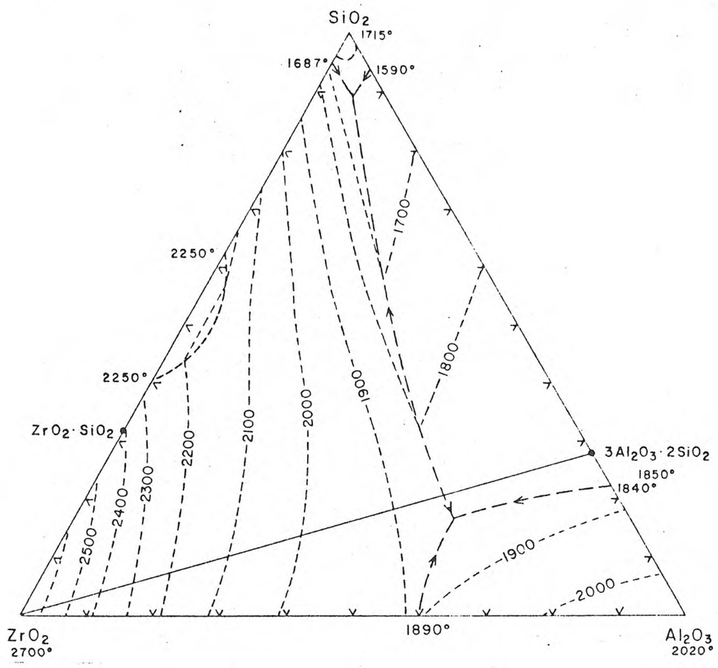
Though the compositional range of the tetragonal phase has not been established, its persistence at high temperatures makes it worth further study. The unit cell parameters, $a = 5.085$ A^o; $c = 5.194$ A^o, are similar to the values of monoclinic ZrO_2,[14] $a = 5.1477$ A^o; $b = 5.2030$ A^o; $c = 5.3156$ A^o; $\beta = 99^o$ 23', suggesting that the phase is similar to ZrO_2, i.e., a distorted fluorite structure. The manner in which aluminum and silicon can be incorporated into such a structure, however, is not at all apparent, so the similarity may be fortuitous. The structure is definitely a tetragonal distortion of a face-centered cubic lattice, but more work is required to establish the compositional range, the stability, and the details of the structure.

C. Hypothetical Liquidus Surfaces

In view of the availability of reasonably good phase equilibria data for the binary systems ZrO_2-SiO_2, ZrO_2-Al_2O_3, and Al_2O_3-SiO_2, it is possible to suggest liquidus surface configurations for the system ZrO_2-Al_2O_3-SiO_2 which will be somewhat more reasonable than that reported by Budnikov and Litvakovskii (Figure 1).

If it is assumed that the revised diagram for the system ZrO_2-SiO_2 (Figure 4) is correct, the liquidus temperatures and the liquid miscibility gap can be incorporated directly and there will be no primary crystallization field for zircon. If it is further assumed that mullite is congruently melting, as shown by Aramaki and Roy,[6] and as indicated as a possible metastable diagram by Aksay and Pask,[7] and that Alper's[5] diagram for the system ZrO_2-Al_2O_3 is correct, the liquidus surface may be revised as shown in Figure 9. The diagram differs from that of Budnikov and Litvakovskii only in detail, most notably in the low-alumina portion, where the liquidus temperatures are much higher. This is in accordance with the observation of Rea,[11] who noted the severe decrease in melting temperatures and deformation ranges caused by addition of alumina to zircon. The trough shown in the cone fusion diagram of Rea in samples containing approximately 20% alumina does not coincide with the phase boundary between the crystallization fields of zirconia and mullite, but because pyrometric cone equivalents are a function of viscosity as well as

Figure 9. Hypothetical liquidus surface for the system ZrO_2-Al_2O_3-SiO_2, based on binary data according to Butterman and Foster,[4] Alper,[5] and Aramaki and Roy.[6]

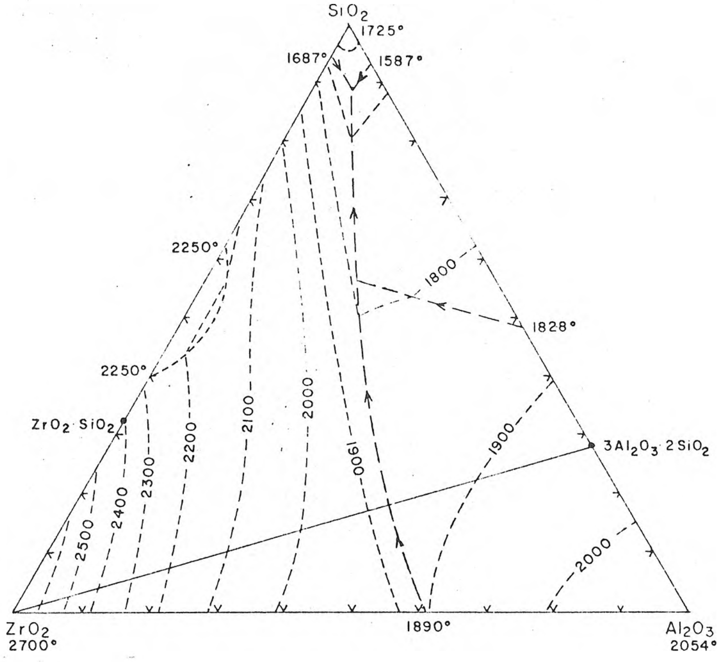

SiO_2
1715°
1687°
1590°
1700
2250°
1800
2250°
1900
2000
2100
2200
2300
2400
2500
$ZrO_2 \cdot SiO_2$
$3Al_2O_3 \cdot 2SiO_2$
1850°
1840°
1900
2000
ZrO_2
2700°
1890°
Al_2O_3
2020°

percentage of liquid, this does not seem to be unreasonable.

Though the crystallization behavior shown by Figure 9 would be expected in actual practice, by virtue of the metastable precipitation of mullite, the true equilibrium surface would necessarily reflect the fact that mullite crystallizes incongruently. A second hypothetical diagram based on the binary data of Butterman and Foster[4] for the system ZrO_2-SiO_2, of Alper[5] for the system ZrO_2-Al_2O_3, and of Aksay and Pask[7] for the system Al_2O_3-SiO_2, is shown in Figure 10. The main feature is the incongruent melting behavior of mullite, with the required ternary peritectic. The overall difference in liquidus configuration between Figures 9 and 10 is quite small, with the sharp decrease in temperatures with addition of alumina and silica to zirconia and the relatively small variation in the low ZrO_2 portion of the system being quite evident in both.

It should be noted that the ternary eutectic in the high SiO_2 portion of the system is most certainly below the dissociation temperature of zircon. Depending on the effect of alumina on the dissociation temperature, therefore, there may be a zircon crystallization field which does not extend to the binary system ZrO_2-SiO_2. In any case, metastable behavior in both systems, Al_2O_3-SiO_2 and ZrO_2-SiO_2, is such a strong possibility that equilibrium crystallization is an ideal not likely to be attained.

Figure 10. Hypothetical liquidus surface for the system ZrO_2-Al_2O_3-SiO_2, based on binary data according to Butterman and Foster,[4] Alper,[5] and Aksay and Pask.[7]


SiO2
1725°
1687°
1587°
2250°
1800
1828°
2250°
ZrO2·SiO2
2200
2100
2000
1900
1900
3Al2O3·2SiO2
2300
2400
2500
2000
ZrO2
2700°
1890°
Al2O3
2054°

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