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## The Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZrO<sub>2</sub> Liquidus Surface: A Discussion

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When 1 atm He instead of O<sub>2</sub> was used during firing, sintered density reached only 95% theoretical density, and no trace of a PbO phase was found in the sample. Thus the lower the oxygen partial pressure in the sintering atmosphere, the greater the PbO loss from the sample and the less effective is the liquid-phase sintering process.

<sup>1</sup> B. Jaffe, R. S. Roth, and S. Marzullo, "Properties of Piezoelectric Ceramics in the Solid-Solution Series Lead Titanate-Lead Zirconate-Lead Oxide: Tin Oxide and Lead Titanate-Lead Hafnate," *J. Res. Natl. Bur. Stand.*, **55** [5] 239-54 (1955).

<sup>2</sup> D. A. Berlincourt, C. Cmolek, and H. Jaffe, "Piezoelectric Properties of Polycrystalline Lead Titanate-Zirconate Compositions," *Proc. IRE*, **48** [2] 220-29 (1960).

<sup>3</sup> R. B. Atkin and R. M. Fulrath, "Point Defects and Sintering of Lead Zirconate-Titanate," *J. Am. Ceram. Soc.*, **54** [5] 265-70 (1971).

<sup>4</sup> A. H. Webster, T. B. Weston, and N. F. H. Bright, "Effect of PbO Deficiency on the Piezoelectric Properties of Lead Zirconate-Titanate Ceramics," *ibid.*, **50** [9] 490-91 (1967).

<sup>5</sup> J. J. Dih, "Electrical Conductivity in Lead Zirconate-Titanate Ceramics"; Ph.D. Thesis, University of California, Berkeley, Calif., 1976; 104 pp.

<sup>6</sup> R. L. Holman, "Intrinsic and Extrinsic Non-stoichiometry in the Lead Zirconate-Titanate System"; Ph.D. Thesis, University of California, Berkeley, 1972; 97 pp.

<sup>7</sup> R. B. Atkin, R. L. Holman, and R. M. Fulrath, "Substitution of Bi and Nb Ions in Lead Zirconate-Titanate," *J. Am. Ceram. Soc.*, **54** [2] 113-15 (1971).

<sup>8</sup> D. C. Lee, "Sintering Sc and Nb Modified Lead Zirconate-Titanate"; M.S. Thesis, University of California, Berkeley, 1970; 35 pp.

<sup>9</sup> R. L. Holman and R. M. Fulrath, "Intrinsic Nonstoichiometry in the Lead Zirconate-Lead Titanate System Determined by Knudsen Effusion," *J. Appl. Phys.*, **44** [12] 5227-36 (1973).

## The Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZrO<sub>2</sub> Liquidus Surface: A Discussion

CHARLES C. SORRELL\* and CHARLES A. SORRELL\*

PHASE equilibria for the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZrO<sub>2</sub> are important for the interpretation of equilibrium or nonequilibrium crystallization in sintered and fused ASZ refractories and of their behavior in service. The only reported ternary liquidus surface data<sup>1</sup> are not consistent with liquidus temperatures reported for the binary systems and should be modified accordingly.

The essential feature is the ternary eutectic at  $\approx 1800^\circ\text{C}$  and 53 Al<sub>2</sub>O<sub>3</sub>, 17 SiO<sub>2</sub>, and 30 wt% ZrO<sub>2</sub>, with uncertainty estimated at  $\pm 2.5$  wt% for each. Mullite is shown as an incongruently melting compound and Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and SiO<sub>2</sub>-ZrO<sub>2</sub> are shown as simple eutectic systems. No primary crystallization field is shown for zircon and the only subsolidus join is between mullite and ZrO<sub>2</sub>, indicating that zircon dissociates in the solid state to ZrO<sub>2</sub> and SiO<sub>2</sub>. In the high-alumina portion investigated, the isotherms are at considerable variance with binary data and the inferred isotherms for the remainder of the system are totally unrealistic.

The systems SiO<sub>2</sub>-ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> have been studied extensively; fortunately, detailed summaries of these studies are available and can be used for suggesting modifications of the ternary system. Buttermann and Foster<sup>2</sup> combined previous data with their own dissociation studies to propose a diagram for the system SiO<sub>2</sub>-ZrO<sub>2</sub> which shows solid-state dissociation of zircon at  $1676^\circ \pm 70^\circ\text{C}$ , liquid immiscibility, and a binary eutectic at  $\approx 95$  wt% SiO<sub>2</sub>,  $1687^\circ\text{C}$ .

The system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> has long been problematical, particularly with regard to the compositional range and melting characteristics of mullite. The diagram of Aramaki and Roy<sup>3</sup> shows that mullite melts congruently at  $\approx 1850^\circ\text{C}$ , with eutectics at  $\approx 94$  wt% SiO<sub>2</sub>,  $\approx 1590^\circ\text{C}$  and  $\approx 22$  wt% SiO<sub>2</sub>,  $\approx 1840^\circ\text{C}$ .

A considerably more detailed study of stable and metastable equilibria in the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> has recently been reported by Aksay and Pask,<sup>4</sup> who showed that mullite melts incongruently at

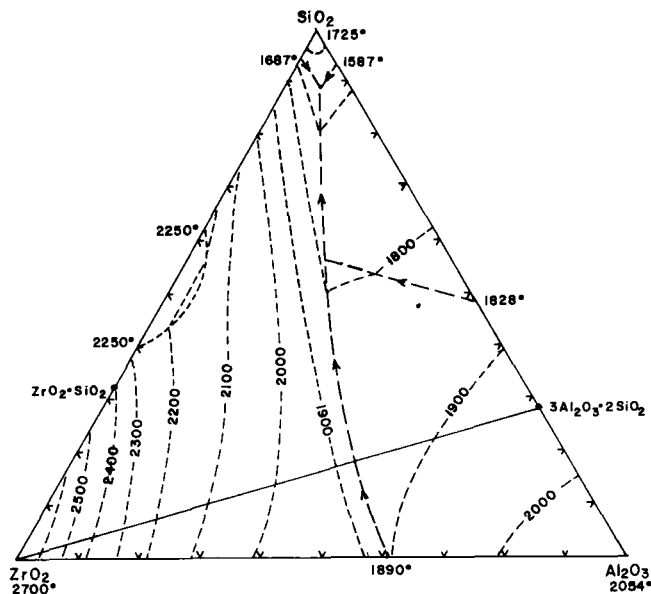


Fig. 1. Hypothetical liquidus surface for the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZrO<sub>2</sub>, based on binary data of Refs. 2, 5, and 4.

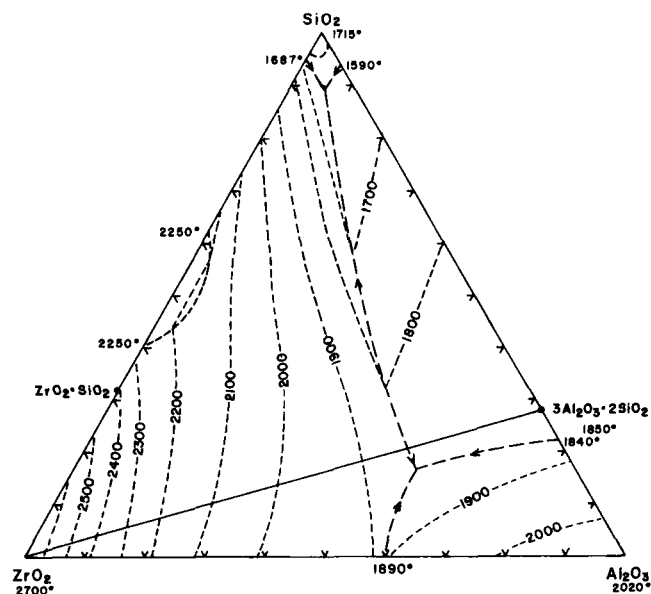


Fig. 2. Hypothetical liquidus surface for the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZrO<sub>2</sub>, based on binary data of Refs. 2, 5, and 3.

$1828^\circ \pm 10^\circ\text{C}$ , with the peritectic at  $\approx 48$  wt% SiO<sub>2</sub> and the eutectic at  $\approx 9$  wt% SiO<sub>2</sub>,  $1587^\circ \pm 10^\circ\text{C}$ . Metastable equilibrium curves, showing the effects of superheating and supercooling, indicate, in general, the reasons for previous disagreement.

Alper<sup>5</sup> melted 16 samples in an induction furnace, using an Ar atmosphere and setters having the same compositions as the samples, to prepare a diagram of the system Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>. The eutectic was placed at  $\approx 40$  wt% ZrO<sub>2</sub>,  $\approx 1880^\circ\text{C}$ , with limited solid solution inferred.

If it is assumed that equilibria are correctly represented by the binary data of Buttermann and Foster,<sup>2</sup> Aksay and Pask,<sup>4</sup> and Alper,<sup>5</sup> the hypothetical diagram shown in Fig. 1, with both a ternary peritectic and eutectic in the mullite-SiO<sub>2</sub>-ZrO<sub>2</sub> triangle, is a better representation of the melting characteristics of the system than is the diagram of Budnikov and Litvakovskii.<sup>1</sup> If, however, it is assumed that mullite melts congruently, as indicated by Aramaki and Roy,<sup>3</sup> and as indicated in the metastable diagram of Aksay and Pask,<sup>4</sup> the hypothetical diagram shown in Fig. 2 differs from that of Budnikov

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and Litvakovskii<sup>1</sup> only in detail in the high-alumina portion.

In either case, the severe decrease in melting temperatures and deformation ranges caused by the addition of alumina to zircon, as reported by Rea,<sup>6</sup> is adequately explained. The trough shown in Rea's cone fusion diagram does not coincide with the boundary between the crystallization fields of  $ZrO_2$  and mullite, but because pyrometric cone equivalents are a function of viscosity as well as percentage of liquid, this behavior does not seem unreasonable.

It should be noted that the ternary eutectic in the high- $SiO_2$  portion of the system is below the reported dissociation temperature of zircon.<sup>2</sup> Depending on the effect of  $Al_2O_3$  on the dissociation temperature, therefore, there may be a zircon crystallization field which does not extend to the binary system  $SiO_2$ - $ZrO_2$ . In any case, metastable behavior in both systems,  $Al_2O_3$ - $SiO_2$  and  $SiO_2$ - $ZrO_2$ , is such a strong possibility that equilibrium crystallization is an ideal not likely to be attained.

<sup>1</sup>P. P. Budnikov and A. A. Litvakovskii, "The  $Al_2O_3$ - $SiO_2$ - $ZrO_2$  System," *Dokl. Akad. Nauk SSSR*, **106** [2] 267-70 (1956).

<sup>2</sup>W. C. Butterman and W. R. Foster, "Zircon Stability and the  $ZrO_2$ - $SiO_2$  Phase Diagram," *Am. Mineral.*, **52** [5-6] 880-85 (1967).

<sup>3</sup>Shigeo Aramaki and Rustum Roy, "Revised Equilibrium Diagram for the System  $Al_2O_3$ - $SiO_2$ ," *Nature (London)*, **184** [4686] 631-32 (1959).

<sup>4</sup>I. A. Aksay and J. A. Pask, "Stable and Metastable Equilibria in the System  $SiO_2$ - $Al_2O_3$ ," *J. Am. Ceram. Soc.*, **58** [11-12] 507-12 (1975).

<sup>5</sup>A. M. Alper, p. 339 in *Science of Ceramics*, Vol. 3. Edited by G. H. Stewart. Academic Press, London, 1967.

<sup>6</sup>R. F. Rea, "Cone Fusion Study of Mixtures of Zirconium Silicate, Silica, and Alumina," *J. Am. Ceram. Soc.*, **22** [3] 95-96 (1939).

## The Binary Phase Diagram $KNO_3$ - $K_2Cr_2O_7$

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The phase diagram of the binary  $KNO_3$ - $K_2Cr_2O_7$  system<sup>1</sup> shows a simple eutectic at composition  $X_{K_2Cr_2O_7} = 0.365$  and  $T = 264^\circ C$ . A cooling curve performed recently during some experiments requiring the use of low-melting eutectics showed anomalous behavior of the temperature for the liquid  $\rightleftharpoons$  solid transformation at the supposed eutectic composition, suggesting an error in this composition. Therefore, the liquidus of the binary solution was determined experimentally, using the cooling curve method.

Reagent-grade  $KNO_3$  and  $K_2Cr_2O_7$  salts in the required proportions were ground together in a mortar and placed in a tubular

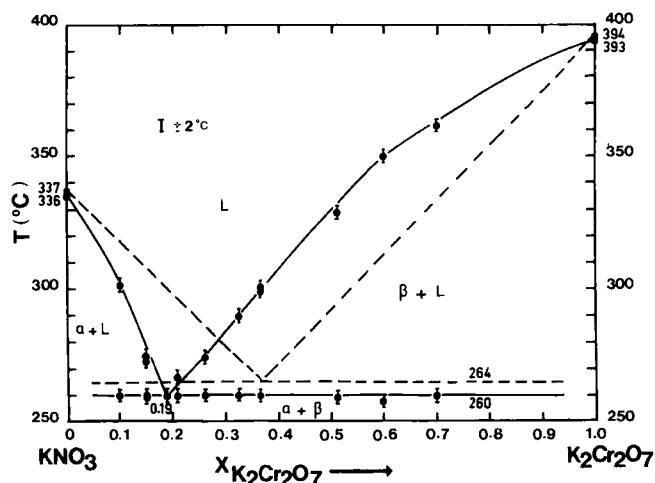


Fig. 1. Phase diagram of  $KNO_3$ - $K_2Cr_2O_7$  system; data points give the results of (●) present work, (■) Ref. 2, and (----) Ref. 1.

heat-resistant glass\* crucible 3.5 cm in diameter. A charge of 45 g was used. The crucible and its charge were suspended in a vertically mounted tube furnace and heated in a slow stream of Ar to the desired temperature, which is  $\approx 50^\circ C$  above the melting points of the pure salts. For intermediate compositions, this temperature lay on the line joining these 2 points. The crucible was held at the selected temperature for 10 to 15 min to allow melting and homogenization of the solution before the cooling curve was determined. The temperature was measured by a sheathed Chromel-Alumel thermocouple placed in the melt. Since the furnace was not insulated, the power input was adjusted to give a relatively slow cooling rate ( $\approx 5^\circ C/min$ ) which was recorded as  $T$  vs  $t$ . Problems of supercooling were reduced by slight agitation of the melt.

From the  $T$ -vs- $t$  traces, it was possible to determine for each composition investigated the liquidus, the presence or absence of a solidus, and the temperature of the univariant line corresponding to the eutectic point. The precision of these graphical determinations was of the order of  $\pm 2^\circ C$ .

Measurements were made on the pure salts and on 7 solutions. The results are summarized in Table I. These values and the reported melting points for the pure salts ( $337^\circ$  and  $394^\circ C$  for  $KNO_3$  and  $K_2Cr_2O_7$ , respectively<sup>2</sup>) were used to construct the corrected diagram, which is shown in Fig. 1. The eutectic composition has been determined to be at 19.0 mol%  $K_2Cr_2O_7$ .

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\*Pyrex, Corning Glass Works, Corning, N.Y.

<sup>1</sup>E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagrams for Ceramists*, 1969 Supplement. Edited by M. K. Reser. The American Ceramic Society, Columbus, Ohio; Fig. 2867.

<sup>2</sup>New Treatise on Inorganic Chemistry, Vol. II (Nouveau Traite de Chimie Minerale, Vol. II). Edited by Paul Pascal. Masson, Paris, 1966.

Table I. Experimental Data for Binary  $KNO_3$ - $K_2Cr_2O_7$  System

| Temp. ( $^\circ C$ ) | $X_{K_2Cr_2O_7}$ (mole fraction) |       |            |       |       |       |       |                   |       |      |      |     |
|----------------------|----------------------------------|-------|------------|-------|-------|-------|-------|-------------------|-------|------|------|-----|
|                      | 0                                | 0.100 | 0.153      | 0.190 | 0.206 | 0.262 | 0.321 | 0.365             | 0.515 | 0.60 | 0.70 | 1.0 |
| $T_{liq}$            | 336                              | 302   | 274<br>272 | 258   | 267   | 275   | 290   | 300<br>299<br>301 | 329   | 350  | 362  | 393 |
| $T_{univ}$           |                                  | 260   | 260<br>259 | 258   | 260   | 260   | 260   | 260<br>260<br>260 | 259   | 258  | 260  |     |

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