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34.—Phase Equilibria in The System $\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2$

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ABSTRACT

A423(CaO/Al₂O₃/TiO₂)

Phase relationships in the system have been studied by the quenching technique and by high-temperature microscopy. In the limiting binary systems, the role of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is discussed. New data are also presented showing that $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ disproportionates to $\alpha\text{-Al}_2\text{O}_3$ and rutile at $1262 \pm 7^\circ\text{C}$. In the $\text{CaO}-\text{TiO}_2$ system it was not found possible to repeat the synthesis of $4\text{CaO} \cdot 3\text{TiO}_2$ reported in the literature. Liquidus relations in the ternary system are dominated by the extensive primary-phase fields of perovskite and aluminous perovskite solid solutions, Al_2O_3 , $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, CaO , and $3\text{CaO} \cdot 2\text{TiO}_2$. Smaller primary-phase fields of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$, and TiO_2 , were also delineated. The nature, location and temperature of 12 liquidus invariant points are tabulated. Applications of the data to predicting the role of TiO_2 in aluminous concretes and refractories are indicated, and the glass-forming properties of some of the high- TiO_2 liquids discussed.

Les équilibres de phases dans le système $\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2$

Les relations d'équilibre des phases dans ce système sont étudiées à l'aide de la technique de la trempe et par microscopie haute température. Le rôle de $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ dans les systèmes binaires limites est discuté. De nouvelles données sont également présentées, montrant que $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ se transforme en Al_2O_3 et en rutile à $1262 \pm 7^\circ\text{C}$. Dans le système $\text{CaO}-\text{TiO}_2$, il n'a pas été possible de reproduire par synthèse $4\text{CaO} \cdot 3\text{TiO}_2$, signalé dans la littérature. Les relations des liquidus dans le système ternaire sont dominées par les zones étendues de phases primaires de perovskite et de solutions solides de perovskite aluminouse, Al_2O_3 , $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, CaO et $3\text{CaO} \cdot 2\text{TiO}_2$. Des zones plus petites de phases primaires de $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ et TiO_2 sont de même délimitées. La nature, l'emplacement et la température de 12 points invariants du liquidus sont consignés sous forme de

tableau. Les possibilités d'utilisation de ces données pour prévoir le rôle de TiO_2 dans les bétons, les réfractaires alumineux, sont indiquées et les propriétés de formateurs de verre, présentées par quelques-uns des liquides à haute teneur en TiO_2 sont discutées.

Phasengleichgewicht im System $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$

Im obigen System wurden die Phasenbeziehungen mittels Abschrecktechnik und Hochtemperaturmikroskopie studiert. In den binären Grundsystemen wird die Rolle des $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ diskutiert. Ferner werden neue Daten angegeben, die eine Disproportionierung von $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ in $\alpha\text{-Al}_2\text{O}_3$ und Rutil bei $1262 \pm 7^\circ\text{C}$ erkennen lassen. Im System CaO-TiO_2 war es nicht möglich, die Synthese von $4\text{CaO} \cdot 3\text{TiO}_2$ zu wiederholen, von der in der Literatur berichtet wird. Die Liquidusbeziehungen in dem ternären System werden weitgehend durch die ausgedehnten Felder der primären Phasen von Perowskit und den festen Lösungen von aluminiumhaltigem Perowskit bestimmt: Al_2O_3 , $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, CaO , und $3\text{CaO} \cdot 2\text{TiO}_2$. Engere Gebiete primärer Phasen von $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ und TiO_2 werden ebenfalls mitgeteilt. Die Art, Lage und Temperatur von 12 liquidusvarianten Punkten sind tabellarisch angegeben. Diese Daten werden zur Vorhersage der Rolle des TiO_2 in Aluminiumzementen und Feuerfestmaterialien benutzt, und es werden die glasbildenden Eigenschaften einiger stark TiO_2 -haltiger Flüssigkeiten diskutiert.

1. PREVIOUS RELATED STUDIES

1.1 $\text{CaO-Al}_2\text{O}_3$

Since RANKIN and WRIGHT'S^{1,2} studies of this system, new data have accumulated. The present state of knowledge about this important binary system may be summarized as follows. The high-alumina $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ phase is generally recognized as containing essential Ca^{2+} . Hence it is not an alumina polymorph, and references to " $\beta\text{-Al}_2\text{O}_3$ " are becoming less frequent. The phases formerly thought to be $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ are now generally known to be $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ respectively. These changes to Rankin and Wright's original phase diagrams have, for example, been accepted and included in the large-scale diagrams published by MUAN and OSBORN³ on behalf of the American Ceramic Society.

Other suggested changes to the phase diagram either are more recent or have not yet been generally accepted. Thus Rankin and Wright fixed the congruent melting of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ at 1605°C (this temperature has been adjusted to agree with the 1948 International

Scale). The studies of AURROL and WURM⁴ and of WELCH and NURSE⁵ show that $\text{CaO} \cdot \text{Al}_2\text{O}_3$ actually melts incongruently. The crystalline product of the incongruent melting is $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$. Likewise, both these studies have shown that $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ melts incongruently to $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ and liquid.

The exact composition and stability of the " $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ " phase has been a source of some contention. Rankin and Wright had no difficulty in obtaining an optically isotropic low-refractive-index phase which they identified as having the composition $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. It was obtained by both solid-state reaction and also by crystallization of appropriate liquids or glasses. They also encountered another phase which was optically birefringent; this phase was believed to be a metastable polymorph of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. In a subsequent study Bussem and Erter (1936)⁶ showed that the isotropic " $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ " phase actually had the $12:7\text{ CaO/Al}_2\text{O}_3$ mole ratio. The two ratios differ by only 0.71% Al_2O_3 . It is now known that $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ can absorb and retain water from ambient laboratory atmospheres, even at comparatively high temperatures. Thus, the product obtained by heating " $12:7$ " at, for example, 1000°C in the ambient laboratory atmosphere will have the composition: $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{Ca(OH)}_2$. The existence of this hydrate and its remarkable thermal stability were first established through the studies of ROY and ROY⁷ and of NURSE.⁸ The hydroxyl nature of the "water", as opposed to molecular H_2O , was further demonstrated by JEEVARATNAM *et al.*⁹; they were able to prepare the fluoride and chloride analogues and exchange OH^- for F^- . These additions to our knowledge of the correct formula and of the role of OH^- and F^- have been further confirmed by a new crystal-structure analysis by WILLIAMS,¹⁰ which shows the details of the crystal structure of the fluorinated phase.

T.g.a. studies made at higher temperatures show that the hydroxyl water is gained or lost reversibly over the temperature range ca. $1100^\circ\text{--}1250^\circ\text{C}$; the dehydroxylated phase obtained at or above 1250°C can be quenched, and it proves to have physical properties (e.g. refractive index, unit cell size, etc.) which differ only slightly from those of the fully hydrated phase. The remaining disagreement between the various studies which is important for present purposes concerns the nature of the " $12:7$ " product obtained between 1250°C and the melting point, and the thermodynamic stability of the $12:7$ phase relative to the other calcium aluminates. The problem has been approached by Jeevaratnam *et al.* by direct chemical analysis of the $12:7$ phase prepared at various temperatures, and by NURSE *et al.*¹¹, who studied its formation in both dry and moist atmospheres

even at subsolidus temperatures, by reaction of the component oxides. The 4:3 phase was identified in two ways: firstly, by its characteristic X-ray powder pattern, and secondly, by its influence on the solidus profile, mixtures of the 4:3 plus 1:1 phases having a higher solidus than those containing mixtures of the 4:3 plus 3:2 phases. The 4:3 phase was found to melt incongruently, yielding CaTiO_3 and liquid, at 1755°C . Figure 2 compares the appearance of the CaO-TiO_2 phase diagram according to Roy *et al.*, and also according to Roth.

Neither author studied the symmetry changes in perovskite (CaTiO_3) itself, but it is known that, at room temperature, CaTiO_3 is orthorhombic, pseudo-cubic. The crystal structure of CaTiO_3 has been described by KAY and BAILEY.¹⁴ It is generally presumed that, at higher temperatures, CaTiO_3 becomes truly cubic. NAVTOR and COOK¹⁵ found evidence of a large heat effect at 1265°C in CaTiO_3 . This heat effect was reversible, and this would fit the observation that the cubic \rightleftharpoons orthorhombic transformation cannot be suppressed, even by relatively rapid quenching. This temperature for the reversible phase transformation should be tentatively incorporated in the lower temperature portions of Figure 2.

1.3 $\text{Al}_2\text{O}_3\text{-TiO}_2$

The $\text{Al}_2\text{O}_3\text{-TiO}_2$ system has been studied principally by LANG *et al.*¹⁶ The results are summarized in Figure 3. A 1:1 phase was found, and an α - and a β -polymorph were characterized. They were unable to determine if $\alpha\text{-Al}_2\text{O}_3\cdot\text{TiO}_2$ melted congruently or just incongruently yielding Al_2O_3 and liquid: the inset shows a possible alternative melting scheme. Although the 1:1 phase is readily preserved to room temperature by quenching, some evidence was also presented that $\text{Al}_2\text{O}_3\cdot\text{TiO}_2$ had a lower limit of thermal stability. At this lower limit it disproportionated to $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 (rutile). No evidence was found to indicate any solid solution between the various crystalline phases.

1.4 $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$

Phase-equilibrium data for the ternary system are very limited. COATES and McMILLAN¹⁷ studied the effect of a number of chemical substituents, including Al_2O_3 , on perovskite. They claimed to have prepared a perovskite having the composition $\text{CaAl}_{0.5}\text{Ti}_{0.5}\text{O}_{2.75}$ by heating the appropriate oxide mixture in air at 1500°C . The resulting product was described as consisting of a single-phase homogeneous cubic perovskite solid solution with $a_0 = 3.809 \pm 0.002\text{\AA}$ and $d = 3.73 \pm 0.06\text{g/cm}^3$. The unit cell and density values were found

to be consistent with the existence of an anion-deficient solid-solution series: that is, a series formed by substitution of 2Al^{3+} for 2Ti^{4+} with the concomitant omission of one O^{2-} . There is, however, an important disagreement concerning the quantitative extent of solid solution as reported in their study, and the results obtained in the present study (see below).

During the preparation of this manuscript, the writers learned that LEA and NURSE¹⁸ had studied phase relations in the high- CaO portions of this system, bounded by CaO , $\text{CaO}\cdot\text{Al}_2\text{O}_3$, and CaTiO_3 . Results of those studies have not been published: however, Dr R. W. Nurse has kindly made his data available to us and the results of the two studies are generally in good agreement.

2. EXPERIMENTAL METHODS

Starting materials included Analar low-alkali CaCO_3 , Cera Al_2O_3 and a special high-purity TiO_2 supplied by British Titan Products. These were dried prior to use at 400°C , 1100°C and 700°C respectively for 24 h. The reagents were chosen for reactivity as well as purity. They were initially in the form of micron-size particles of calcite, $\alpha\text{-Al}_2\text{O}_3$ (corundum) and rutile respectively. Weighed quantities of the reagents were moistened with acetone and ground together in an agate mortar. The ground mix was dried and then

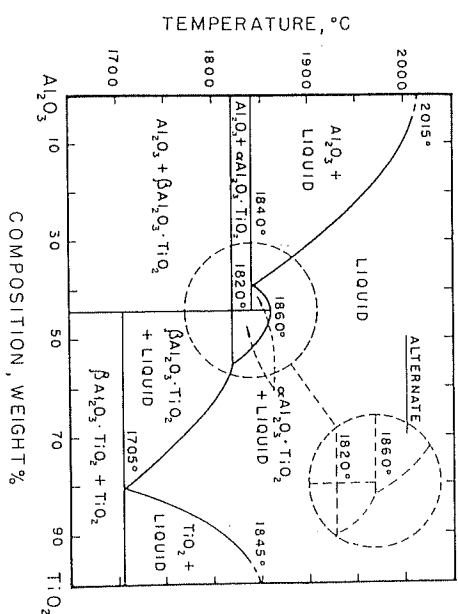


Figure 3.—Phase diagram for the system $\text{Al}_2\text{O}_3\text{-TiO}_2$ (after LANG *et al.*, 1952). LANG *et al.* were not certain if $\text{Al}_2\text{O}_3\cdot\text{TiO}_2$ melted congruently or incongruently. The alternative melting scheme is shown in an insert.

ignited repeatedly at subsolidus temperatures, with repeated intermediate grindings. Some mixtures used for high-temperature microscopy were also subjected to a further attrition of 5 min. in a tungsten carbide vessel, using a Glen Creston analytical mixer mill. This treatment reduced the mean particle size to less than 1 μ m.

Approximately 85 ternary compositions were prepared and used for heating-experiments. For studies of the phase distribution at subsolidus temperatures, portions of these compositions were heated in platinum foil envelopes or crucibles at constant temperature until an apparent equilibrium had been attained. For studies of the liquidus surface, standard quenching-furnaces were used. This equipment and technique, its limitations and accuracy, have already been described.² A newer technique, the hot-stage microscope, was used to supplement quenching-furnace studies. A commercial instrument based on the design of WELCH¹⁹ was used. This microscope furnace was found to be valuable both for reconnaissance runs at temperatures below 1550°C, but mainly for use at temperatures above the limits of platinum resistance furnaces: e.g., above 1550–1575°C, where primary reliance was placed on the high-temperature microscope. A number of runs were duplicated both in quenching furnace and on the high-temperature microscope, with identical results. No evidence was found that indicated a change in composition of the runs as, for example, might occur if one or more of the components were volatile.

Phases present in quenched samples were examined both by conventional petrographic techniques and by X-ray diffraction. Powder patterns were obtained on a Philips diffractometer and also on a Guinier-de Wolf focusing camera. Single crystals of the calcium titanates were also prepared and these crystals were examined with the aid of rotation and Weissenberg photographs. Density determinations were made with a Beckman air-comparison pycnometer.

3 RESULTS AND DISCUSSION

3.1 Phase Relations at Subsolidus Temperatures

The range of Al³⁺-containing oxygen-deficient perovskite solid solutions postulated by Coates and McMillan would lie along the join CaTiO₃-Ca₂Al₂O₅ (or CaAlO_{2.5}). The Al³⁺ end-member does not have a stable existence in the CaO-Al₂O₃ system. A series of compositions was prepared whose compositions lay on or in close proximity to this join. These compositions were heated at temperatures ranging from 1300° to 1500°C. Equilibrium was not, in general, attained at or below 1300°C, but above this temperature

equilibrium was judged to have been attained in runs of a few days' duration. However, many runs made at temperatures above 1370°C were found to contain a liquid phase. At subsolidus temperatures where compositions reacted fully, that is between ca. 1300° and 1370°C, mixtures which lay off the CaTiO₃-Ca₂Al₂O₅ join always gave perovskite plus at least one other crystalline phase; therefore it was concluded that the Al³⁺-substituted perovskites had compositions lying along the join CaTiO₃-Ca₂Al₂O₅. Results of heating experiments made on compositions lying on this join are shown in Table 1. These experiments show that an extensive range of Al³⁺-containing solid solutions exist. Room-temperature examination shows that CaTiO₃ itself and the low-Al³⁺ solid solutions are orthorhombic; with increasing Al³⁺ content the symmetry changes from orthorhombic to tetragonal and, finally, at or near the limit of Al³⁺ substitution, the solid solutions are cubic. The single-phase regions would be expected to be separated by two-phase regions of (orthorhombic + tetragonal) and (tetragonal + cubic) solid solutions.

Table 1
Results of Heating Experiments on the Join CaTiO₃-CaAlO_{2.5}

CaAlO _{2.50} (mole %)	Time (h)	Temperature (°C)	Phases present	
			X-ray	Petrographic
6.0	24	1420	Orthorhombic perovskite	P*
6.0	600	1300	Orthorhombic perovskite	P*
12.0	24	1420	Orthorhombic perovskite	P*
12.0	600	1300	Orthorhombic perovskite	P*
18.0	24	1420	Orthorhombic perovskite	P*
18.0	600	1300	Orthorhombic perovskite	P*
21.5	24	1420	Orthorhombic perovskite	P*
21.5	600	1300	Orthorhombic perovskite	P*
23.25	12	1400	Tetragonal perovskite	P*
25.0	24	1420	Cubic perovskite	P+L
25.0	100	1350	Cubic perovskite	P
25.0	600	1300	Cubic perovskite + C ₁₂ A ₇	P + C ₁₂ A ₇
27.5	90	1420	Cubic perovskite	P+L
27.5	22	1350	Cubic perovskite + C ₁₂ A ₇	P + C ₁₂ A ₇
27.5	600	1300	Cubic perovskite + C ₁₂ A ₇	P + C ₁₂ A ₇

Abbreviations: The perovskites are all perovskite solid solutions. P* = optically anisotropic perovskite. P = isotropic perovskite. C₁₂A₇ = 12CaO·7Al₂O₃.

No evidence was found that any of the compositions studied lay in either of these two-phase regions. Therefore it either must be presumed that the two-phase regions comprise only a very narrow range of compositions, or else that the change in symmetry is gradual, e.g., a continuous phase change. However, if the lattice parameters of the quenched solid solutions are examined at room temperature (Figure 4), it appears that the symmetry changes are discontinuous. Data shown in Figure 4 represent unit-cell data

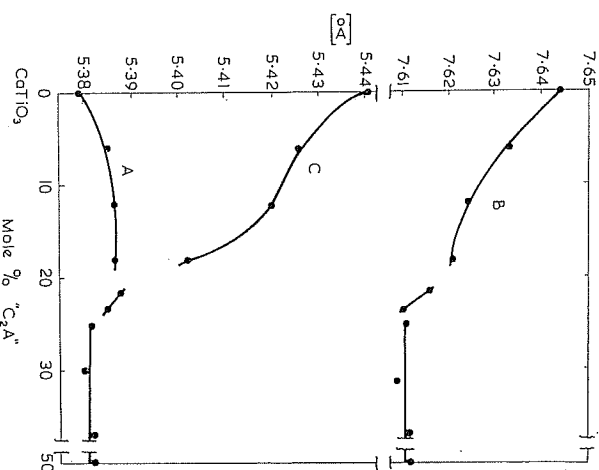


Figure 4.—The variation in unit-cell parameters of perovskite solid solutions. Three ranges of solid solution are shown: with increasing Al_2O_3 content these are orthorhombic, tetragonal and cubic. In order to facilitate comparison, all the cell dimensions have been converted to the larger orthorhombic cell.

determined at 25°C , for samples which were reacted at 1370°C and then quenched. Each solid solution was examined microscopically for the possible presence of additional phases. While it was not possible to detect small quantities of non-cubic perovskite in the presence of cubic perovskite, on account of the very low birefringence of the non-cubic solid solutions, it was easy to recognize the presence of a liquid phase: this readily undercools and is preserved to room temperature as a glass. This high-index glass stands out with strong

relief against the very high refractive index subhectral perovskite grains. At or below 1370°C , however, the limit of solid solution was marked by the appearance of other crystalline phases, principally $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, which was easily recognizable by its low refractive index.

Within the area of homogeneous single phase formation, it can be seen that the change in unit cell size is rather non-ideal. In order to facilitate this comparison, the unit cell sizes of the tetragonal and cubic cells have been converted to those of the corresponding orthorhombic cell by means of the transformation matrix:

$$\begin{aligned} \sqrt{2}a_{\text{cubic}} &= a_{\text{ortho}} = a_{\text{avg}} \\ 2a_{\text{cubic}} &= b_{\text{ortho}} = c_{\text{avg}} \\ \sqrt{2}a_{\text{cubic}} &= c_{\text{ortho}} = a_{\text{avg}} \end{aligned}$$

The densities of a number of these homogeneous solid solutions were also measured, and these results are shown in Figure 5. From the unit cell dimensions, the unit cell volume, V , is readily calculated. The larger orthorhombic cell was used in all cases: for the solid solutions containing 6.0, 12.0, 18.0, 21.5, 23.25 and 25.0 mole %

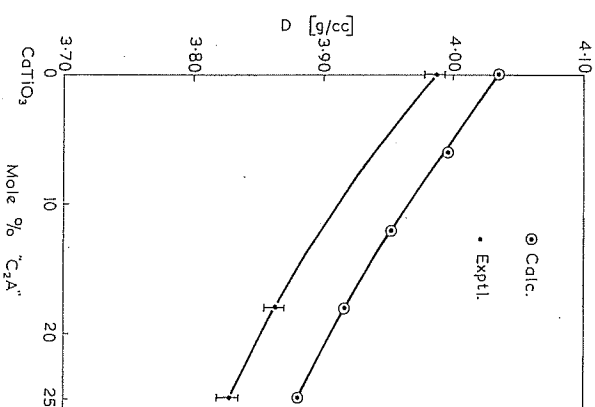


Figure 5.—Densities of homogeneous, single-phase, perovskite solid solutions containing Al^{3+} . The short vertical line segments terminated by bars indicate the error in measurement of the observed density.

3.2 The Liquidus Surface

Figure 8 shows the configuration of the liquidus surface. The primary-phase fields have been delineated by quenching runs on approximately 85 ternary compositions. The critical quenching runs—those which bracket some phase change, fix the temperature

and location of a boundary curve or invariant point, etc.—are shown in Table 2, copies of which will be supplied on request by the authors. These data have been used in the construction of Figures 8–14.

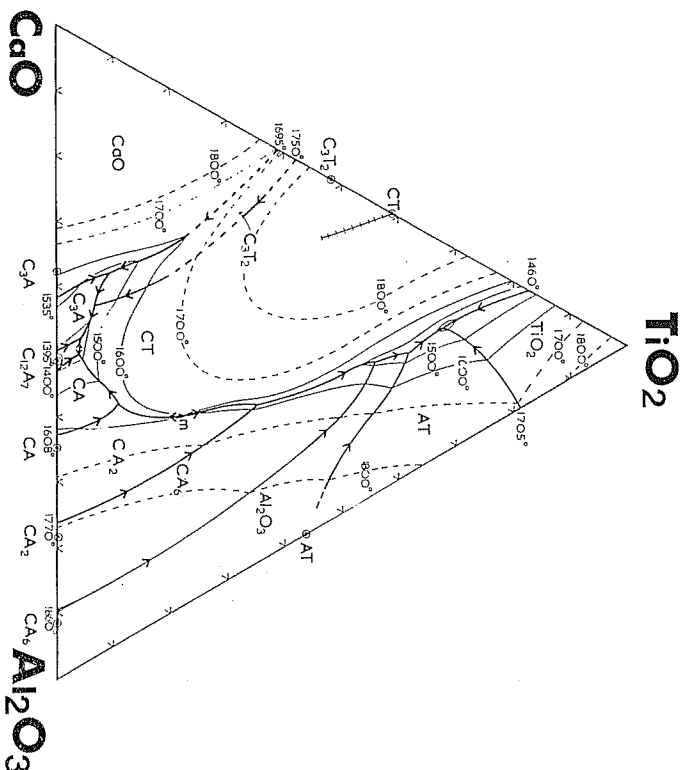


FIGURE 8.—Liquidus surface of the $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$ system. The direction and limit of perovskite solid solutions are shown by a cross-ruled line. The nature, temperature and composition of liquidus invariant points are given in Table 3.

At higher ($\text{CaO} + \text{TiO}_2$) contents, the primary fields of crystallization of the two calcium titanates sweep across the liquidus surface, creating a large primary field of crystallization of perovskite and a narrower tongue-like primary field of crystallization of $3\text{CaO} \cdot 2\text{TiO}_2$. The calcium aluminates, especially $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$, have rather small primary-phase fields. Thus, in the vicinity of the $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ composition, a number of compositions containing only 4–6 wt% TiO_2 actually have CaTiO_3 as their primary crystalline phase. At higher alumina contents the primary-phase fields of $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ and Al_2O_3 extend long tongue-like areas toward a series of invariant points

which are located at relatively high TiO_2 contents. The primary-phase fields of rutile and that of $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ have a relatively limited extent. The diagram shows two areas in which relatively low melting points are encountered: one centred near the eutectic between TiO_2 , Al_2O_3 , TiO_2 and CaTiO_3 , and the other close to the binary and ternary eutectics involving $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ as a crystalline phase. These two areas of low melting-temperatures are separated by a thermal maximum (shown as point *m* in Figure 8) along the univariant boundary curve which separates the primary-phase

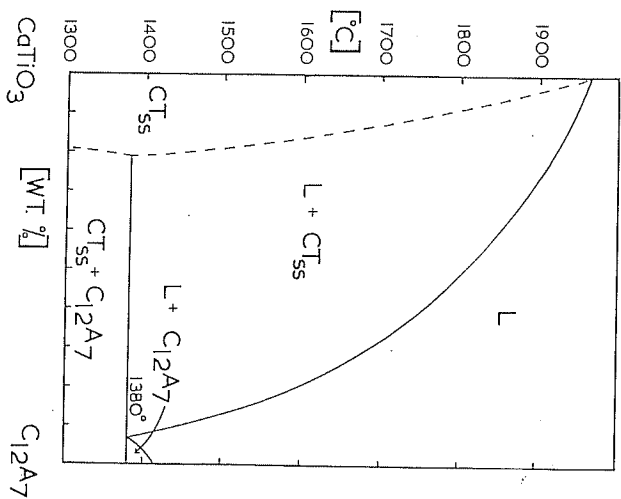


Figure 9.—The pseudo-binary join perovskite- $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$.

fields of perovskite and $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$. Moving away from these low-melting compositions, liquidus temperatures rise rapidly in the primary-phase field of perovskite; this is evidenced by the close spacing of isotherms in the perovskite primary-phase field. The very non-ideal extent of the various primary-phase fields means that a large number of the liquidus invariant points are peritectics. A summary of the nature, location and temperature of these invariant points is given in Table 3. Another consequence of these peritectic reactions is that relatively few of the subsolidus joins remain true

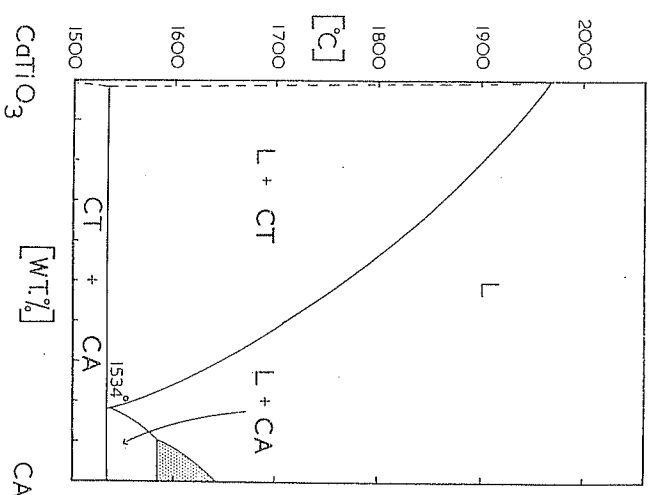


Figure 10.—The pseudo-binary join perovskite- $\text{CaO} \cdot \text{Al}_2\text{O}_3$.

binary systems at liquidus temperatures. As an example of this, note how the primary-phase fields of Al_2O_3 and of $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ transgress the $\text{CaTiO}_3-\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ join. This, plus the decomposition of $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ at lower temperatures, means that this join is binary only between 1257°C and 1435°C ; the latter is the peritectic temperature at which incongruent melting begins. The three joins which constitute essentially binary systems are $(\text{CaTiO}_3-\text{CaO} \cdot 2\text{Al}_2\text{O}_3)$, $(12\text{CaO} \cdot 7\text{Al}_2\text{O}_3-\text{CaTiO}_3)$ and $(\text{CaO} \cdot \text{Al}_2\text{O}_3-\text{CaTiO}_3)$; these are shown in Figure 9. In two cases the perovskite phase is an aluminous solid solution which means, strictly speaking, that the joins are not binary. However, on the $\text{CaTiO}_3-12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ join (Figure 9) the direction of perovskite solid solutions is towards a hypothetical end-member whose composition may be written as " $12\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ ". Thus the direction of solid solution is so nearly coincident with the join in question, which extends from perovskite to $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, that very little error results in projecting the observed data as if it were a true binary system. In another case, shown in Figure 11, the compositions of perovskites which are in equilibrium with either $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ or liquid along the join $\text{CaTiO}_3-\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ are

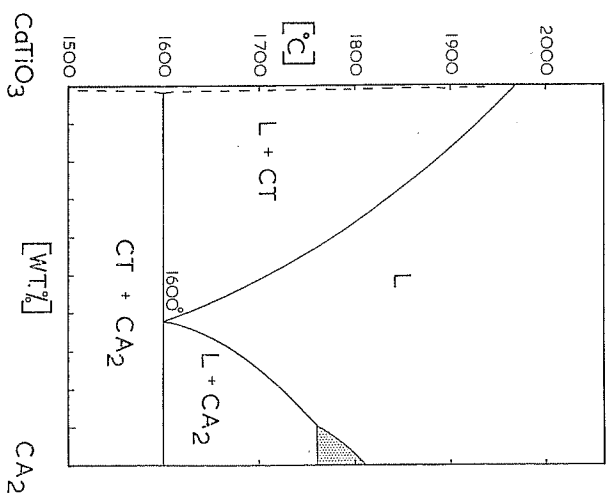


Figure 11.—The pseudo-binary join perovskite-CaO-2Al₂O₃.

always very low in Al₂O₃, therefore no serious error arises in projecting the results as a binary system. The eutectic in this binary system becomes, very nearly, a thermal maximum along the ternary univariant boundary curve. Another, slightly different, quasi-binary situation arises along the join (CaO-Al₂O₃-CaTiO₃) Figure 10. In the present study it has not been possible to decide the exact location of the invariant point (CaO-Al₂O₃+CaO-2Al₂O₃+CaTiO₃+liquid) with respect to the join in question. Hence it is not certain if this invariant point is a eutectic or a peritectic. It is tentatively shown in Table 3 as a eutectic, which means that, except for the incongruent melting of CaO-Al₂O₃ and a range of adjacent compositions, the system would be binary. This incongruent melting of CaO-Al₂O₃ itself at 1605±7°C has been confirmed by a number of runs made on the high-temperature microscope. The peritectic melting reaction is reversible with falling temperatures, provided that several hours are allowed for the dialuminate crystals to react with liquid. Contrary to assumptions which are sometimes made about the advantages of high-temperature microscopy, it was not found that equilibrium was attained any faster on the high-temperature microscope than by conventional quenching furnace techniques.

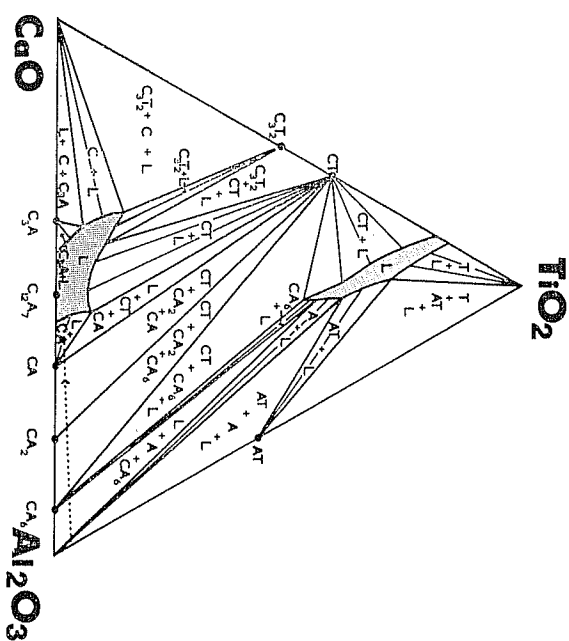


Figure 12.—Isothermal section of the CaO-Al₂O₃-TiO₂ system at 1500°C. The section has been simplified by omission of several small two-phase regions, as well as by showing the perovskite as pure CaTiO₃. The dotted line shows a range of compositions which are discussed in the text.

The direction of the univariant boundary curve separating the primary phase fields of the mono- and dialuminates in the ternary system has also been determined from appropriate compositions by means of standard quenching-techniques, and a reasonable extension of these data would also indicate an incongruent melting point of CaO-Al₂O₃. However, on the CaO-Al₂O₃-CaTiO₃ join, any quantities of dialuminate which would be present at liquidus temperatures as a result of this incongruent melting would be small. Hence as in the previous cases, the results may be shown as a binary system without serious error.

3.3 The "4CaO, 3TiO₂" Phase

This phase was first described by ROTH.¹³ In the present study, no 4:3 phase was encountered in the ternary system. CaTiO₃ was observed to grow as small cubes, optically isotropic or very nearly so, and 3CaO·2TiO₂ was observed as elongated laths or needles having a moderately high birefringence and parallel extinction. The habit and optical properties of these crystals fitted descriptions of the 3:2 phase given in the literature and, moreover, the same crystalline

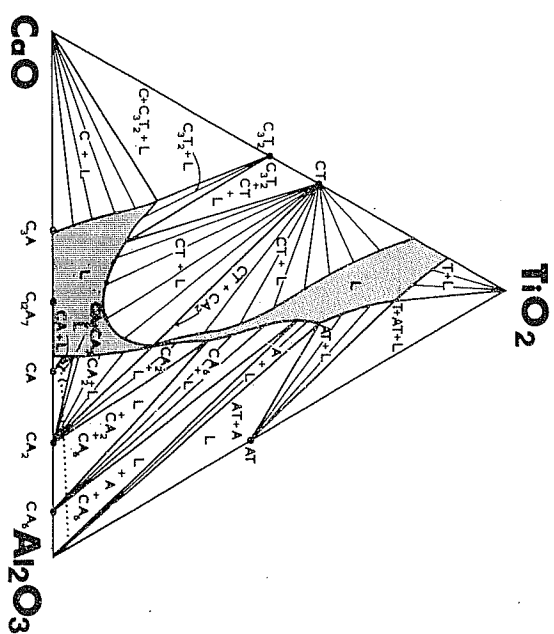
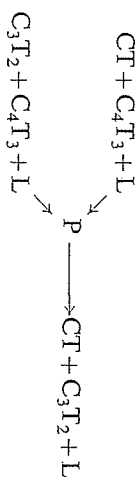


Figure 13.—Isothermal section of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2$ system at 1600°C ; for additional comments see caption, Figure 12, and text.

3:2 phase appeared to be in equilibrium along the appropriate univariant boundary curve, with either CaTiO_3 or CaO , at temperatures as high as 1700°C . X-ray powder patterns could be obtained of the 3:2 phase and on at least one occasion a quenching run yielded crystals large enough for single-crystal rotation photographs. The non-appearance of a 4:3 phase at the liquidus was, at this stage of the investigation, tentatively ascribed to its disappearance, by peritectic reaction at some quite high temperature, according to the following scheme of peritectic ($=P$) reaction:



However, in order to check that the birefringent needle-like phase was, in fact C_3T_2 , an attempt was made to reproduce Roth's syntheses of both C_3T_2 and C_4T_3 from the appropriate $\text{CaO}-\text{TiO}_2$ compositions. C_3T_2 was readily prepared, but the writers consider that the existence of a 4:3 phase must still be open to question. The reasons for this are as follows. If $\text{CaO} + \text{TiO}_2$ mixtures are sintered

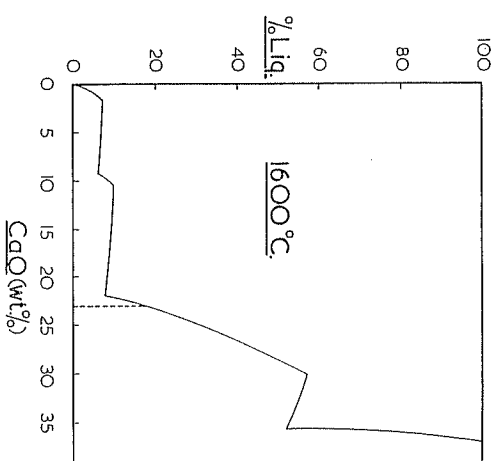
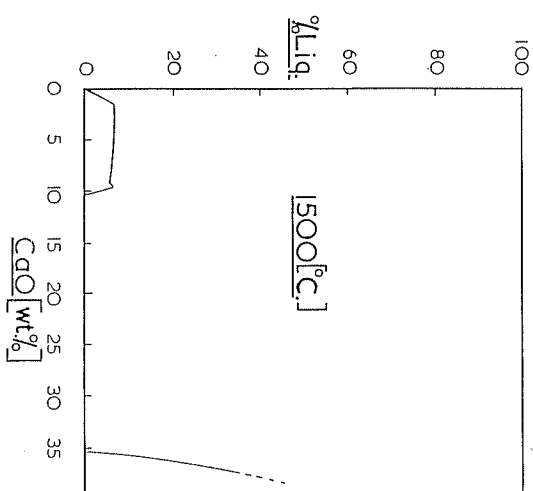


Figure 14.—Variation in the proportion of liquid present in $\text{CaO}-\text{Al}_2\text{O}_3-\text{TiO}_2$ compositions having the $\text{Al}_2\text{O}_3:\text{TiO}_2$ ratio 96:4 at (top) 1500°C , and (bottom) 1600°C . These compositions are also projected in the appropriate iso-thermal sections in Figures 12 and 13 respectively.

Table 3
Location and Nature of Invariant Points

Phases present	Type	Temperature (°C)	Composition (wt %)		
			Al ₂ O ₃	CaO	TiO ₂
CaO + C ₃ T ₂ + C ₃ A	Peritectic	1462 ± 0.5	33.5	57.0	9.5
C ₃ T ₂ + C ₃ A + CT	Peritectic	1432 ± 4	39.5	53.5	7.0
C ₃ A + CT + C ₁₂ A ₇	Eutectic	1369 ± 2	45.5	50.0	4.5
CT + C ₁₂ A ₇ + CA	Eutectic	1368 ± 4	49.0	47.0	4.0
CT + CA + C ₁₂ A ₇	Eutectic	1534 ± 5	52.5	36.5	11.0
CT + CA ₂ + CA ₆	Peritectic	1558.5 ± 3.5	41.0	24.0	35.0
CT + CA ₆ + Al ₂ O ₃	Peritectic	1476.5 ± 1.5	24.0	20.0	56.0
CT + Al ₂ O ₃ + AT	Peritectic	1435 ± 1	20.0	18.0	62.0
CT + AT + TiO ₂	Eutectic	1390	13.0	19.0	68.0
CT + C ₁₂ A ₇	Eutectic*	1380 ± 5	49.5	46.5	4.0
CT + CA	Eutectic*	1534 ± 5	52.5	36.5	11.0
CT + CA ₂	Eutectic*	1600 ± 5	45.0	30.5	24.0

*These systems are quasi-binary. The reasons for this are given in the text.

at temperatures below ~1500°C in the absence of a flux, the products which are obtained are fine grained and cannot readily be identified by optical means; it is necessary to use X-ray powder diffraction. Both C₃T₂ and CT have very similar powder patterns, and that reported for C₄T₃ is also very similar (but not identical) to those reported for both C₃T₂ and CT. The reported similarity between the X-ray powder patterns of all three phases lies mainly in the similarity of the stronger diffraction maxima: the distinction between the phases lies in the weaker X-ray reflections. The C₄T₃ composition was heated at temperatures between 1300°C and 1600°C for periods ranging from a few days to 30 days: under these conditions, Roth obtained the 4:3 phase readily. However, Guinier photographs did not give any consistent pattern amongst the weaker X-ray reflections which might have been indicative of a 4:3 phase; furthermore, none of the sets of weaker reflections which were obtained showed a marked similarity to Roth's powder data for the 4:3 phase. The stronger X-ray reflections of all three calcium titanate phases can be indexed on a cubic pseudo-cell having $a \approx 3.8 \text{ \AA}$ but the true unit cells must have a lower symmetry. Therefore, an attempt was made to sort out the problem by examining single crystals of the calcium titanates. Crystals were grown in three different ways: from CaO-TiO₂ charges sintered at 1600°C for 350 h, from CaO-Al₂O₃-TiO₂ melts, and from various fluxed compositions. PbO-Bi₂O₃ fluxed compositions were very successful in growing large crystals, often 1–2 mm

maximum size. Unfortunately these crystals all turned out to be either perovskite, or a perovskite-like phase having a doubled cell and Bi₂O₃ sheets between the perovskite layers; this latter phase was described by AURVILLIUS (1950).²⁰ Consequently no further work was done on these crystals, or on PbO-Bi₂O₃ fluxed compositions. Crystals were also extracted from a composition containing: CaO=54.0, Al₂O₃=38.0, and TiO₂=8.0 wt%, held at 1427°C for 12 h. At this temperature, the composition contained a few needles ca. 50 μm long in glass. One of these needles gave rotation photographs indicating an orthorhombic unit cell with $a=5.44 \text{ \AA}$, $b=5.40 \text{ \AA}$, $c=3.85 \text{ \AA}$. Unfortunately the crystal was not good enough to tell if the c axis repeat was the true repeat or if it was only a pseudo-repeat: the latter appears most probable. The use of LiF (15 wt%) as a flux yielded better crystals. The 3:2 composition mixed with LiF was heated for 72 h at 1560°C. Optical examination indicated that the quenched run contained needles or laths of C₃T₂, plates of CT, and glass. A lath which gave sharp extinction and appeared to be internally homogeneous was selected. X-ray examination showed that the crystal was not, in fact, homogeneous. The crystal proved either to be an intergrowth of two phases or else to contain two polytypes of the same phase; it is not certain which is the correct explanation. Both individuals of this composite crystal had orthorhombic symmetry and, moreover, each individual had identical a and b axes. One individual had: $a=5.44 \text{ \AA}$, $b=5.40 \text{ \AA}$, and $c=19.25 \text{ \AA}$; the other individual had axes (designated by primes): $a'=5.44 \text{ \AA}$, $b'=5.40 \text{ \AA}$, $c'=26.95 \text{ \AA}$. The two crystals had their a^* and a'^* directions and their b^* and b'^* directions in common: thus the composite behaved optically as a single crystal. Moreover, both individuals exhibited a strong pseudo repeat in the c^* direction; pseudo c and pseudo c' were 3.85 Å. From the rotation photographs about c^* it was apparent that true c^* and c'^* were related exactly by having $5c_p^* = 7c_p'^*$ where c_p indicates the pseudo-repeat. At least two crystals from this run gave identical c -axis rotation photographs and in both cases the two cells accounted for all the reflections observed in powder photographs of the bulk composition. One of these crystals known to contain two individuals was crushed: it gave a powder pattern essentially identical with that of 3CaO.2TiO₂ which had been prepared from the sintered unfluxed 3:2 CaO-TiO₂ composition. At this stage it may be concluded that the tetragonal unit cell for C₃T₂, which was deduced by Roth (from powder data alone), is probably not correct. If Roth's powder data are compared with those obtained in the present study, it is observed that, for CaO-TiO₂ compositions, no

patterns were obtained which were exactly like those of Roth's 4:3 phase. Instead, the 4:3 composition gave powder patterns which exhibited considerable variation in the weaker reflections which were supposed to be consistent and diagnostic for the 4:3 phase. The stronger perovskite-like reflections were, of course, always present. The variations in the weaker reflections were found to be dependent on two factors: the temperature at which the preparation had been made, and the CaO/TiO_2 ratio of the starting material. At any one temperature the patterns of weak reflections arising from the C_3T_2 phase were different, comparing samples which had a trace of excess CaO with those which had a trace of excess perovskite. These variations could be explained if the polytypism of " C_3T_2 " were influenced both by temperature and also by the solid solution of a small excess of either, or both, CaO and TiO_2 . Alternatively, there may be several other crystalline phases each of which have rather narrow ranges of thermal stability, and whose compositions lie between C_3T_2 and C_4T_3 . It is tentatively concluded that the former explanation is more likely to be correct, and that no additional phases exist which, in this temperature range, have compositions lying between C_3T_2 and CT . A further relevant observation which has been made concerns the effect of Al_2O_3 on the powder patterns of the various forms of C_3T_2 . Even small Al_2O_3 additions (ca. 1 mole % Al_2O_3) to the C_3T_2 composition, or to compositions between C_3T_2 and C_4T_3 , have a very marked effect on the powder patterns which are recorded from heated specimens. These small alumina additions are found to produce a pattern which is essentially identical to that which Roth records as characteristic of the "4:3" phase; moreover, the same pattern is obtained consistently over a range of temperatures from 1300°–1600°C, and its appearance is not sensitive to minor variations in $\text{CaO}:\text{TiO}_2$ ratio. Again the explanation of this behaviour is not certain, but it is tentatively concluded that Al and, possibly, excess Ti enter into solid solution in the 3:2 phase, thereby altering the polytype distribution. This possibility has been shown schematically in Figures 6 and 7 by showing a small region of homogeneous single-phase formation in the vicinity of the C_3T_2 composition, which extends along the binary edge as well as projecting into the ternary system. This region is stippled in both figures. Compositions within or adjacent to this area warrant further study. In this connection it should be pointed out that the pseudo-cubic symmetry of the calcium titanates greatly complicates the experimental problems in distinguishing the various phases, and that powder X-ray patterns, unless of the highest quality, are unlikely to be of much assistance.

3.4 The Binary and Quasi-binary Joins

Phase relations on the join $\text{CaTiO}_3\text{--}12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ are shown in Figure 9. Liquidus temperatures drop from perovskite toward a eutectic at 1380°C. The primary phase field of C_{12}A_7 is very small; consequently the eutectic is displaced very close to the C_{12}A_7 composition itself. The initial slopes of the liquidus profiles leading away from the eutectic are rather different, that of the perovskite liquidus having the steeper gradient. The perovskite solid solution in equilibrium with the eutectic liquid is comparatively rich in Al , as may be seen from Figure 4. The direction marking the compositions of these solid solutions is nearly, but not exactly, coincident with this join: to this extent the system is quasi-binary.

Figure 10 depicts phase relations on the join $\text{CaTiO}_3\text{--}\text{CaO} \cdot \text{Al}_2\text{O}_3$. The composition of the perovskite solid solutions which appear on this join are essentially pure CaTiO_3 . The eutectic between $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and CaTiO_3 is at 1534°C. Because of the incongruent melting of the monoaluminate to dialuminate, a small region of the diagram contains a non-binary phase ($\text{CaO} \cdot 2\text{Al}_2\text{O}_3$); the extent of this region is indicated by the stippled area.

The phase relations on the $\text{CaTiO}_3\text{--}\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ join are shown in Figure 11. The composition of the perovskite solid solutions in equilibrium with $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ or with liquid are, as in the previous example, always very close to pure CaTiO_3 . The eutectic, at 1600°C, marks the highest range of solidus temperatures which have been encountered amongst compositions containing all three components. $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ itself melts incongruently, and this small region of non-binary melting relations is shown by a stippled area.

4. APPLICATIONS

4.1 Phase Constitution of Aluminous Cements containing TiO_2

The distribution of titanium may be examined with the aid of the subsolidus phase diagrams (Figures 6 and 7). Some refractory products, such as aluminous cements, are apt to contain, at most, a small percentage of titanium. The subsolidus compatibility triangles and two-phase regions involving the calcium aluminates all contain perovskite, or an aluminous perovskite solid solution, as the titanium-bearing phase; hence it would be predicted that, in the absence of an iron-bearing phase, the titanium would be present as perovskite. Cements prepared by fusion processes may contain some glass; however, the liquidus diagram shows that liquids close to the C_{12}A_7 and CA compositions become saturated with respect to perovskite at total TiO_2 contents of only a few percent: therefore at any reasonable liquidus temperature the liquid phase would probably not be

capable of dissolving much TiO_2 . The effect of SiO_2 and iron oxide on these calculations is not known, but it seems unlikely that SiO_2 , dissolved in the melt, would be apt to enhance the solubility of TiO_2 .

4.2 The TiO_2 -containing Glasses

The system $\text{CaO-Al}_2\text{O}_3$ is noted for its glass-forming tendencies. Liquids in the vicinity of the 12:7 composition undercool readily, forming colourless glasses which have good infra-red transmission. During the present study, a number of TiO_2 -containing liquids based on the $\text{CaO-Al}_2\text{O}_3$ system were found to quench to glasses. The refractive indices of these glasses rises rapidly with increasing Ti content, as would be expected from the high molar refractivity of the TiO_2 component. It is difficult to saturate the high- Ti liquids in titanium, even at $1600^\circ\text{--}1700^\circ\text{C}$, as titanium, even if added as rutile, tends to re-precipitate as perovskite, and this perovskite redissolves slowly until the saturation value, shown by the appropriate isotherm in Figure 8, is eventually reached. The presence of undissolved perovskite did not seem to act as a nucleating agent for the subsequent crystallization of the glass during quenching.

An interesting feature of this system is the existence of yet another region of glass formation. This region lies in the vicinity of the $\text{CT-AT-Al}_2\text{O}_3$ and CT-AT-TiO_2 invariant points, and is bounded approximately by the 1500°C isotherm. Quench packets, containing 20–30 mg of liquid and quenched from an appropriate temperature into mercury, yielded homogeneous glasses which proved, under microscopic examination, to be free from quench growths. These glasses had a refractive index greater than 1.82 (which was the highest refractive index oil available). Attempts to prepare 5-g batches of these glasses by quenching platinum crucibles containing the appropriate melts were, however, only partially successful. The glass partially crystallized during the water quench. No experiments were undertaken on 'stabilizers' for the glass, but it may be of interest to glass technologists that these liquids, containing ca. 75% TiO_2 , can be quenched to yield glasses at all.

4.3 Phase Changes in High-alumina Refractories containing Titania

Bauxites used in alumina refractories often contains several percent TiO_2 . The role of this titania has been examined recently by CALDWELL *et al.*,²¹ who examined the phase constitution and the distribution of phases in new and in used brick, and also discussed the relevant available phase-equilibria data. They showed that $\text{Al}_2\text{O}_3\text{-TiO}_2$ was present in fired refractories and that, in service conditions, a zone enriched in $\text{Al}_2\text{O}_3\text{-TiO}_2$ formed at a distance of

15–20 mm behind the hot face. Data presented in the present study cannot of course be used to assess the effects of SiO_2 , but a simplified example, showing the effects of CaO attack on an alumina refractory, may prove illustrative. Taking a hypothetical refractory containing 96% Al_2O_3 –4% TiO_2 , this composition would contain two phases after firing: $\alpha\text{-Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3\text{-TiO}_2$ (ca. 8%). If, in service conditions, the refractory were used in a temperature gradient, the $\text{Al}_2\text{O}_3\text{-TiO}_2$ kept at temperatures below 1262°C should disproportionate to TiO_2 and Al_2O_3 ; in practice, the reaction is sluggish and unlikely to proceed during normal cooling of refractories, but it may well proceed in the appropriate zones of a refractory mass which is maintained in a temperature gradient. This disproportionation should manifest itself in the zone which was at, or just below, the disproportionation temperature, 1262°C .

Another case which may be considered is the effect of CaO on a titania-containing alumina refractory. Should the refractory pick up CaO during service, the bulk composition would shift along the line marking all compositions having a 96:4 ratio of Al_2O_3 to TiO_2 . The position of this line, and the phase changes which would occur, are best seen by projection upon the appropriate isothermal section or sections. Two such sections, one at 1500°C , the other at 1600°C , are shown in Figures 12 and 13 respectively. The path of changing compositions caused by CaO pick-up, and assuming no loss of Al_2O_3 or TiO_2 by draining out of a liquid phase, etc., follows the bold dotted line, in the direction of the arrow. The position of these lines is identical on both isothermal sections. The sequence of phase changes is similar but not identical at the two temperatures. The most significant feature, at both 1500°C and 1600°C , is that the addition of CaO causes the rapid disappearance of the $\text{Al}_2\text{O}_3\text{-TiO}_2$ phase and causes the rapid appearance of a liquid phase. Formation of this liquid phase is controlled by the liquidus invariant points involving CA_6 and Al_2O_3 as crystalline phases: because these invariant points are very low in temperature, liquid formation commences at temperatures as low as 1435°C . Because the invariant points are located at comparatively high TiO_2 contents, and because the appropriate isotherms lie comparatively close to the invariant points, the proportion of liquid formed is not large. This proportion of liquid may either be calculated directly from the appropriate isothermal section or, alternatively, read from the auxiliary graphs presented as Figure 14. At 1500°C it may be seen that, with increasing CaO content, the percentage of liquid first increases rapidly, then remains approximately constant, and then falls to zero, across a broad range of compositions. The range of compositions having relatively high

solidus temperatures are those which lie on the joins CT-CA and, especially, on the join CT-CA₂. The intervening three-phase triangle CT-CA-CA₂ also gives compositions with high solidus temperatures, as does the neighbouring triangle CT-CA₂-CA₆. The join CT-CA₂ is a pseudo-binary system, and it will be recalled that the intersection of the join with the univariant boundary curve separating the primary-phase fields of perovskite and CA₂ creates a maximum on the liquidus. Thus, while compositions on this join, or close to it, may not necessarily have especially high liquidus temperatures, they do have high solidus temperatures. At 1500°C a wide range of calcium aluminate compositions containing TiO₂ are more refractory—if solidus temperatures are taken as the criteria of refractoriness—than are nearly pure Al₂O₃-TiO₂ refractory compositions which contain only a few percent CaO. The limiting case of this superior refractoriness is encountered at 1600°C, where only one lime-containing composition is entirely solid: this is the composition which lies on the perovskite-CA₂ join, and at this point, shown in Figure 14 (bottom), by a dashed vertical line segment, the proportion of liquid becomes nil.

It is difficult to predict exactly the sequence of mineralogical changes which might be encountered in service conditions. Assuming that the refractory was subject to a temperature gradient, and that CaO pick-up occurred at the hot face which was maintained at ca. 1500°–1600°C, the refractory might well develop at least six distinct zones. From the hot face inwards, these would be:

- (1) A thin surface zone of a calcium aluminate liquid, containing crystals of the lime-rich aluminates CA and CA₂, plus possibly a trace of perovskite.
- (2) A zone of solid material containing CA₂ + CT and, with falling temperatures, CA₂ + CA₆ + CT.
- (3) A zone of alumina-rich phases, such as CA₆, plus CT and liquid.
- (4) A solid zone containing AT + Al₂O₃ + CT.
- (5) A solid zone in which the AT disproportionates to Al₂O₃ + TiO₂. And, finally,
- (6) The essentially unreacted brick.

With these factors in mind, it might well be possible to infer the modifying effects of SiO₂ and iron oxides using microscopic, chemical and mineralogical analyses of the zones developed in used refractories. The principal result of the present analysis is to show how a zone of low refractoriness may develop well behind the hot face: the development of liquid in this zone and the volumetric effects

of the disproportionation of Al₂O₃-TiO₂ might well affect the performance of the refractory.

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