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The Join Calcium Monoaluminate-Calcium Fluoride

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The system $CaO—Al_2O_3—CaF_2$ is important in cement and slag technology and in metallurgy. A section of this system, the pseudo-binary join $CaO \cdot Al_2O_3—CaF_2$, has been studied and the phase diagram established. This join is of particular interest since $CaO \cdot Al_2O_3$ is one of the main constituents of high alumina cement.

Quenching in sealed platinum capsules followed by microscopic and X-ray examination was the principal method used. The only compound on the join is $3CaO \cdot 3Al_2O_3 \cdot CaF_2$ which melts congruently at 1507 ± 1.5° C and forms one eutectic with $CaO \cdot Al_2O_3$ at 11% CaF_2 and 1498 ± 5° C and another with CaF_2 at 97.5% CaF_2 and 1405 ± 10° C. There is a wide zone of liquid immiscibility. The m.p. of CaF_2 was determined to be 1422 ± 1° C.

Attempts to use high temperature microscopy to study this system are described.

1. Introduction

The system $CaO—Al_2O_3—CaF_2$ has assumed considerable importance in cement technology and in metallurgy. The join $CaO \cdot Al_2O_3—CaF_2$ within this ternary system is of particular interest since calcium monoaluminate is one of the main constituents of high alumina cement.

Rankin and Wright [1] reported that $CaO \cdot Al_2O_3$ melts congruently at 1600° C but later Nurse *et al* [2] have shown that it melts just incongruently at 1602 ± 5° C to give $CaO \cdot 2Al_2O_3$ and liquid.

While no phase diagram has so far been published for the join $CaO \cdot Al_2O_3—CaF_2$, a ternary compound $3CaO \cdot 3Al_2O_3 \cdot CaF_2$ existing within it, was reported by Leary [3]. This compound was discovered during investigations on the effect of CaF_2 on the system $CaO—Al_2O_3$ and on the cementitous properties of calcium monoaluminate. Leary reported that $3CaO \cdot 3Al_2O_3 \cdot CaF_2$ was hexagonal and uniaxial negative with refractive indices $N_0 = 1.628$ and $N_e = 1.618$ and m.p. of 1507 ± 2° C. Later, Litvinova and Raichenko [4] reported a ternary compound with the same optical properties but attributed to it the formula $2CaO \cdot Al_2O_3 \cdot CaF_2$.

Gutt and Jeevaratnam [5] studied the synthesis and properties of $3CaO \cdot 3Al_2O_3 \cdot CaF_2$. This compound could be obtained from $CaCO_3$, Al_2O_3 and CaF_2 by heating in air at 1400° C for 30 min. The loss of fluorine was negligible. If, however, the heating was prolonged or the temperature raised, only $12CaO \cdot 7Al_2O_3$ and $CaO \cdot Al_2O_3$ were produced, with loss of fluorine. Gutt [6] employed DTA with samples held in sealed platinum capsules and reported that $3CaO \cdot 3Al_2O_3CaF_2$ melted congruently at 1505 ±2° C confirming Leary's original value [3].

Brisi and Rolando [7] studied the decomposition of $CaO \cdot Al_2O_3$ in the presence of chloride or fluoride and also solid state equilibria in the system $CaO—Al_2O_3—CaF_2$. According to these authors the ternary compound $3CaO \cdot 3Al_2O_3 \cdot CaF_2$ was in equilibrium with $CaO \cdot Al_2O_3$, CaF_2, $CaO \cdot 2Al_2O_3$ and with $11CaO \cdot 7Al_2O_3 \cdot CaF_2$, which is derived by substitution of oxygen by fluorine in $12CaO \cdot 7Al_2O_3$.

At the outset of the present work there was, as has been outlined above, a divergence of opinion about the formula of the ternary compound on the join $CaO \cdot Al_2O_3—CaF_2$ and its equilibrium relations with the end components of the join were not known. The major objective of the present work was to establish the phase diagram. A secondary objective was to compare the results obtainable for this system by quenching and by high temperature microscopy respectively.

2. Quenching

2.1 Experimental

The quenching procedure adopted was selected at the Building Research Station and its essential feature was the use of sealed platinum capsules. Several series of quench runs were then made, some at BRS and some at the Baikov Institute, the final series at the latter.

The mixes were prepared from $CaCO_3$, Al_2O_3 and CaF_2. For the final series calcium monoaluminate was made first and CaF_2 was then added.

To check whether the join was binary, decarbonated mixes made from $CaCO_3$, Al_2O_3 and CaF_2 were annealed in sealed 5 Rh/95 Pt capsules (at BRS) for 50 h at 1200° C in an electric furnace. The products were subjected to X-ray analysis by means of a de Wolff focusing camera. The results given in table I show that all samples except for No. 2 gave phases on the join. The trace of $12CaO\cdot 7Al_2O_3$ in sample 2 was regarded as a disequilibrium product and the join was treated as binary.

TABLE I

Sample no.	Wt percentage of CaF_2	Phases present
CA2	10%	$C_3A_3CaF_2 + CA$ (with traces of $C_{12}A_7$)
CA4	20%	Almost pure $C_3A_3CaF_2$
CA7	40%	$C_3A_3CaF_2 + CaF_2$
CA9	60%	$C_3A_3CaF_2 + CaF_2$
CA11	80%	$CaF_2 + C_3A_3CaF_2$

To calibrate the quench furnaces used at BRS and at the Baikov Institute the m.p. of the compound $CaO\cdot SiO_2$ was determined, giving results within 1.5° C of the generally accepted value of 1544° C. In the final series the 6/30 Rh—Pt thermocouple was employed and especially calibrated by measuring the m.p. of Cu, Ni and Pd as well as $CaO\cdot SiO_2$. Samples were placed in platinum tubes about 15 mm long, 3 to 4 mm in diameter with a wall thickness of 0.10 mm. Both ends of the tubes were welded either electrically or in oxy-acetylene flame. The packets were suspended in the hottest zone of the furnace where the temperature gradient was experimentally established to be zero over 30 mm.

The period of heating was 1.5 h if samples were placed in a cold furnace or 45 min if they were introduced into a hot furnace. In any case 20 min was allowed at the test temperature, to reach equilibrium. The swelling of packets provided an indication of no leakage. The products of quenching were examined by microscopy and X-ray analysis.

2.2. Results of Quench Studies

The results of quenching are presented in figure 1. Liquidus temperatures are accurate to ± 2.5° C and solidus temperatures to the left of the eutectic between $CaO\cdot Al_2O_3$ and $3CaO\cdot 3Al_2O_3\cdot CaF_2$ to ± 2.5° C and otherwise to ± 5° C. The ternary compound melts congruently at 1507° C. There is a eutectic between $CaO\cdot Al_2O_3$ and $3CaO.3Al_2O_3\cdot CaF_2$ at 11% CaF_2 and 1448° C. A wide zone of liquid immiscibility has been delineated over the composition range 34 to 95% CaF_2 and temperature range 1472° C to beyond 1550° C. A tendency towards immiscibility was suspected in compositions having between 25 and 34% CaF_2, because of the development, in this composition range, of two glasses, one transparent and the other brownish. This behaviour in the 25 to 34% CaF_2 range was not, however, sufficiently reproducible and the liquidus temperture shows a gradual fall. In view of this the beginning of the immiscibility zone is taken to be at 34% CaF_2 at which point the liquidus becomes horizontal. The immiscibility is very pronounced over the range 50 to 70% CaF_2 where a clear transparent glass and a brownish spotted glass are obtained.

The eutectic between $3CaO\cdot 3Al_2O_3\cdot CaF_2$ and CaF_2 occurs at 97.5% and 1405° C, the m.p. of CaF_2 being determined as 1422° C. (It is noteworthy that precise liquidus temperature was difficult to assess in the region 90 to 97.5% CaF_2.) A point of interest is the occurrence of quench growth of CaF_2 in compositions containing 20% or more of CaF_2. This could not be prevented and was clearly detectable by both microscopy and X-ray analysis. Liquid and glass composition in this system are therefore different.

3. High Temperature Microscopy

With the view to examining the melting behaviour of compositions on the join in an open atmosphere, a study of compositions up to 30% CaF_2 was attempted by means of high temperature microscopy technique, developed at the Building Research Station [8].

To find out if there was any loss of fluorine on

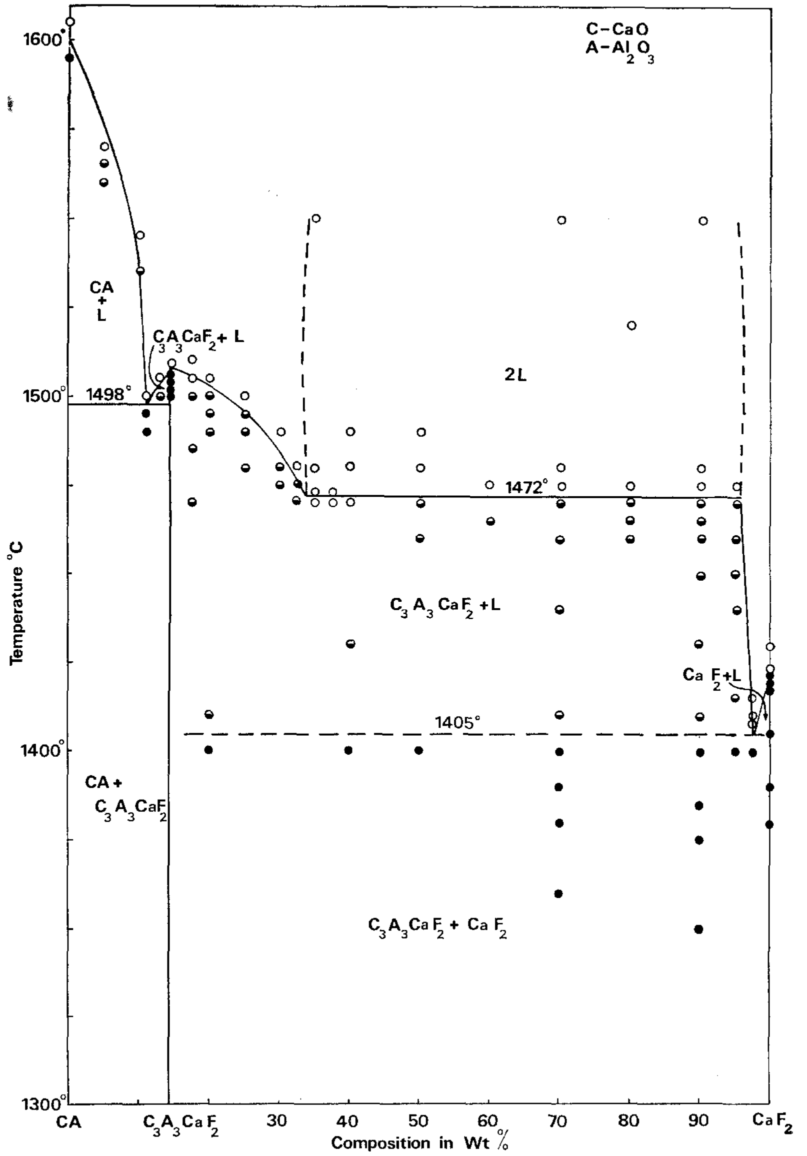

Figure 1 The join CA-CaF$_2$

the hot stage during the period of heating needed to make measurements, beads of a composition on the join containing 5.6% fluoride were held on the stage for 40 sec and were collected and analysed. The fluoride content after heating was 5.5%. Since the loss of fluorine was negligible and since the ternary compound $3CaO \cdot 3Al_2O_3 \cdot CaF_2$ could be prepared in an open atmosphere without any significant loss of fluorine [5] it seemed reasonable to proceed.

Compositions for this part of the investigation were prepared as follows. The samples were decarbonated (1.5 h at 1000° C) ground and melted in large sealed platinum capsules made from a platinum tube of 4.8 mm outer diameter and 0.15 mm in wall thickness. These homogeneous samples were mounted on the hot stage for study, the 5/20 Rh/Pt thermocouple being used. Readings were the same in air and argon and therefore the latter was used to prolong the working life of the thermocouples. The results of high temperature microscopy are given in table II.

TABLE II

No. of sample	Percentage of CaF_2 (wt %)	Temperature of initial melting °C	Liquidus temperature °C	Primary phase	Second phase if noted
1	5%	1360	1585	Birefringent imperfect plates	—
2	10%	1359	1561	Same	—
$C_3A_3CaF_2$	14.4%	1360	1557	Birefringent greyish plates which were often imperfect	—
3	15%	1360	1555	Same	—
4	20%	1361	1482	Same	Hexagonal isotropic crystals resembling C_3A
5	25%	1350	1505	Same	—
6	30%	1352	1440	Hexagonal isotropic crystals resembling C_3A	Birefringent rectangular plates

4. General Discussion and Conclusions

Quenching in sealed platinum capsules followed by X-ray and microscopic examination has proved to be a satisfactory method for the study of the system $CaO \cdot Al_2O_3$—CaF_2. Since quench growth of CaF_2 is so predominant X-ray analysis alone could give rise to misleading results and so microscopy is essential to distinguish between the genuine high temperature phases and those formed during cooling. High temperature microscopy provided very useful preliminary data indicating whether particular phases can be quenched and helping to select temperature ranges for quench studies. The differences between the quench data and high temperature microscopic observations are almost certainly due to compositional changes occurring in the sample on the hot stage. The phase diagram presented in fig. 1 is based on quench data. It has been confirmed that the only ternary compound present on this join is $3CaO \cdot 3Al_2O_3 \cdot CaF_2$ and this composition, given by Leary, is correct. Its phase relations have been delineated as has been discussed.

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