JOURNAL OF MATERIALS SCIENCE 8 (1973) 1278–1282

The phase equilibrium diagram of the ternary subsystem CaO-$CaO \cdot Al_2O_3$-11 $CaO \cdot 7$ $Al_2O_3 \cdot CaF_2$

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On the basis of the experimental results obtained from the study of high-temperature equilibrium relations of seven pertinent joins the phase diagram of the subsystem CaO–$CaO \cdot Al_2O_3$–11 $CaO \cdot 7$ $Al_2O_3 \cdot CaF_2$ has been constructed. In this diagram the delineation of the boundary curves of the primary fields of CaO, 3 $CaO \cdot Al_2O_3$, $CaO \cdot Al_2O_3$ and the 11 $CaO \cdot 7$ $Al_2O_3 \cdot CaF_2$ solid solution has been improved over our previously published phase diagram of the system CaO–Al_2O_3–CaF_2 [1]. The isotherms have also been drawn more precisely to give a better idea about the topography of the portion investigated.

1. Introduction

The crystallization behaviour of tricalcium aluminate, 12 $CaO \cdot 7$ Al_2O_3 and calcium monoaluminate with small additions of calcium fluoride is of special importance in cement technology and metallurgy. However, in our recently published phase equilibrium diagram of the system CaO–Al_2O_3–CaF_2 [1] this region has not been investigated and discussed to the necessary extent. The studies of Brisi and Rolando [2, 3] about the solid-state decomposition of tricalcium aluminate and calcium monoaluminate in the presence of calcium fluoride and chloride also do not give any idea about the high-temperature and liquidus relations of the above compounds. Volkonskii *et al* have demonstrated the stability of calcium fluoroaluminate up to 1450°C only [4], which is much below the melting point of the aforesaid compound.

The compatibility diagram of the system CaO–Al_2O_3–CaF_2 [5] shows that the compound 11 $CaO \cdot 7$ $Al_2O_3 \cdot CaF_2$ coexists with CaO, C_3A†, CA, C_3A_3Fl and CaF_2 (Fig. 1). In this article, the high-temperature equilibrium relations of the following joins have been described: C_3A–CA, CaO–$C_{11}A_7Fl$, C_3A–$C_{11}A_7Fl$, C_{12} A_7–$C_{11}A_7Fl$, $C_{11}A_7Fl$–CA, C_3A–I, and CA–II, where I and II denote the intermediate compositions 55% $C_{11}A_7Fl$ + 45% CA and 42% $C_{11}A_7Fl$ + 58% C_3A respectively. From the aforesaid joins, the equilibrium diagram of the subsystem CaO–CA–$C_{11}A_7Fl$ has been constructed. The experimental techniques adopted for the above studies were the same as in [6].

2. Description of individual joins

2.1. Join C_3A–CA

This join represents a part of one of the most controversial binary systems, the main controversy lying in the fact whether the phase $C_{12}A_7$ could be obtained in a strictly anhydrous state. Although this phase was previously reported [7] as a congruently melting compound with a melting point of 1415°C, later it was shown [8] that this compound is stable only in the hydrated form $C_{12}A_7H$, and so should not be included in the binary system.

In the present study, the entire join was not reinvestigated. Only the melting points of C_3A, $C_{12}A_7$ and CA were checked. While our observations on the melting behaviour of C_3A and CA matched well with the findings of [9], the melting behaviour of $C_{12}A_7$ as determined by us was significantly different. The peculiarity of this compound was that it did not give any sharp melting point and on quenching in sealed

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†CaO = C, Al_2O_3 = A, CaF_2 = Fl, H_2O = H

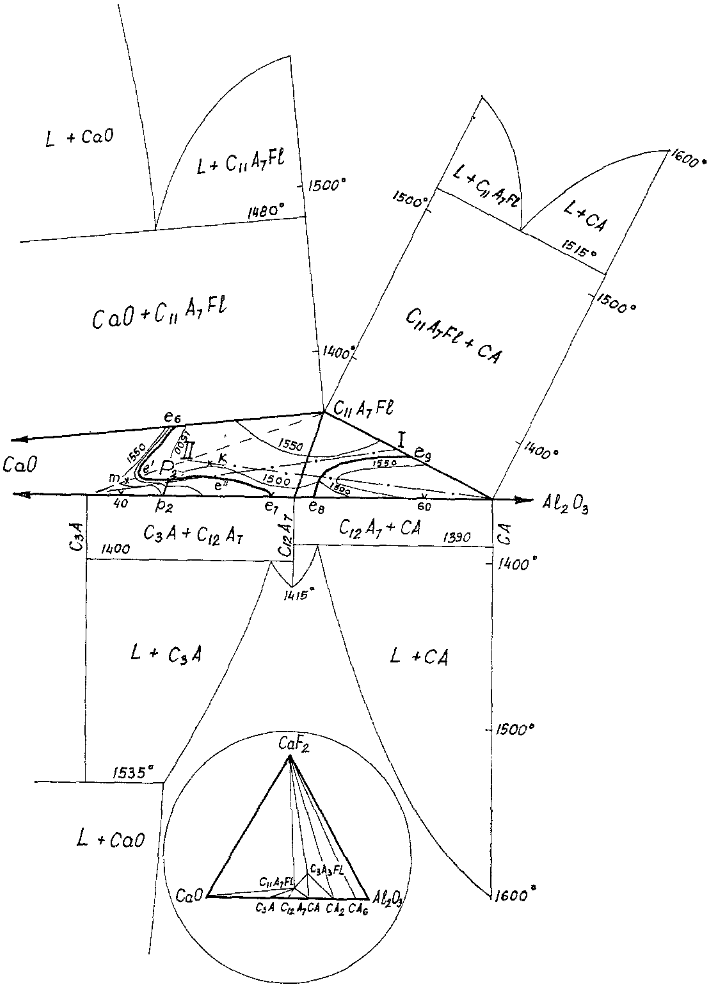

Figure 1 The phase equilibrium diagram of the subsystem CaO–$CaO \cdot Al_2O_3$–$11\,CaO \cdot 7\,Al_2O_3 \cdot CaF_2$ with the diagrams of its binary sides. The circular inset shows the compatibility triangles of the system CaO–Al_2O_3–CaF_2.

platinum capsules glass was found to coexist with unmelted crystals of $C_{12}A_7$ from 1380 to 1415°C. The refractive index of this glass coexisting with $C_{12}A_7$ crystals at 1390°C was 1.635. At 1415°C no primary crystals of $C_{12}A_7$ were left. However, quench crystals of $C_{12}A_7$ were noticed from 1415 to 1450°C which could be easily differentiated from the primary crystals. Under these circumstances this compound was considered to have its melting temperature at 1415°C. The coexistence of glass and crystals of $C_{12}A_7$ over a significant range of pre-melting temperature could not be explained at the present moment but an explanation may be sought in the structural peculiarities of this compound. In order to verify the presence of hydroxyl ions in $C_{12}A_7$ this compound was synthesized in hermetic platinum capsules by sintering for 25 min at 1370 to 1380°C after preliminary dehydration at the tip of welding gas flame, and subjected to infra-red spectroscopic examination. In contrast to the observations of Nurse *et al* no absorption band was found around 3550 cm^{-1} (Fig. 2), which indicated the anhydrous condition of $C_{12}A_7$.

In view of the above observations it was concluded that $C_{12}A_7$ should be included in the binary system and the phase diagram given in [9] cannot be fully accepted. Therefore, in the present study a hybrid form of the diagram was adopted: the field of $C_{12}A_7$ was taken from [7] and the rest from [9] as shown in Fig. 1.

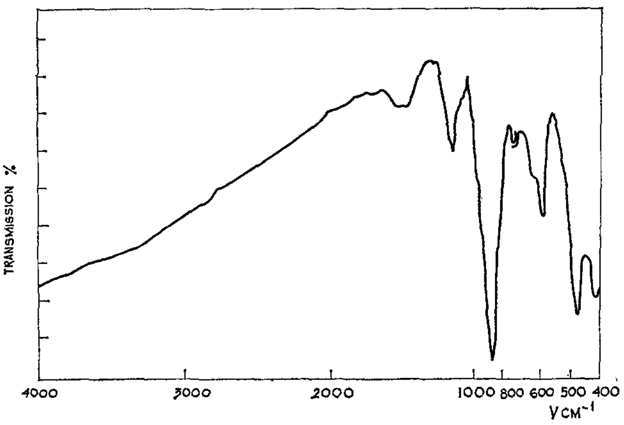

Figure 2 Infra-red spectra of 12 CaO·7 Al_2O_3.

2.2. Joins CaO–$C_{11}A_7Fl$ and $C_{11}A_7Fl$–CA

These joins represent simple eutectic systems with the following characteristics of the eutectics: e_6 (18.2% CaO + 81.8% $C_{11}A_7Fl$) at 1480° ± 10°C and e_9 (50% CA + 50% $C_{11}A_7Fl$) at 1515° ± 10°C (Fig. 1).

2.3. Join C_3A–$C_{11}A_7Fl$

There is no primary field of C_3A in this diagram. The liquidus has a minimum at 22% $C_{11}A_7Fl$ + 78% C_3A and 1468° ± 5°C. The final crystallization takes place by peritectic reaction at 1455° ± 10°C (Fig. 3a). Isothermal heating of various initially homogeneized compositions in this system for 40 to 50 min leaves disequilibrium phases which are shown in brackets in Fig. 3a. The disequilibrium crystals of CA are generally found inside $C_{11}A_7Fl$. Below the solidus unreacted CaO was often observed.

2.4. Join $C_{12}A_7$–$C_{11}A_7Fl$

The phase equilibrium relation of this join has already been indicated [1]. However, in this paper the actual experimental diagram is furnished (Fig. 3b). In this context it may be noted that in this system the refractive index of the crystalline phase varies from 1.608 ($C_{12}A_7$) to 1.602 ($C_{11}A_7Fl$) and that of glass from 1.672 to 1.664 respectively.

2.5. Joins C_3A–I and CA–II

In order to be able to determine more precisely the positions of isotherms, boundary curves and invariant points in the subsystem CaO–CA–$C_{11}A_7Fl$ these two transverse joins were studied.

The join C_3A–I contains two characteristic points: one at 74% C_3A and another at 62% C_3A. The first one corresponds to the intersection of the join with the peritectical p_2P_2 and the second one to the intersection of the join with the eutectical e_7P_2 (Fig. 1). Between these two intersection points there is a small primary field of C_3A (Fig. 4a). In the subsolidus region the join is divided into two independent sections by the trace of the join $C_{12}A_7$–$C_{11}A_7Fl$. As there is complete solid solution along this join, the projection of the solid solution zone was expected to appear in the plane of the section C_3A–I. However, as it could not be experimentally detected, in Fig. 4a only the trace of the solid solution plane has been indicated. The delineation of the crystallization fields exactly tallies with the experimental results with the exception of two points. At the points corresponding to 76.5% C_3A and 1470°C and 85.2% C_3A and 1460°C the presence of $C_{11}A_7Fl_{ss}$ could not be detected, although the appearance of this phase was otherwise expected.

The major part of the join CA–II (Fig. 4b) has been constructed from the experimental results with the exception of the dotted portion on the left which was extrapolated from the finally constructed ternary diagram. The characteristic point on the liquidus at 42% CA corresponds to the intersection of the join with the cotectic line e_8–e_9 (Fig. 1). The horizontal line at 1445°C (Fig. 4b) corresponds to the temperature of peritectic transformation P_2 involving the reaction $CaO + L \rightleftharpoons C_3A + C_{11}A_7Fl$. This is in perfect agreement with the solidus temperature of the join C_3A–$C_{11}A_7Fl$ (Fig. 3a).

Although the experimental results in general

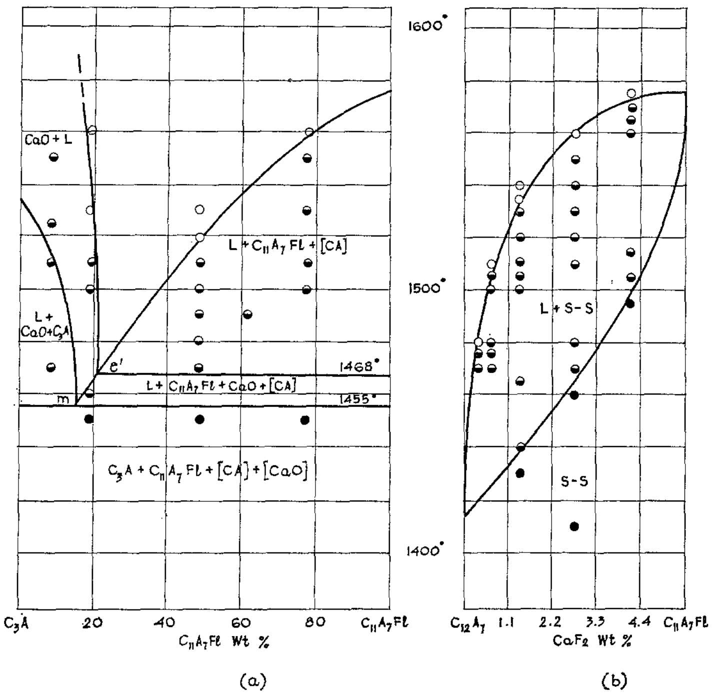

Figure 3 (a) The phase equilibrium diagram of the join 3 CaO·Al_2O_3–11 CaO·7 Al_2O_3·CaF_2; (b) The phase equilibrium diagram of the join 12 CaO·7 Al_2O_3–11 CaO·7 Al_2O_3·CaF_2.

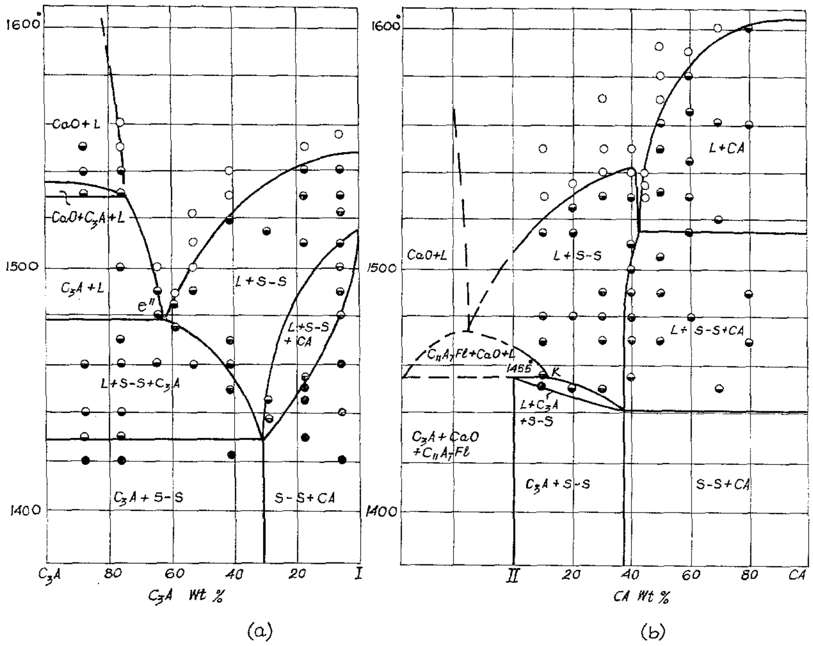

Figure 4 (a) The phase equilibrium diagram of the join 3 CaO·Al_2O_3–I. (b) The phase equilibrium diagram of the join CaO·Al_2O_3–II.

satisfy the delineation of fields as given in Fig. 4b, only in the compositions ranging from 60 to 80% CA and in the temperature interval from 1450 to 1520°C could no glass be detected, which may well be due to its extremely small quantity.

3. Ternary subsystem CaO–CA–$C_{11}A_7Fl$

There is only one variation of the ternary diagram that satisfies all the experimental joins and that is presented in Fig. 1. The subsystem contains three compatibility triangles, the final crystallization of which takes place at P_2, e_7 and e_8.

The position of the ternary peritectic P_2 (44.3% Al_2O_3 1.1% CaF_2, 54.6% CaO) signifying crystallization of CaO + C_3A + $C_{11}A_7Fl$ has been localized by the intersection of two rays: one from $C_{11}A_7Fl$ through the point K in the section CA–II (Figs. 1 and 4b) and the other from CaO through m in the section C_3A–$C_{11}A_7Fl$ (Figs. 1 and 3a). In drawing the first ray it was assumed that at the ternary peritectic P_2 crystallizes the end phase $C_{11}A_7Fl$ and not its solid solution.

In the triangle $C_3A - C_{12}A_7 - C_{11}A_7Fl$ there is crystallization of $C_3A + C_{11}A_7Fl_{ss}$, the lowest temperature of crystallization being the point e_7. Similarly in the triangle $C_{12}A_7$–CA–$C_{11}A_7Fl$ there is crystallization of CA + $C_{11}A_7Fl_{ss}$, the lowest temperature of crystallization being e_8.

The trend of the surface e_6–e_7 is somewhat unusual. If we go strictly by the experimental results of the pertinent joins, then one may come across a temperature minimum followed by a maximum in the surface as follows: te_6, 1480°C (Fig. 1); te', 1468°C (Fig. 3a); te'', 1478°C (Fig. 4a); and te_7 1400°C (Fig. 1). Theoretically it is possible to have such a trend [10] but the rise in the present case is only 10°C which is within the limits of experimental error and hence cannot be guaranteed. So in our interpretation the e_6 e_7 line is shown as a continuously descending one from e_6 to e_7 with a very gentle slope from e_6 to e''. The isotherms in Fig. 1 give a general impression about the topography of the area investigated.

4. Conclusions

1. The phase equilibrium diagram of the ternary subsystem CaO–CaO·Al_2O_3–11 CaO·7 Al_2O_3·CaF_2 has been constructed.
2. The detailed investigation of this portion of the system CaO–Al_2O_3–CaF_2 renders the delineation of primary fields of 3 CaO·Al_2O_3, CaO·Al_2O_3 and the solid solution of 12 CaO·7 Al_2O_3 and 11 CaO·7 Al_2O_3·CaF_2 more accurate and makes the high temperature topography more comprehensible.
3. The ternary peritectic P_2 has the composition of 54.6% CaO + 1.1% CaF_2 + 44.3% Al_2O_3 and temperature of 1455° ± 10°C.
4. The zone of solid solution between 12 CaO·7 Al_2O_3 and 11 CaO·7 Al_2O_3·CaF_2 is restricted to the plane of the section.

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Received 12 January and accepted 23 February 1973.