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The Phase Equilibrium Diagram of the System CaO-Al_2O_3-CaF_2

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The phase equilibria of the system CaO-Al_2O_3-CaF_2 have been studied by quenching in sealed platinum capsules followed by microscopic and X-ray examination of quenched products. The established phase diagram contains five ternary eutectics, two ternary peritectics and two invariant points of four-phase monotectic transformations. The system Al_2O_3-CaF_2 has been established to be the stable diagonal of the reversible reciprocal system $Al_2O_3 + 3CaF_2 = 3CaO + 2AlF_3$. In the high-fluoride region a wide zone of liquid immiscibility has been found. The system also shows such rarely noticed but theoretically possible phenomena as the transformation of peritecticals into eutecticals and occurrence of three different primary fields under single continuous zone of liquid immiscibility.

1. Introduction

Due to the growing importance of the system CaO-Al_2O_3-CaF_2 in metallurgy a systematic study of the system was started in the laboratories of Baikov Institute of Metallurgy of the USSR Academy of Sciences, Moscow. The following is a brief account of our findings on the phase equilibria of the system under consideration. The details are being published in various scientific journals of the Soviet Union.

A more or less complete review of the previous literature relating to this system has already been made [1, 2]. Without going into the details of the analysis we may put forward the major conclusions drawn, which served as a basis in designing the experiments on phase equilibria of the system:

1. The equilibrium study of the system is rendered difficult because of the presence of CaF_2 which evaporates at high temperatures and easily interacts with the material of the crucibles, with the furnace atmospheres and with the chemical components of the specimens themselves. Such interactions may lead not only to a change of composition but also to disturbance of the normal order of crystallisation. Therefore for studying the equilibrium relations of the given system an experimental procedure has to be devised which will give reproducible results.
2. The system Al_2O_3-CaF_2 is a reversible reciprocal system involving the following equation:

$$Al_2O_3 + 3CaF_2 = 3CaO + 2AlF_3 \qquad (1)$$

However, the previous equilibrium studies had not been initiated from this consideration. Therefore the phase diagram of the system Al_2O_3-CaF_2 needs a thorough reconstruction.

3. The equilibrium relations of the binary systems CaO-Al_2O_3 and CaO-CaF_2 need partial verification with respect to the following:
(a) The primary field of $C_{12}A_7$† in the system CaO-Al_2O_3, the controversy lying in the fact whether this phase could be obtained in a strictly anhydrous state.
(b) The presence of liquid immiscibility in the high-fluoride region and the nature of the liquidus curve in the primary field of CaO in the system CaO-CaF_2.
4. There was no complete diagram for the system CaO-Al_2O_3-CaF_2. Although the part CaO-CaF_2-C_5A_3 was studied by Eitel in 1938 [3], even this partial investigation cannot be regarded as complete since the diagram of Eitel does not include any primary field of C_3A and the compound C_5A_3 is now regarded as metastable.

2. Experimental

Before starting the actual investigation a few sets

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†CaO = C, Al_2O_3 = A, CaF_2 = Fl.

of preliminary experiments were conducted. The results of the more important ones are given below:

1. By studying simultaneously the same set of samples by high temperature microscopy in an open atmosphere and DTA and quenching in sealed platinum capsules it has been shown that the equilibrium relations of the system CaO-Al_2O_3-CaF_2 in a closed fluorine-bearing atmosphere sharply differ from those in open atmospheres, and for establishing the phase diagram of the system it is necessary to adopt the method of quenching in sealed platinum capsules [2, 4].
2. In the section Al_2O_3-CaF_2 by sub-solidus sintering of various compositions in both hermetic capsules and open platinum crucibles it was found that below the solidus Al_2O_3 and CaF_2 are the only two co-existing phases. According to the theory of reciprocal systems [5] the sub-solidus stability of Al_2O_3 and CaF_2 signifies that the diagonal connecting them in the reciprocal system CaO-Al_2O_3-AlF_3-CaF_2 is the stable one, and consequently the ternary system CaO-Al_2O_3-CaF_2 may be studied as an independent unit.
3. Attempt was made to gather some preliminary information about the quenchability of the melts of the given system. It was found that in the high-fluoride region (with more than 35% CaF_2 approximately) and in the high-lime region (with more than 60% CaO approximately) melts could not be quenched into a transparent glass. The high-fluoride melts, however, could be quenched to a brownish opaque striated mass, which is easily differentiated under the microscope from all other phases. The quench crystals of CaF_2 could also be differentiated from its primary crystals, but this differentiation could not be made in the case of CaO crystals. Based on these observations it was decided that all samples, after quenching, must be thoroughly analysed optically and X-ray patterns must be interpreted on the basis of these observations.

The actual quench experiments were carried out in sealed platinum capsules using a vertical tubular graphite furnace. The details of the experimental procedure are given in [2, 4, 6]. It was expected that the reaction shown by equation 1 would take place within the capsules. The equilibrium concentration of the reaction product CaO in the purely binary system Al_2O_3-CaF_2 as well as the development of P_{AlF_3} within the capsules were estimated thermodynamically [6]. Under the actual experimental conditions the equilibrium concentrations of CaO did not appear to exceed the amount that is normally present as an impurity in the analytically pure chemicals used in the experiments, and the pressure inside the capsules was equal to the atmospheric pressure or slightly more than that due mainly to the thermal expansion of the atmosphere that remained inside after the sealing of the capsules. That the capsule pressure was very near to that of the atmosphere is corroborated by the swelling of capsules made of sufficiently plastic platinum foils during heat-treatment, which was not always to their ultimate capacity and maintained a balance with the outer atmosphere.

3. Results and Discussion

The equilibrium relations of the following sections were studied: CA_2-CaF_2, CA-CaF_2, $C_{12}A_7$-CaF_2, C_3A-CaF_2, C_3A_3Fl-CA_2, C_3A_3Fl-$C_{11}A_7Fl$, CaO-$C_{11}A_7Fl$, C_3A-$C_{11}A_7Fl$, $C_{12}A_7$-$C_{11}A_7Fl$, $C_{11}A_7Fl$-CA and CaO-AHϕ6‡ (fig. 1). Apart from these internal sections the binary systems Al_2O_3-CaF_2 and CaO-CaF_2 were also investigated. The system CaO-CaF_2 could not be studied only by the method of quenching due to the difficulties already mentioned. So, the liquidus relations of this system were studied by the capillary method [7]. In the remaining binary system CaO-Al_2O_3, which has already been studied by various authors and in sufficient details, only a few important points were checked.

Before the equilibrium relations of various sections above the solidus were studied, a compatibility diagram of the entire system was established by solid-state sintering of selected samples in hermetic capsules [2, 8].

The phase diagram of the ternary system CaO-Al_2O_3-CaF_2 was constructed from the partial phase diagrams of the internal sections studied. In this respect a few models were assumed on the basis of the diagrams of the internal partial sections and on the overall preliminary conception of the system. Then rejecting those models which did not satisfy all the available information, the most satisfactory model was selected. In fact this approach has been quite effective in the present system. Even the invariant points could be fixed within a very narrow range of variation, the internal sections having provided good controlling points. How-

‡A binary composition 30 wt% Al_2O_3 + 70 wt% CaF_2.

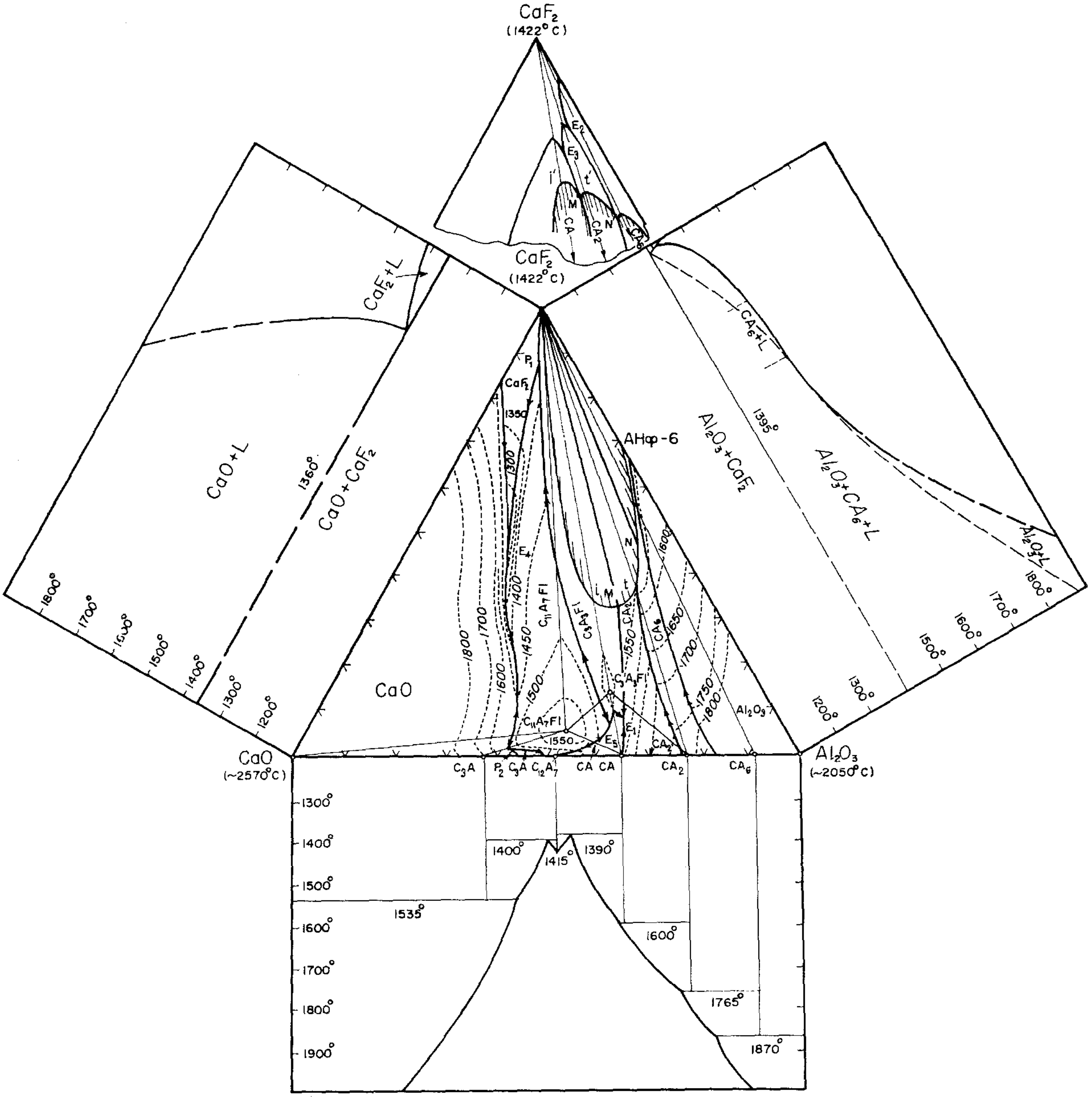

Figure 1 The phase diagram of the system $CaO-Al_2O_3-CaF_2$ along with the diagrams of its binary sides. The top fragment shows the portion with more than 95% CaF_2. Dashes along the border of the liquid immiscibility zone indicate the probable conode directions.

ever, these aspects as well as the internal sections are not discussed here, as they have been and are being detailed elsewhere. Only the salient features of the ternary diagram are given below:

1. The diagram contains the primary fields of CaO, CaF_2, Al_2O_3 and all other stable binary aluminates. The compound CA, which melts just incongruently in the binary system, behaves as a congruently melting compound in the ternary system.
2. The peritecticals originating from the binary peritectics of CA_2 and CA_6 become eutecticals with the increase of CaF_2 content.
3. In this system there are two congruently melting ternary compounds C_3A_3Fl and $C_{11}A_7Fl$ which are characterised by peritectic inter-

TABLE I Invariant points in the system CaO-Al_2O_3-CaF_2

Denotation	Type	Composition			Temperature °C	Corresponding triangle	Nature of equilibrium
		CaO	Al_2O_3	CaF_2			
E_1	Eutectic	31.0	61.0	8.0	< 1498°	CA-C_3A_3Fl-CA_2	L = CA + C_3A_3Fl + CA_2
E_2	,,	0.4	~ 2	97-98	~ 1390°	CA_2-CaF_2-CA_6	L = CA_2 + CaF_2 + CA_6
E_3	,,	0.9	~ 2.5	96-97	~ 1385°	C_3A_3Fl-CaF_2-CA_2	L = C_3A_3Fl + CaF_2 + CA_2
E_4	,,	38.0	22.0	40.0	1230°	CaO-$C_{11}A_7$Fl-CaF_2	L = CaO + $C_{11}A_7$Fl + CaF_2
E_5	,,	35.0	58.5	6.5	< 1475°	CA-$C_{11}A_7$Fl-C_3A_3Fl	L = CA + $C_{11}A_7$Fl + C_3A_3Fl
P_1	Peritectic	6.0	6.0	88.0	1355°	$C_{11}A_7$Fl-CaF_2-C_3A_3Fl	L + C_3A_3Fl = $C_{11}A_7$Fl + CaF_2
P_2	,,	56.2	42.5	1.3	1460°	CaO-$C_{11}A_7$Fl-C_3A	L + CaO = C_3A + $C_{11}A_7$Fl
M	Points of 4 phase monotectic reaction	18.0	48.5	33.5	1472°	—	$L_M = L_{M^1}$ + C_3A_3Fl + CA_2
M^1		1.5	4.0	94.5			
N	,,	8.0	45.0	47.0	1515°	—	$L_N = L_{N^1}$ + CA_2 + CA_6
N^1		1.0	6.0	93.0			
CaF_2	Compound	—	—	100.0	1422° ± 1.5	—	Congruent melting
C_3A_3Fl	,,	30.5	55.4	14.1	1507° ± 1.5	—	Congruent melting
$C_{11}A_7$Fl	,,	43.7	50.7	5.5	1577° ± 2.5	—	Congruent melting

transformation.

4. The diagram of the binary system Al_2O_3-CaF_2 shows that below the solidus Al_2O_3 and CaF_2 are the co-existing phases, while above it, at least in the interval 70 to 80% CaF_2, there is total absence of Al_2O_3 and presence of CA_6 (fig. 1). These results indicate that this section belongs to the group of reversible reciprocal systems.

5. There is complete solid solubility between $C_{12}A_7$ and $C_{11}A_7$Fl, the rise of the liquidus being steep from 1415° (mp of $C_{12}A_7$) to 1577° C (mp of $C_{11}A_7$Fl) over an increase of 5.5% CaF_2. The zone of solid solution is confined to the plane of the section $C_{12}A_7$-$C_{11}A_7$Fl. The maximum difference of refractive index of these two compounds is 0.006, and in this system the refractive index of any composition in the crystalline state is less than that of the corresponding glass.

6. The diagram, as a whole, contains nine invariant points, of which five are ternary eutectics, two ternary peritectics and two points of four-phase monotectic transformations. The characteristics of the invariant points are given in table I.

7. In the high-fluoride high-alumina region of the diagram there is a wide zone of liquid immiscibility. It is practically a closed one and just touches the binary side Al_2O_3-CaF_2. Below the immiscibility zone there are primary fields of C_3A_3Fl, CA_2 and CA_6. It appears that in the section CA-CaF_2 passing through the zone of liquid immiscibility there is a sharp stratification of liquids, which give rise to two distinctly separate types of quenched melts. In the section CA_2-CaF_2, also passing through the zone of liquid immiscibility, one can find the micro-liquation structure formed by the inclusion of one type of quenched melt into another. This structure indicates the probable occurrence of emulsion-type of liquation in the melts. This type of texture of the quenched melts could be seen in the join CaO-AHϕ6 from 12.5% CaO up to the binary side Al_2O_3-CaF_2. Further, the liquidus curve of the latter has an S-shaped form, it being suggestive of the presence of a zone of metastable liquid immiscibility. These observations indicate that the degree of immiscibility in this system is gradually reduced from the join CA-CaF_2 to Al_2O_3-CaF_2.

The lines ii′ (a part of the section CA-CaF_2) and tt′ (a part of the section CA_2-CaF_2) form two separate usual conodes and the lines MM′ and NN′ are the two special conodes, along which the four-phase reactions take place. These two conodes give rise to two minima at two different temperatures.

8. Traces of three horizontal platforms separated by sharp temperature falls were experimentally determined in the liquidus curve of the transverse join CaO-AHϕ6 passing through the zone of liquid immiscibility [6]. This type of liquidus is rather unusual and was explained by supplementing theoretically a few fields which were experimentally almost undetectable because of their extremely restricted spatial extensions. However, possibilities of other explanations, such as the occurrence of three liquid equilibria, cannot be ruled out at the present stage without further investigation of this zone of liquid immiscibility.

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