

## Phase diagram of CaO–Al<sub>2</sub>O<sub>3</sub> system

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### Abstract

The CaO–Al<sub>2</sub>O<sub>3</sub> system was studied by differential thermal analysis method in content interval from 0 to 60 mass% CaO. The absence of congruently melting compounds in argon atmosphere was confirmed and the coordinates of eutectic and peritectic points redefined. The heats of these transformations were measured and then the enthalpies of fusion of aluminates were calculated. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* Phase diagram; CaO–Al<sub>2</sub>O<sub>3</sub>

### 1. Introduction

The CaO–Al<sub>2</sub>O<sub>3</sub> system is involved in practical applications in the cement and concrete industry, in steel-making and refining of steel, in abrasive and refractories production. Due to such broad use the phase diagram of this system was studied many times [1–7], reviewed in [8], but in spite of more recent investigation [7] some handbooks give older versions or compilations [9,10]. The enthalpies of fusion of calcium aluminates, reviewed in [11], were calculated from indirect data and differ by large margins. The only calorimetric study was aimed to determine the enthalpy of incongruent decomposition of 3CaO·Al<sub>2</sub>O<sub>3</sub> [12] (306±31 J/g). So it was important to confirm the latest version of the diagram and directly define the mentioned enthalpies by quantitative differential thermal analysis (DTA).

### 2. Experimental

Samples were prepared from chemical grade calcined oxides (1 h at 1000°C) with compositions from 0 to 60 mass% CaO, step 2.5%. Both crucibles and furnace heater were made from molybdenum, enabling us to reach 2150°C and melt all samples.

In the preliminary work calcia-rich melts were found to corrode the crucible at elevated temperatures in vacuum. It could be supposed that the samples of 40–60 mass% CaO (as more CaO, is stronger) join into corrosion reactions with the molybdenum: 2CaO + Mo = 2Ca + MoO<sub>2</sub> and 3CaO + Mo = 3Ca + MoO<sub>3</sub>. The products of these reactions are much more volatile than the source substances. This is confirmed by mass-spectra measurement of Ca and MoO<sub>2</sub> pressures in the same conditions [13]. The colour of the samples after melting in vacuum changes together with CaO content due to corrosion from transparent/white at 0–10 mass% CaO to transparent/light dirty yellow at 40 mass% CaO and to transparent/brown at 60 mass% CaO. The last sample has a huge weight loss (more than 30%) after heating it up to 2100°C in vacuum but no loss after heating it to 1700°C in argon. The wettability also could be considered as a measure of affinity. Really, the liquid alumina did not change colour, did not react with the molybdenum crucible and only slightly wet it even at 2100°C in vacuum. A drop of the sample of 40 mass% CaO melted just above of liquidus temperature (1550°C) in argon was also found to form a sphere but in vacuum it wet molybdenum very well and its colour become darker. So after such preliminary results all experiments on diagram determination were carried out, not in vacuum, but in argon atmosphere (1.3 atm) to prevent rapid removing of products from the sample surface and reduce reaction rate. Nevertheless, the impurity of Mo in the samples, determined by X-ray fluorescence microanalysis, is less than 0.01 mass% for pure alumina

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and increases up to 1 mass% for the sample with 60 mass% CaO.

The differential thermal analysis cell was equipped with three equal crucibles. In addition to two convenient crucibles, the third crucible contains pure alumina that permits calibration of thermocouple (tungsten-rhenium 5/20) in situ by melting of  $\text{Al}_2\text{O}_3$  at the same time as measurement of the sample in the neighbouring crucible. The method, tested by melting of pure Al, KBr, Cu,  $\text{CaF}_2$ , Fe, Pt with the calibrated thermocouple, has an accuracy of temperature determination better than  $\pm 10^\circ\text{C}$  up to  $2100^\circ\text{C}$ . As an additional precaution against corrosion only the samples with 0–20 mass% CaO were heated up to  $2100$ – $2130^\circ\text{C}$  for calibration at the  $\text{Al}_2\text{O}_3$  melting point. The others were heated to just  $50$ – $80^\circ\text{C}$  above the liquidus line and were calibrated after main high temperature series by the melting of pure copper put directly into sample crucible. So, alumina ( $2050^\circ\text{C}$  and  $1100\text{ J/g}$  [10]) and copper ( $1084.62^\circ\text{C}$  and  $205\text{ J/g}$  [10]) were the main substances for temperature and heat calibration of the cell. The calorimetric properties of the cell were found by determining the dependence between heat of transition and correspondent DTA peak area by melting of 14 pure substances with well known fusion enthalpies (In, Sn, Pb, Sb, Al, KBr, NaCl, Ag, Cu, Be,  $\text{CaF}_2$ , Fe, Pt,  $\text{Al}_2\text{O}_3$ ). Details of similar methods of temperature and enthalpy calibration of the cell are described in [14]. All these calibrations enable us to define clearly, temperatures (better than  $\pm 10^\circ\text{C}$ ) as well as heat effects (better than  $\pm 10\%$ ) of transitions.

Heating rates were 5, 10, 20, 60 and  $100\text{ K/min}$ , with high temperature annealing before each new heating. Every sample was heated 3–8 times for better statistical determination of parameters of transitions. The outline characteristics of the resulting diagram (Fig. 1, Table 1) are peritectic melting of all aluminates and absence of  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  ( $\text{C}_{12}\text{A}_7$ ) in a dry atmosphere, as was pointed out in [7]. As it was there found,  $\text{C}_{12}\text{A}_7$  forms in the presence of less than 1 mass% of the water absorbed in the solid and does not form after removal of this water. The existence of this compound in the presence of traces of water is confirmed in our work by the appearance of  $\text{C}_{12}\text{A}_7$ -containing eutectic peaks at  $1403\pm 5^\circ\text{C}$  on the first melting (synthesis) of the sample (trace water was gained by CaO during grinding in air of the oxide mixture but removed after melting). None of the substances exhibits polymorph transitions.

The heat effects in the system were calculated from peak areas of DTA curves. When arranged by increasing of content in the sample of definite aluminate or eutectic, the correspondent peritectic or eutectic peak areas shows linear growth according to lever rule (Fig. 2), so that statistically proofed value for the stoichiometric content was found (Table 2). The full fusion enthalpies of calcium aluminates were derived as sum of

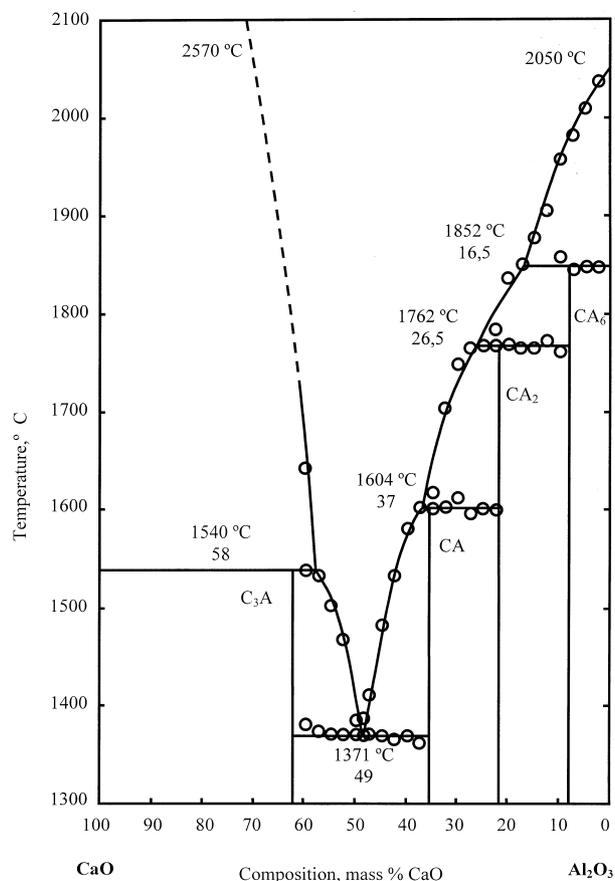


Fig. 1. Obtained diagram of the CaO– $\text{Al}_2\text{O}_3$  system.

Table 1  
Invariant points in the CaO– $\text{Al}_2\text{O}_3$  system

Reaction	CaO content (mass%)	Temperature ( $^\circ\text{C}$ )	Source
$\text{Al}_2\text{O}_3 = \text{L}$	0	2050	[10]
$\text{CA}_6 = \text{Al}_2\text{O}_3 + \text{L}$	$16.5 \pm 1$	$1852 \pm 7$	This research
$\text{CA}_2 = \text{CA}_6 + \text{L}$	$26.5 \pm 1$	$1762 \pm 5$	
$\text{CA} = \text{CA}_2 + \text{L}$	$37 \pm 1$	$1604 \pm 5$	
$\text{C}_3\text{A} + \text{CA} = \text{L}$	$58 \pm 1$	$1371 \pm 5$	
$\text{C}_3\text{A} = \text{CaO} + \text{L}$	$49 \pm 1$	$1540 \pm 5$	
$\text{CaO} = \text{L}$	100	2570	[10]

peritectic reaction heat plus calculated heat of melting of remaining solid (Table 3). For example, the fusion enthalpy of  $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$  ( $\text{CA}_6$ ) is the sum of  $410\pm 40\text{ J/g}$  for peritectic decomposition of this aluminate and  $650\pm 20\text{ J/g}$  for obtaining liquid from remaining  $\text{Al}_2\text{O}_3$ . The last value derived from following. Due to lever rule, decomposition of 1 g of  $\text{CA}_6$  at  $1852^\circ\text{C}$  provide  $8.47/16.5 = 0.513\text{ g}$  of liquid with 16.5 mass% CaO and  $0.487\text{ g}$  of  $\text{Al}_2\text{O}_3$  crystals. Heat needed to melt these crystals is the hidden heat of melting ( $1100\cdot 0.487 = 536\text{ J}$ ). The fusion enthalpies of  $\text{CA}_3$ , CA and  $\text{CA}_2$  were calculated

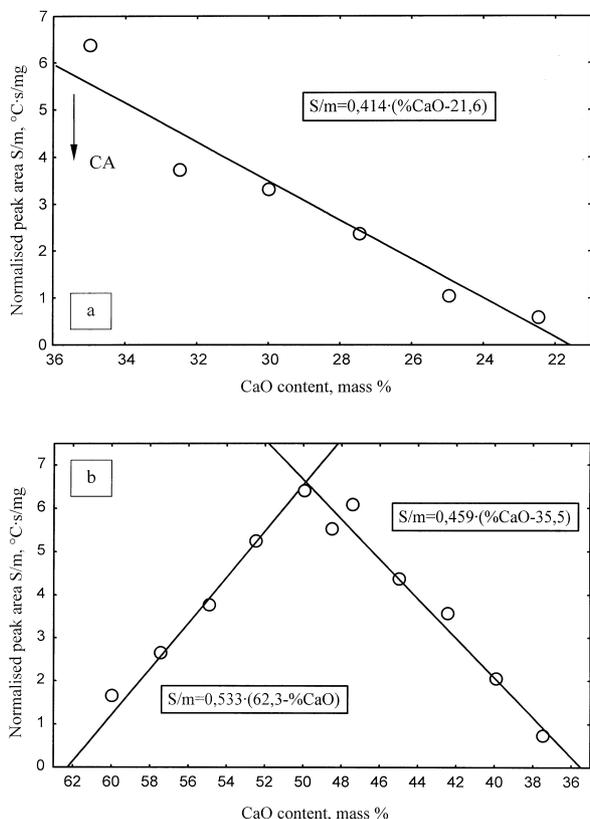


Fig. 2. Dependence of the peak size of peritectic decomposition of CA (a) and eutectic  $C_3A-CA$  (b) from the specimen composition.

Table 2  
Heats of invariant transitions in the CaO- $Al_2O_3$  system

Reaction	Enthalpy $\Delta H$		Source
	J/g	kJ/mol	
$Al_2O_3 = L$	$1100 \pm 10$	$112 \pm 1$	[10]
$CA_6 = Al_2O_3 + L$	$410 \pm 40$	$270 \pm 30$	This research
$CA_2 = CA_6 + L$	$490 \pm 40$	$130 \pm 10$	
$CA = CA_2 + L$	$440 \pm 50$	$70 \pm 10$	
$C_3A + CA = L$	$360 \pm 40$	–	
$C_{12}A_7 + CA = L$	$410 \pm 50$	–	
$C_3A = CaO + L$	$320 \pm 80$	$85 \pm 20$	
$CaO = L$	930	52	[10]

by the same way using fusion enthalpies of CaO,  $CA_2$  and  $CA_6$ .

According to Tables 1 and 3 one can see correlation between composition, melting point and fusion enthalpy of calcium aluminates (Fig. 3). Comparison with collected data [11] lead to conclusion that data recommended in [12,15–18] are close to the results of this research, whereas those derived from mass-spectra measurements [11] are 2–3 times less.

Table 3  
Fusion enthalpies in the CaO- $Al_2O_3$  system

Reaction	Enthalpy $\Delta H$		Source
	J/g	kJ/mol	
$Al_2O_3 = L$	$1100 \pm 10$	$112 \pm 1$	[10]
$CA_6 = L$	$1060 \pm 50$	$710 \pm 30$	This research
$CA_2 = L$	$810 \pm 50$	$210 \pm 10$	
$CA = L$	$530 \pm 50$	$84 \pm 10$	
$C_3A + CA = L$	$360 \pm 40$	–	
$C_{12}A_7 + CA = L$	$410 \pm 50$	–	
$C_3A = L$	$540 \pm 100$	$145 \pm 30$	
$CaO = L$	930	52	[10]

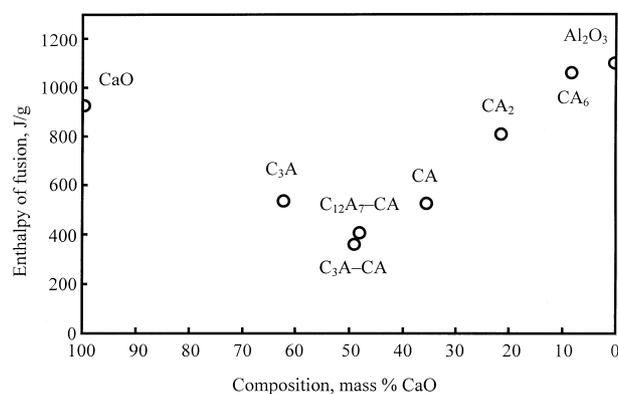


Fig. 3. Correlation between composition and enthalpy of fusion of the compounds and of the two eutectics in the CaO- $Al_2O_3$  system.

### 3. Conclusion

This investigation of CaO- $Al_2O_3$  system confirms the general view of diagram obtained in [7] with little divergence in temperature and composition values. It seems to be the first determination of all fusion enthalpies in one research. Results show a strong correlation between composition, melting temperature and fusion enthalpy of calcium aluminates.

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