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Phase diagram of the system $CaCl_2$–$CaCO_3$

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Abstract

The chloride-rich part of the system $CaCl_2$–$CaCO_3$ has been investigated by differential scanning calorimetry (DSC). The phase diagram is of an eutectic type. The eutectic mixture contains 30 mol% $CaCO_3$ and melts at 635°C. Experimental data suggest the existence of a double salt $CaCl_2 \cdot CaCO_3$, which decomposes to single salts at 628°C.

Keywords: DSC; Calcium chloride; Calcium carbonate; Phase diagram

1. Introduction

Calcium chloride and calcium carbonate are very common salts used for many chemical and metallurgical purposes, separately and together. And yet there are very few data on their binary system. P. Niggli [1] stated that it formed an eutectic at 30 mol% $CaCO_3$ that melted at 622°C. He also suggested the formation of a double salt $CaCl_2 \cdot CaCO_3$. N.A. Toropov and I.G. Luginina [2] synthesised this compound and presented its X-ray diffraction spectrum. I.F. Poletaev et al. [3] found the composition of the eutectic to be 33 mol% $CaCO_3$ and the temperature to be 630°C. They investigated only liquidus line and did not find the double chloride–carbonate compound.

2. Experimental

Seventeen compositions between pure $CaCl_2$ and 50 mol% $CaCO_3$ were studied in NETZSCH STA 409 EP instrument. This apparatus allows differential scanning calorimetry (DSC) and thermal gravimetry (TG) measurements to be carried out simultaneously. Alumina crucibles and reference material were used. The instrument was previously calibrated against standard substances with known melting points: Sn (231.9°C), Pb (327.5°C), Zn (419.6°C), Al (660.3°C) and NaCl (801°C). All experiments were carried out in the atmosphere of dry CO_2 to prevent the decomposition of calcium carbonate. The temperature error was ±2°C.

The samples were prepared directly in the apparatus as follows. Anhydrous calcium chloride was prepared from $CaCl_2 \cdot H_2O$ (Aldrich ACS reagent, 98+% purity). A study of the thermal decomposition of calcium chloride dihydrate [4] showed that most of the water could be removed by slow heating of the salt up to 200°C. A known amount of $CaCl_2 \cdot H_2O$ was placed in the crucible and heated at the rate of 0.5°/min up to 300°C. Then, the salt was taken to 800°C and dry CO_2 was passed over it for 10 h. The mass loss was registered, and this value was taken from the initial weight of the sample. The required amount of $CaCO_3$ was thoroughly weighed and added to the crucible with anhydrous calcium chloride. Calcium carbonate

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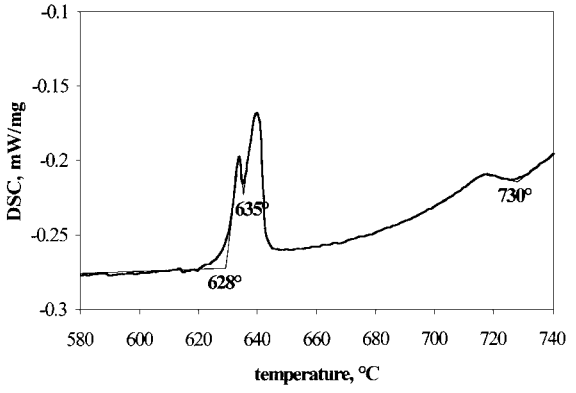

Fig. 1. Heating curve of $CaCl_2$–$CaCO_3$ (15 mol%) at 20°/min.

used was Aldrich ACS reagent (99+% purity). Prior to use, it was kept in an oven for 48 h at 75°C. The salts were fused in the crucible, kept in the liquid state for some time to homogenise the mixture, then frozen. The prepared sample was heated up at 2°/min and the heating curve was registered.

3. Results

An example of the DSC trace obtained is given in Fig. 1. Onset points of the peaks on the heating curves were taken for temperatures of phase transitions, the end of the peak for the temperature of liquidus being as shown in the figure. Two sharp peaks can clearly be seen at temperatures of 628 and 635°C.

The measurements are summarised in the Fig. 2, resulting in the phase diagram of the system $CaCl_2$–$CaCO_3$. The eutectic temperature obtained (635°C) is higher than reported in previous papers [1,3]. This must be because, in these papers, the temperatures were determined in the cooling cycle, while in our work, we used the heating cycle. In our experiments, a substantial overcooling phenomenon occurred, thus the cooling curve could not be used for the measurements of phase transitions.

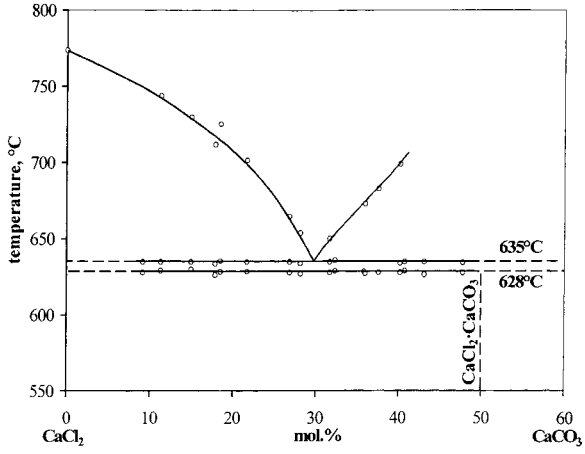

Fig. 2. Phase diagram of the system $CaCl_2$–$CaCO_3$.

The composition of the eutectic mixture is found to be 30 mol% $CaCO_3$ in good agreement with [1]. The peak at 628°C was observed on all the heating curves obtained between pure calcium chloride and 50 mol% $CaCO_3$. This phase transition happens in the solid state and may be attributed to the decomposition of the double compound $CaCl_2 \cdot CaCO_3$ to single salts.

Acknowledgements

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References

[1] P. Niggli, Zeitschrift fur Anorganische und Allgemeine Chemie 106 (1919) 126.
[2] N.A. Toropov, I.G. Luginina, Neorganicheskie Materialy 5 (1969) 914.
[3] I.F. Poletaev, A.P. Lyudomirskaya, A.I. Ismailov, N.D. Tsiklina, Zhurnal Neorganicheskoi Khimii 21 (1976) 2281.
[4] E.B. Freidina, D.J. Fray, In: B. Mishra (Ed.), EPD Congress 1999, TMS, San Diego, CA, 1999, p. 169.