ELSEVIER

Thermochimica Acta 356 (2000) 97–100

thermochimica acta

www.elsevier.com/locate/tca

Study of the ternary system $CaCl_2$–NaCl–CaO by DSC

E.B. Freidina, D.J. Fray*

Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, UK

Received 27 August 1999; accepted 2 February 2000

Abstract

The chloride-rich part of the ternary system $CaCl_2$–NaCl–CaO has been investigated. Ten vertical cross sections below 20 mol% CaO were studied by differential scanning calorimetry. A liquidus surface corresponding to primary crystallisation of $CaCl_2$ and three secondary crystallisation lines was determined. The constructed ternary phase diagram was found to be of a simple eutectic type, E=500°C (48 mol% $CaCl_2$, 47 mol% NaCl, 5 mol% CaO) is suspected. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Differential scanning calorimetry (DSC); Calcium chloride; Sodium chloride; Calcium oxide; Phase diagram

1. Introduction

The binary system, $CaCl_2$–CaO, has many chemical and metallurgical uses. Its phase diagram was studied by Wenz et al. [1] and displayed a eutectic mixture, which melts at 750°C and contains 6.5 mol% CaO. For various purposes it is useful to reduce the melting point of the salt mixture. This can be achieved by adding to the melt other components, such as chlorides — as for instance, NaCl. Calcium chloride forms with sodium chloride a relatively low melting eutectic [2]: 500°C, 46 mol% $CaCl_2$ in comparison with the temperatures of fusion for pure salts (771–778°C for $CaCl_2$ and 778–801°C for NaCl, according to different sources [3]). Calcium oxide melts at a very high temperature — 2614°C [4]; hence, if there is any low-melting region in its mixture with calcium and sodium chlorides, it must be expected in the chloride-rich part of the diagram. The solubility of lime in the $CaCl_2$–NaCl melt was studied by Boghosian et al. [5]. According to this work, it is very low in pure NaCl: 0.001 mol% at 850°C, but increases significantly with the $CaCl_2$ content in the system. In the present work, the calcium chloride corner of the ternary phase diagram $CaCl_2$–NaCl–CaO has been investigated by differential scanning calorimetry.

2. Experimental

Thermal experiments were performed in the NETZSCH STA 409 EP instrument. This apparatus allows DSC and TG (thermogravimetry) measurements to be taken simultaneously. Crucibles and the reference material were made from alumina. The instrument was previously calibrated against standard substances with known melting points: Sn (231.9°C),

---

* Corresponding author. Tel.: +44-1223334306; fax: +44-1223334567.
E-mail address: djf25@hermes.cam.ac.uk (D.J. Fray)

PII: S0040-6031(00)00454-8

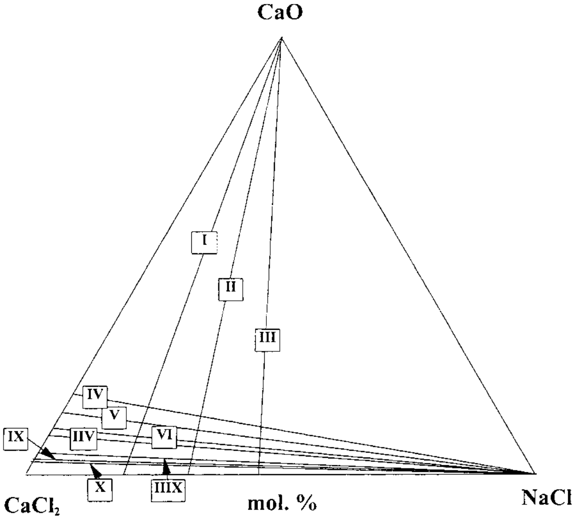

Fig. 1. Positions of 10 vertical sections on the composition triangle.

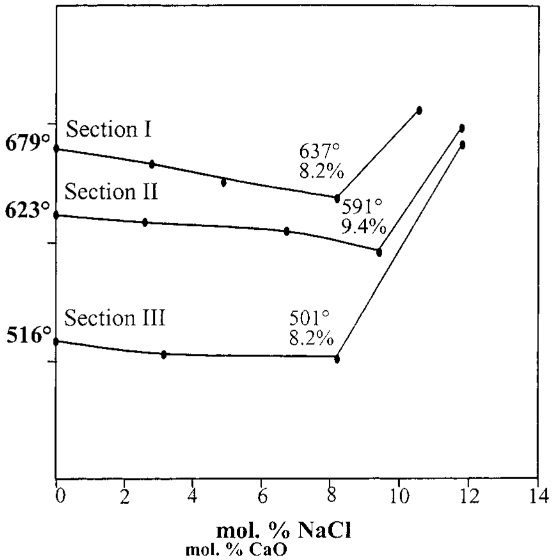

Fig. 2. Liquidus curves for sections I, II and III.

Pb (327.5°C), Zn (419.6°C), Al (660.3°C) and NaCl (801°C). All the tests were carried out in an atmosphere of argon, which was dried over silica gel and molecular sieves. The temperature error was ±2°C.

Sodium chloride (Aldrich A.C.S. reagent >99% purity) was kept at 75°C for 48 h before use. Calcium oxide was prepared by thermal decomposition of $CaCO_3$ (Aldrich A.C.S. reagent, >99% purity) at 1000°C. The preparation of anhydrous calcium chloride from $CaCl_2{\cdot}H_2O$ (Aldrich A.C.S. reagent, >98% purity) is described elsewhere [6]. The samples were made directly in the apparatus. A known amount of $CaCl_2{\cdot}H_2O$ was placed in the crucible and heated to 300°C at the rate of 0.5°/min. The salt was melted at 800°C and dry Ar 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 CaO (or NaCl) was carefully weighed and added to the crucible with anhydrous calcium chloride. 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. After that, the remaining salt was added and the procedure repeated. The end of the peak on the heating curve was taken as the liquidus temperature.

3. Results and discussion

Ten vertical cross sections of the composition triangle, indicated in Fig. 1, were investigated. The liquidus curves of these sections are shown in Figs. 2–4. The compositions and the temperatures

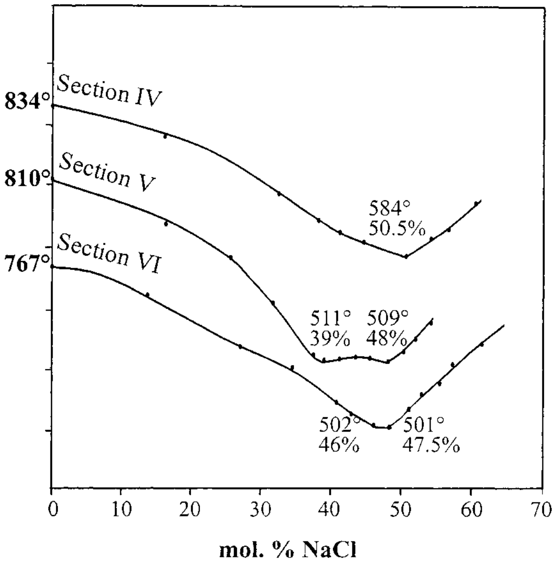

Fig. 3. Liquidus curves for sections IV, V and VI.

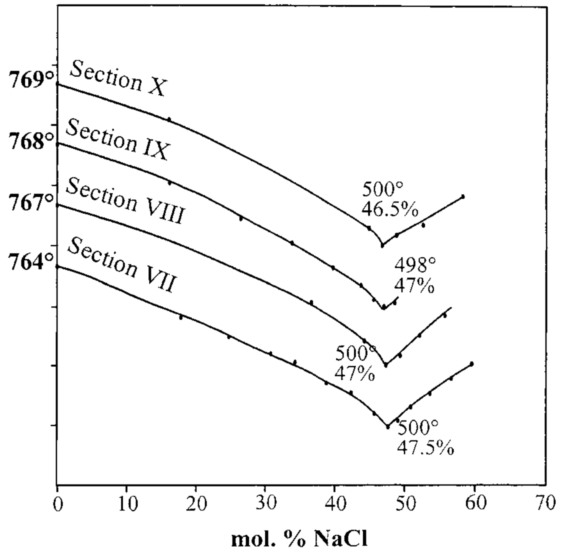

Fig. 4. Liquidus curves for sections VII, VIII, IX and X.

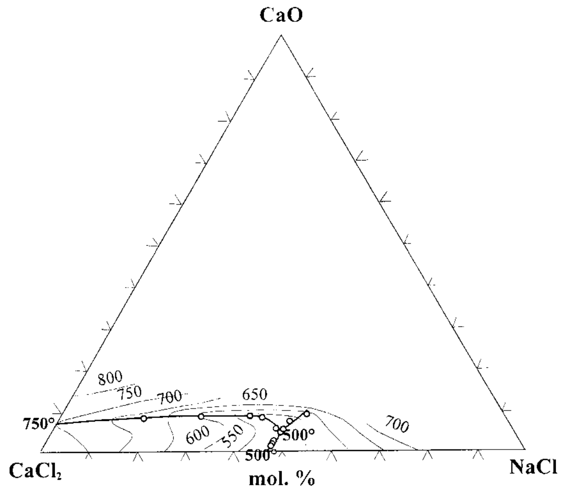

Fig. 5. $CaCl_2$–NaCl–CaO phase diagram.

of deflection points on the liquidus curves are given in Table 1. Projected on the base triangle, they form secondary crystallisation lines. Fig. 5 represents the ternary diagram, constructed from these projections. We determined the ternary eutectic point by extrapolation: E=500°C, 47.0 mol% NaCl, 48.0 mol% $CaCl_2$, 5 mol% CaO.

A comparison with the study of Boghosian et al. [5] reveals that our data suggest much higher solubility of calcia in the $CaCl_2$–NaCl melt. This disagreement can be explained. Several recent publications, devoted to the solutions of oxides in the chloride melts [7–9], report that a discrepancy between the results of solubility measurements by different methods can be as high as an order of magnitude. The authors attribute this to the fact that these solutions often form a finely dispersed colloidal fluid. The size of the colloidal particles may vary from nano- to micrometers. For instance, particles of size 11–32 nm were found by X-ray diffraction in the melts $CaCl_2$–CaO [7]. In a colloidal form, a molten salt mixture may contain much higher amounts of the oxide than its true

Table 1
Compositions and temperatures of deflection points on the liquidus curves

Section	Composition of the section (mol%)	First point[a]		Second point[a]	
		(mol%)	T (°C)	(mol%)	T (°C)
I	(19.2NaCl, 80.8$CaCl_2$)–CaO	8.2 (1)	637		
II	(32.7NaCl, 67.3$CaCl_2$)–CaO	9.4 (1)	591		
III	(45.8NaCl, 54.2$CaCl_2$)–CaO	8.2 (1)	501		
IV	(18.5CaO–81.5$CaCl_2$)–NaCl			50.5	584
V	(14.2CaO–85.8$CaCl_2$)–NaCl	39.0 (2)	511	48.0 (2)	509
VI	(10.8CaO–89.2$CaCl_2$)–NaCl	46.0 (2)	502	47.5 (2)	501
VII	(9.3CaO–90.7$CaCl_2$)–NaCl	47.5 (2)	500		
VIII	(4.9CaO–95.1$CaCl_2$)–NaCl	47.0 (2)	500		
IX	(3.9CaO–96.1$CaCl_2$)–NaCl	47.0 (2)	498		
X	(2.4CaO–97.6$CaCl_2$)–NaCl	46.5 (2)	500		

[a] (1), CaO; and (2), NaCl.

solubility. DSC measurements, carried out in the present work, can only determine the transition of a solid to a liquid. However, given that the composition of the binary eutectic between $CaCl_2$ and CaO extrapolated from this work correspond closely with the values presented by Wenz [1] indicates that our data is confirmed. Furthermore, the direct visual observation of some samples above the melting points, determined by DSC experiments, suggested that they were clear homogenous liquids.

Acknowledgements

The authors would like to thank Engineering and Physical Sciences Research Council for financial support.

References

[1] D.A. Wenz, I. Johnson, R.D. Wolson, J. Chem. Eng. Data 14 (2) (1969) 252.
[2] A. Seltveit, H. Flood, Acta Chem. Scand. 12 (5) (1958) 1030.
[3] E.M. Levin, C.R. Robbins, H.F. McMurdie, Phase Diagrams for Ceramists, The American Ceramists Soc., Columbus, OH, 1964.
[4] CRC Handbook of Chemistry and Physics, 74th Edition, CRC Press, Boca Raton, FL, 1994.
[5] S. Boghosian, Aa. Godø, H. Mediaas, W. Ravlo, T. Østvold, Acta Chem. Scand. 45 (1991) 145.
[6] E.B. Freidina, D.J. Fray, In: B. Mishra (Ed.), EPD Congress 1999. TMS, San Diego, CA, 1999, p. 169.
[7] B.D. Antonov, V.P. Stepanov, N.P. Kulik, Coll. J. 60 (4) (1998) 442.
[8] N.M. Barbin, A.P. Pekar', V.N. Nekrasov, L.E. Ivanovskii, Melts 6 (2) (1992) 87.
[9] N.P. Kulik, V.P. Stepanov, B.D. Antonov, S.I. Dokashenko, Doklady Ross. Akad. Nauk 343 (1) (1995) 65.