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Thermochimica Acta 447 (2006) 41–44

thermochimica acta

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Solubility of $AlPO_4$ in cryolite melts

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Received 11 January 2006; received in revised form 18 January 2006; accepted 19 January 2006
Available online 8 June 2006

Abstract

The solubility of aluminium orthophosphate in cryolite melts was determined. Part of the binary phase diagram of the system Na_3AlF_6–$AlPO_4$ was investigated. The eutectic point was determined to be at 43.7 mass% (or 57.2 mol%) $AlPO_4$ and (696 ± 1) °C. It is suggested that in pure molten cryolite melts the orthophosphate ion dissociates partly into a metaphosphate ion and an oxide ion.

Keywords: Aluminium orthophosphate; Cryolite; Solubility; Aluminium electrolysis; Phosphorus

1. Introduction

The motivation for the present study was the established deleterious effect of phosphorus in aluminium production. Phosphorus impurities originate from the raw materials, mainly from the primary alumina (Al_2O_3), which may contain 4–11 ppm P_2O_5 [1], probably in the form of phosphate. The interest in the effect of phosphorus in aluminium production has increased significantly since the process was changed to a more closed system so that a substantial fraction of the impurities in the off gases are being recycled together with the alumina passing through the dry scrubbers. The Faradaic efficiency for aluminium production in modern cells is typically 92–96%. Further increase in efficiency depends on controlling the content of impurities in the system, in particular phosphorus. It has been postulated [1] that each 100 ppm phosphorus (P) in the electrolyte reduces the current efficiency by 1%. Furthermore, there is a restriction on the phosphorus content in aluminium, especially for cast alloys [2].

To avoid problems due to phosphorus, it is necessary to enhance the understanding of the behaviour of phosphorus in industrial cells. Firstly, it is of interest to determine the phase diagram of phosphate in cryolite. In an earlier work, del Campo [3] studied the system Na_3AlF_6–$Na_4P_2O_7$ and found a eutectic at 748 °C and 71.7 mass% $Na_4P_2O_7$. With its high solubility and low volatility sodium pyrophosphate was assumed to be a compound suited for fundamental studies. However, the pyrophosphate ion was found to dissociate into ionic phosphate species, either ${PO_4}^{3-}$ or ${PO_3}^{-}$. The choice of aluminium orthophosphate as the compound to be investigated in the present study was based on the assumption that phosphorus is most likely present as a orthophosphate in primary alumina.

2. Experimental

The measurements were performed in a closed furnace with water-cooling, as shown in Fig. 1. The furnace consisted of a steel cylinder filled with insulating material. Kanthal wires were used as heating elements. The cell was placed inside a Pythagoras tube, which was closed with tight lids at either end. The atmosphere inside the furnace during the measurements was argon, which was flushed through the cell at a constant rate. The temperature of the furnace was controlled by a Pt–PtRh10% thermocouple, inserted horizontally through the steel cylinder of the furnace, touching the Pythagoras tube.

The chemicals used are: Na_3AlF_6, hand-picked, natural Greenland cryolite, kept at 200 °C in a heating chamber before use. Crystal grains with coloured appearance were discarded. $AlPO_4$, Riedel-de-Haën anhydrous, technical grade, kept at 200 °C in a heating chamber before use. Ar, argon 4.0 (99.99%), AGA, used as received.

The cryolite was not analysed for impurities, but the melting point was 1011 °C, showing that it was of high purity.

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doi:10.1016/j.tca.2006.01.021

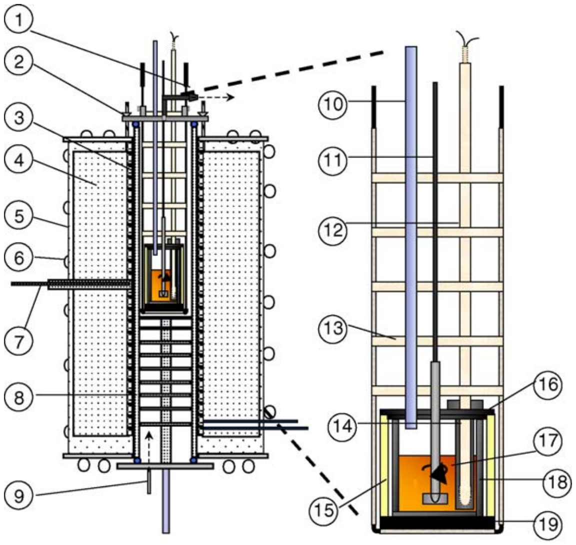

Fig. 1. Cross section of furnace (left) and cell (right). (1) Gas outlet, (2) fixation screws for cell set-up, (3) Kanthal heating element, (4) insulating material, (5) steel cylinder, (6) water-cooling pipes, (7) thermocouple for furnace temperature control, (8) Pythagoras tube, (9) gas inlet, (10) feeding tube of quartz, (11) nickel stirrer mounted on stainless steel, (12) thermocouple (TC), (13) alumina radiation shields, (14) graphite TC protection, (15) alumina casing, (16) graphite lid, (17) melt, (18) nickel crucible, and (19) graphite supporter.

About 150 g of natural cryolite was placed in a nickel crucible (55 mm diameter, 60 mm height. For measurements up to 4 mol% $AlPO_4$, the phosphate was added in the form of pressed tablets during the experiment. The feeding tube was inserted above the melt shortly before addition and immediately retracted as soon as the tablets had been added. For experiments with melts containing 5 mol% $AlPO_4$ or more, the components were mixed before loading the crucible. The crucible was placed inside the furnace, as shown in Fig. 1, and the furnace was tightly closed to the ambient atmosphere. Before heating, the cell was flushed with argon for at least 10 h. Thereafter the furnace was heated approximately 20 °C above the estimated liquidus temperature of the melt. The temperature of the melt was controlled by a Pt–PtRh10% thermocouple placed inside an alumina tube and protected from the melt by an outer graphite tube. The thermocouple was calibrated with respect to the melting point of silver.

When molten, the mixture was stirred with a nickel stirrer at 300 rpm for at least 1 h, in order to ensure homogeneity. If $AlPO_4$ was added as tablets to the molten cryolite, the mixture was stirred for at least 2 h under the same conditions. The temperature was recorded during the experiment. The cooling rate was set at $0.7\,K\,min^{-1}$. For the determination of the liquidus and solidus arrests, the slow cooling rate and the vigorous stirring were intended to prevent possible under-cooling of the melt. The solidified melt was crushed, and the existing phases were determined by means of XRD.

The experimental set-up for the measurements of the liquidus curve of orthophosphate-rich side was the same as shown in Fig. 1. Instead of the graphite protection tube for the thermocouple a closed nickel tube was used. The weighed-in mixture consisted of cryolite and an excess amount of aluminium orthophosphate (66.4 mol%). When a liquid phase had been formed, stirring was started and maintained for at least 2 h. Thereafter the stirring was stopped so that dispersed solid phosphate particles could settle. The time allowed for settling was at least 2 h. Subsequently, a quartz tube was immersed 1 cm into the melt, and with the help of a syringe attached to the upper end of the tube, a melt sample was sucked into the tube and the tube was withdrawn. The sampling lasted less than 10 s. The quartz tubes were broken and the melt samples were carefully collected, crushed in an agate mortar, dissolved in a 30% aluminium chloride solution and analysed by atomic emission spectrometry.

For each run a new bath of cryolite and aluminium orthophosphate was prepared.

3. Results and discussion

The results obtained by thermal analysis are presented in Tables 1–3.

Table 1
Temperatures of primary crystallization in the system Na_3AlF_6–$AlPO_4$ at the cryolite-rich side

x' ($AlPO_4$) (mol%)	x ($AlPO_4$) (mass%)	T (°C)
0.00	0.00	1011.0
0.00	0.00	1011.0
0.51	0.30	1010.2
0.99	0.58	1009.2
1.96	1.15	1007.0
2.87	1.69	1005.2
4.04	2.39	1003.7
4.98	2.96	1002.3
10.03	6.08	994.4
14.97	9.28	981.4
19.99	12.67	964.5
30.00	19.94	918.4
39.91	27.84	851.7
50.01	36.76	755.9

Table 2
Results of solidus temperature measurements in the system Na_3AlF_6–$AlPO_4$

x' ($AlPO_4$) (mol%)	x ($AlPO_4$) (mass%)	$T_{solidus\ 1}$ (°C)	$T_{solidus\ 2}$ (°C)
19.99	12.67	691.0	564.5
39.91	27.84	702.4	–
50.01	36.67	695.0	565.0
60.87	47.47	695.0	557.0

Table 3
Results of the temperature of primary crystallization in the system Na_3AlF_6–$AlPO_4$ at the aluminium orthophosphate-rich side

x' ($AlPO_4$) (mol%)	x ($AlPO_4$) (mass%)	T (°C)
59.97	46.53	905.9
59.80	46.36	922.6
61.39	48.02	997.3
61.60	48.24	1041.8

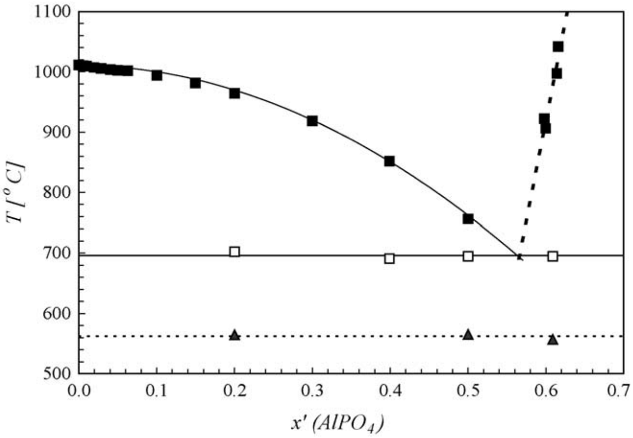

Fig. 2. Phase diagram of the system Na_3AlF_6–$AlPO_4$ determined by thermal analysis (■ liquidus data; □ solidus data; ▲ phase transition).

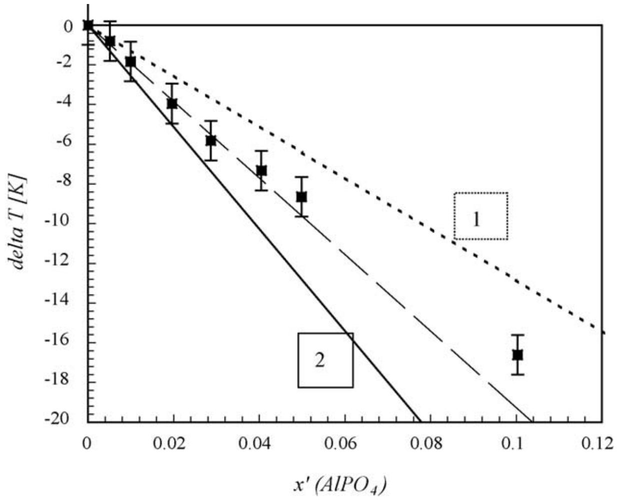

Fig. 3. Calculated curves according to equation (1) for $\nu = 1$ and 2 new species, respectively, as marked in the plot. Experimental data are plotted as filled squares.

The estimated uncertainty in the temperature measurements was estimated to be ±1 °C. The error in concentration of the mass percent data was caused by the uncertainty in weighing and a loss of approximately 1.5 mass% of the total amount of melt due to evaporation. The loss by evaporation was determined by weighing the cell before and after each experiment. A total error of ±0.02 mol% of $AlPO_4$ was derived.

The phase diagram for the Na_3AlF_6–$AlPO_4$ system was found to be a simple binary eutectic, Fig. 2. The phosphate-rich side was only investigated up to 61.6 mol% $AlPO_4$. The eutectic point was found at 57.2 mol% $AlPO_4$ at 695.9 °C.

While the second arrest on the cooling curve for a simple binary system represents the temperature where the melt is completely solidified, i.e. the solidus, the third arrest represents the phase transition of the cryolite phase. "the cubic high-temperature β-phase of cryolite transforms at 563 ± 2 °C to the low-temperature α-phase, a monoclinic modification of Na_3AlF_6" [1].

Investigations by XRD on solidified samples showed that Na_3AlF_6 and $AlPO_4$ were the only solid phases present.

The number of species originating from a substance A added to a molten salt B can be determined from the equation for freezing point depression which can be simplified to

$$\Delta T = \frac{RT_f^2}{\Delta H_f}\nu x_A \tag{1}$$

if only small additions of A are made to the melt B. T_f is the temperature of fusion for the pure solvent B (in this case cryolite), ΔH_f the enthalpy of fusion for solvent B and ν is the number of particles formed when A dissolves in B.

A plot according to Eq. (1) shows how many new species are formed when adding $AlPO_4$ to cryolite. Since the enthalpy of fusion for pure cryolite is known, i.e. ΔH_f (Na_3AlF_6) = 106.7 kJ/mol [4], theoretical curves based on Eq. (1) can be calculated, assuming different numbers of new species.

The experimental results do not fit to a dissolution scheme involving either one or two new particles. This is not in agreement with the findings by Chrenková et al. [5], who reported one new species when aluminium orthophosphate was added to cryolite.

Assuming that the orthophosphate dissociates partly into metaphosphate, as postulated in reaction (2),

$$K_{eq}[PO_4^{3-}] = [PO_3^{-}][O^{2-}] \tag{2}$$

the results presented in Fig. 3 are in agreement with Eq. (2), since the data points show an upwards curvature. In a melt containing additional oxide species, e.g. from alumina, the dissociation reaction will be shifted more to the left. In cryolitic melt containing alumina the main phosphate species will be the orthophosphate. The enthalpy has to be positive, so there will be an increase in dissociation of the orthophosphate with increasing temperature. Hence, it can be concluded that the three main factors influencing reaction (2) are the concentration of $AlPO_4$, the concentration of additional oxide and the temperature.

In the work by Chrenková et al. [5], the melting point of the natural, hand-picked Greenland cryolite that was used at 1004 °C. Normally the melting point of pure cryolite lies between 1009 and 1012 °C [1], as found in the present work. This indicates that the cryolite used by Chrenková et al. was rather impure. Since oxides are likely to be present among the impurities in cryolite, it is possible that in the work by Chrenková et al. Equilibrium (2) was shifted more to the left due to the presence of additional oxide. As a consequence, the results of those measurements indicated the presence of only one new species, i.e. PO_4^{3-}.

In Na_3AlF_6–NaF–$AlPO_4$ melts Tkatcheva et al. [6] found the ratio between oxygen and phosphorus to be four, also in the presence of Al_2O_3. This does not necessarily imply that the PO_4^{3-} anion is the only stable phosphorus-containing anion, but rather that the P and O components do not escape from the melt by forming volatile species. If we assume that the metaphosphate ions and oxide ions are stable species in cryolite – phosphate melts, the present results are supported by the findings of Tkatcheva et al.

To confirm that the phosphate ion dissociates to some extent in molten cryolite when adding $AlPO_4$, additional work in this type of melt, e.g. by Raman spectroscopy, should be performed as the next step.

Acknowledgement

Financial support received from the Norwegian Research Council and the Norwegian Aluminium Industry and provided for this study through the PROSMAT program is greatly appreciated.

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