Thermochimica Acta, 92 (1985) 513-516
Elsevier Science Publishers B.V., Amsterdam

INVESTIGATION ON THE Na_3AlF_6-Al_2O_3 SYSTEM BY DTA

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ABSTRACT

The Na_3AlF_6-Al_2O_3 sytem with a constant molar ratio of NaF/AlF_3=3 was investigated by DTA method. The alumina content was changed between 0-10 mass percent. The following data were determined: the liquidus and solidus temperatures, the entalpies of the melting and solidification, the entalpy of cryolite phase transition and the entalpy of alumina dissolution in cryolite.

INTRODUCTION

During the aluminium electrolysis the alumina is introduced into the melted cryolite by crustbreaking of the solidified bath crust. The alumina partly dissolves in the bath and cooled it. The other part of alumina is coated with the solidified electrolyte or under certain conditions go through the layer of liquid aluminium to the cathode and there forms a deposit of sludge. These processes cause a significant change in the temperature and composition of the bath and hence the current efficiency.

EXPERIMENTAL METHOD

The measurements were carried out in a high temperature furnace of Mettler TA 1 vacuum thermoanalyzer in flowing air /17 1/h/ atmosphere. DTA-20 thermoelement, PtRh 10 crucible of 0.9 cm^3 covered by lid of the same material and α-Al_2O_3 reference were used. The weight of the sample was 100 mg. It was heated up to 500 ^oC with a heating rate 15 ^oC/min, after it was measured between 500 and 1015 ^oC with heating and cooling rate of 4 ^oC/min. The DTA and TG curves were registrated simultaneously.

The thermoanalyzer was calibrated with ICTA standards /Ag_2SO_4, K_2SO_4, K_2CrO_4, $BaCO_3$/.

In course of the investigations of cryolite-alumina system 0, 1, 3, 5, 6 and 10 mass % alumina were added to the cryolite and the samples were heated up after homogenizing.

Proceedings of ICTA 85, Bratislava

RESULTS AND DISCUSSION

The phase diagram of Na_3AlF_6-Al_2O_3 system involving our data can be seen in Fig.1. The temperature values obtained from the cooling curves are smaller than the data of Z. F. Lungyina /1/. This may be explained by the loss of fluor content. Grjotheim and his coworkers /2/ established that the vapour pressure above the melted cryolite-alumina contains about 90 mole% $NaAlF_4$ gas. The $NaAlF_4$ gas condenses on the crucible wall so the loss of $NaAlF_4$ cannot be seen on the TG-curves. However the vapour pressure decreases with increasing content of alumina in the liquid mixture /3/.

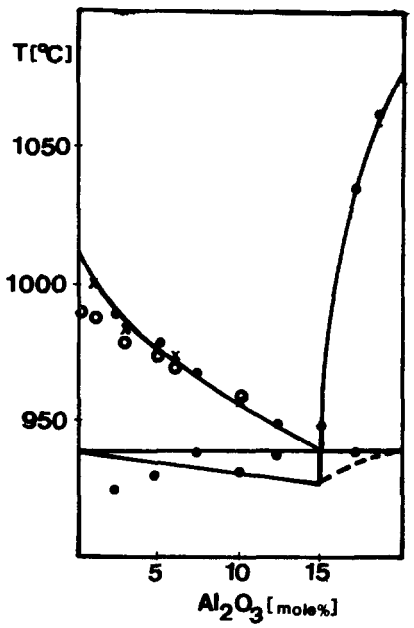

Figure 1
The phase diagram of Na_3AlF_6-Al_2O_3 system

Our measurements:
x-melt., o-solid.

The transition entalpy of cryolite $\Delta H_{trans.}$=46±4 J /g was determined from the heating curves. This value agrees well with literary data /4/. A higher value of it /$\Delta H_{trans.}$= 54±4 J/g/ could be obtained from the cooling curve in the case of small alumina content in cryolite. This can be explained by the loss of $NaAlF_4$ during the measurements.

The melting entalpy of cryolite $\Delta H_{melt.}$=460±16 J/g differs

from the literary value /4/. From the cooling curves the value of $\Delta H_{sol.}$ =480±16 J/g was obtained for the solidification entalpy.

Heating the cryolite-alumina system two reactions take place at the same time: the melting of the cryolite and the dissolution of the alumina. These two processes cannot be separated in the DTA curves, except if the alumina is added to the melt on the temperature of melted cryolite.

In the Table 1. we summarized the dissolution entalpy of alumina in cryolite together with literary values /5/, not accepted the extreme high values /6/.

Table 1. Dissolution entalpy of alumina in cryolite.

Al_2O_3 content /mole %/	$\Delta H_{diss.Al_2O_3}$ /kJ/g/	$\Delta H_{diss.Al_2O_3}$ /kJ/g/ /6/
1	2,09	2,05
3	1,64	1,59
5	1,51	1,43
6	1,49	1,43
10	1,93	1,43

CONCLUSIONS

The melting temperature of cryolite-alumina system decreases with increasing content of alumina up to 10 %.

The transition entalpy of cryolite $\alpha \rightarrow \beta$ obtained from the heating and cooling curves are 46 J/g and 54 J/g respectively.

The melting entalpy of cryolite is 460 J/g and the solidification entalpy is 480 J/g.

The dissolution entalpy of alumina in cryolite-alumina system depends on the alumina content, as can be seen in the Table 1.

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