

Reactions of sulphides in molten cryolite

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Abstract

The freezing point depression of cryolite (Na_3AlF_6) by the addition of Al_2S_3 and FeS was investigated. It was found that for contents of up to 10 wt.% Al_2S_3 , it brings into the melt three new species. X-ray analysis of solidified melts of the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$ showed that it contained chiolite, $\text{Na}_5\text{Al}_3\text{F}_{14}$ and Na_2S . Chiolite originates from a reaction between Na_3AlF_6 and AlF_3 . This suggests that the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$ is a part of the reciprocal system NaF , $\text{AlF}_3/\text{Na}_2\text{S}$, Al_2S_3 . The solubility of FeS in cryolite melt is so low that it cannot be determined by the thermal analysis. When FeO is added to the $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$ melt, Fe^{2+} cations and S^{2-} anions react under the formation of solid FeS . A similar reaction was observed for Ni^{2+} and S^{2-} ions.

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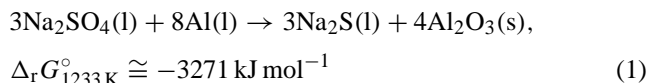
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1. Introduction

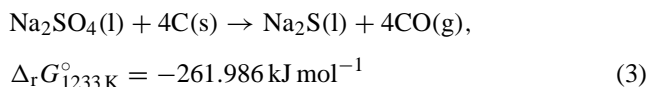
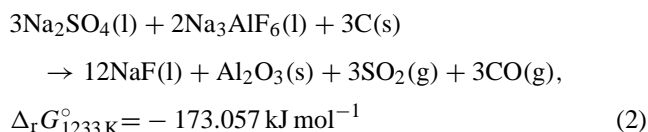
Aluminium is produced by the electrolysis of alumina dissolved in cryolite-based melts. Besides cryolite (Na_3AlF_6) and alumina, the electrolyte contains an excess of AlF_3 with respect to Na_3AlF_6 , and 3–6 wt.% CaF_2 . Other additives like LiF and/or MgF_2 can be present as well. The electrolyte may also contain impurities, like iron, silicon, phosphorus, sulphur, etc. [1]. The impurities are introduced into the electrolyte with the alumina or fluoride salts or they originate from the carbon anodes. The main constituents of the gas leaving the cell are as follows: CO_2 , CO , CF_4 , C_2F_6 , HF , SiF_4 , H_2O , hydrocarbons, SO_2 , H_2S , COS , CS_2 , together with some solid particulate emissions. In this paper, we will discuss the behaviour of the sulphur compounds in aluminium cells, in particular, the solubility of Al_2S_3 in molten cryolite.

Sulphur originates mainly from two sources. Petroleum coke used for the production of carbon anodes contains 0.7–4 wt.% sulphur. Cryolite and aluminium fluoride also

contain sulphur, mainly as sulphates (up to 1%). Sulphur leaves the aluminium cell mainly as SO_2 , with minor amounts of COS , CS_2 and H_2S [2,3]. The phase diagram of the system $\text{Na}_3\text{AlF}_6\text{--AlF}_3\text{--Al}_2\text{O}_3\text{--Na}_2\text{SO}_4$ was investigated by Delmárová and Malinovský [4]. Danielik and Gabcova [5] studied the system $\text{Na}_3\text{AlF}_6\text{--NaF--Na}_2\text{SO}_4$. Baimakov and Vetyukov [6] reported that metallic aluminium dissolved in electrolyte reduces sulphates to sulphides:



Shvartsberg [7] studied losses of sulphur from cryolite melts. He found that at a temperature of 1000 °C sulphate ions are reduced by graphite. He explained his observations by the following reaction schemes:



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In most cases, no experimental evidence of the reactions mentioned above has been given. The Gibbs energies of the reactions were calculated using the JANAF tables [8]. No data on the solubility of sulphides in cryolite-based melts are available. In preliminary experiments on the reduction of sulphates dissolved in cryolite melts by metallic aluminium, we found by X-ray diffraction analysis that the solidified melt contained Al_2S_3 . In this paper, we will present results of the study of the phase diagram of the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$.

2. Experimental

2.1. Chemicals

Handpicked Greenland cryolite, Al_2S_3 (99.9% metal basis, Alfa Aesar), FeS (99.9% metal basis, Merck) and FeO (99.9%, Aldrich) were used. The other chemicals were of the grade “pro analysis”.

2.2. Apparatus

The liquidus curve of cryolite (Na_3AlF_6) in the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$ was determined by thermal analysis under an argon atmosphere. Since Al_2S_3 reacts with moisture, the use of inert atmosphere was of primary importance in the preparation of the samples and during the measurements. Mixtures of 150–200 g of handpicked and crushed Greenland cryolite and Al_2S_3 powder with known composition were prepared in a glove box under low-humidity atmosphere and transferred into the pyrolytic boron nitride

(BN) crucible (60 mm diameter, 55 mm height). Platinum cannot be used because it reacts with Al_2S_3 . The BN crucible was placed in a vertical furnace, under argon atmosphere. A sketch of the apparatus is shown in Fig. 1. The temperature was measured with a Pt/Pt10Rh thermocouple located inside a hot-pressed boron nitride protection tube. The stirrer was made from hot-pressed boron nitride and rotated with a speed of about 300 rpm.

The melt was heated about 20°C above the liquidus temperature when the stirring was started. The stirring lasted for 60 min before cooling was initiated with a rate of $0.7^\circ\text{C min}^{-1}$. The slow cooling rate and the vigorous stirring were applied in order to prevent or reduce super-cooling of the melt. As a further measure to avoid super-cooling was to add small crystal seeds of cryolite were added to the melt during cooling. The precision of the temperature measurement was 0.1°C , the reproducibility was $\pm 0.4^\circ\text{C}$.

A similar apparatus was used to investigate the influence of the addition of FeS on the temperature of primary crystallisation of cryolite.

3. Results and discussion

In Fig. 2, the liquidus temperature of cryolite (Na_3AlF_6) is plotted as a function of the addition of up to 0–1.5 mol% Al_2S_3 . By addition of small amounts of Al_2S_3 , we can assume ideal behaviour of molten Na_3AlF_6 . The curves in Fig. 2 correspond to the theoretical prediction of the temperature of primary crystallisation of cryolite based on the Le Chatelier–Schröder equation [9,10]:

$$\ln x(\text{Na}_3\text{AlF}_6) = \frac{\Delta H_{\text{fus}}^\circ(\text{Na}_3\text{AlF}_6)}{Rk_{\text{St}}} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T} \right) \quad (4)$$

where $x(\text{Na}_3\text{AlF}_6)$ is the mole fraction of cryolite in the mixture, $\Delta H_{\text{fus}}^\circ(\text{Na}_3\text{AlF}_6)$ the enthalpy of fusion of cryolite ($=106.7 \text{ kJ mol}^{-1}$ [1]), T_{fus} the temperature of fusion of pure cryolite (1284 K) and T the temperature of its primary crystallisation. R is the gas constant and k_{St} the Stortenbeker factor [11], which equals the number of new foreign species that Al_2S_3 brings into the solution. It can be seen that Al_2S_3 forms (when added in small amount) three new species in cryolite melts.

By analogy with the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{O}_3$ [12], we may assume that the composition of these species is of the form $\text{Al}_2\text{SF}_6^{2-}$, which is a complex of the bridging type, i.e. Al–S–Al. However, it can also be explained by the formation of any other species containing only one S atom, e.g. AlSF_2^- species by analogy with the species that Hjuler et al. [13] assumed to be formed in $\text{NaCl--AlCl}_3\text{--Al}_2\text{S}_3$ melts.

In Fig. 3, the liquidus temperature for higher additions of Al_2S_3 is shown. For additions above 15 mol% Al_2S_3 , the decrease in the temperature of primary crystallisation of cryolite is surprisingly large. This observation can be explained by the metathetical reaction, where one product

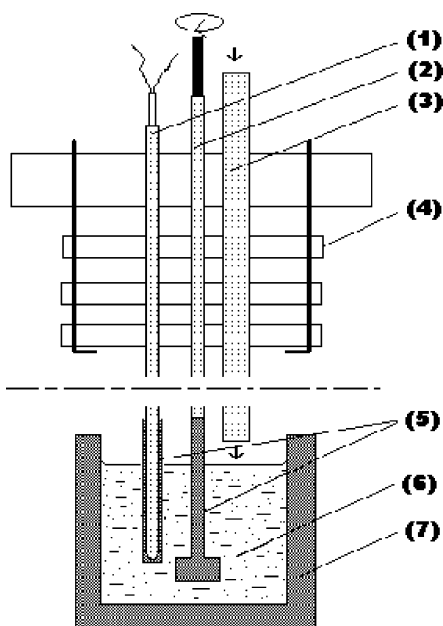


Fig. 1. Experimental apparatus: (1) Pt/Pt10Rh thermocouple; (2) stirrer; (3) Alsint tube for adding small crystal seeds; (4) radiation shields; (5) hot-pressed boron nitride protection of stirrer and thermocouple; (6) melt; (7) pyrolytic BN crucible.

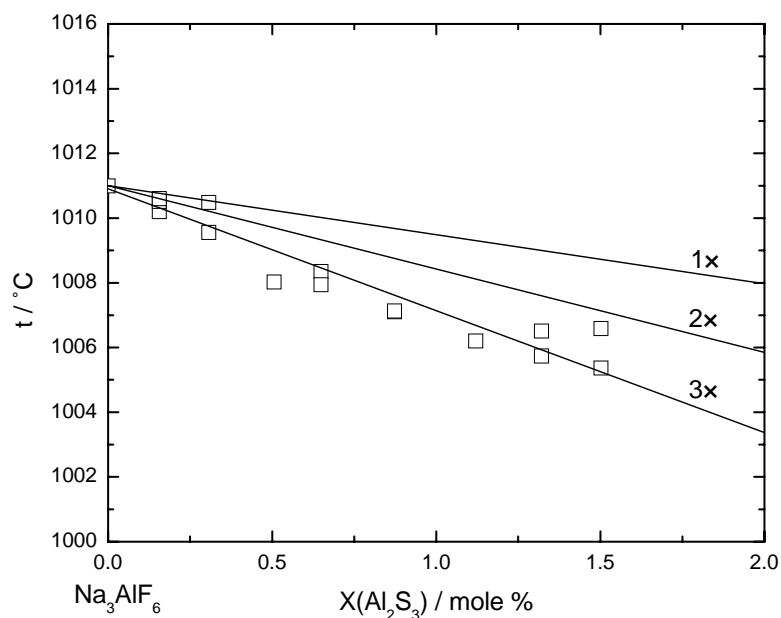
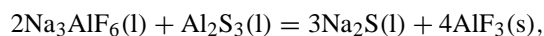


Fig. 2. Liquidus temperatures of cryolite as a function of the amounts of Al_2S_3 added (0–1.5 mol%). Full lines: calculated according to Eq. (4) for new species 1–3.

is AlF_3 :



$$\Delta_r G_{1273\text{ K}}^\circ = 72.633 \text{ kJ mol}^{-1},$$

$$\Delta_r G_{973\text{ K}}^\circ = 54.313 \text{ kJ mol}^{-1} \quad (5)$$

The standard Gibbs energy of this reaction is positive. However, the activity of AlF_3 in cryolite melts is very low [14] because of complex formation. X-ray analysis of the solid-

ified melts in the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$ showed that they contained Na_2S and chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$), which is an incongruently melting compound in the system $\text{Na}_3\text{AlF}_6\text{--AlF}_3$. This observation indicates that the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$ is part of the reciprocal system NaF , AlF_3 // Na_2S , Al_2S_3 .

The excess of AlF_3 (in the form of chiolite) in the samples with the addition of 10, 20, 30, and 40 mol% Al_2S_3 was determined by a standard X-ray method. It was found that the content of AlF_3 increased from 3.6 wt.% for the addition of

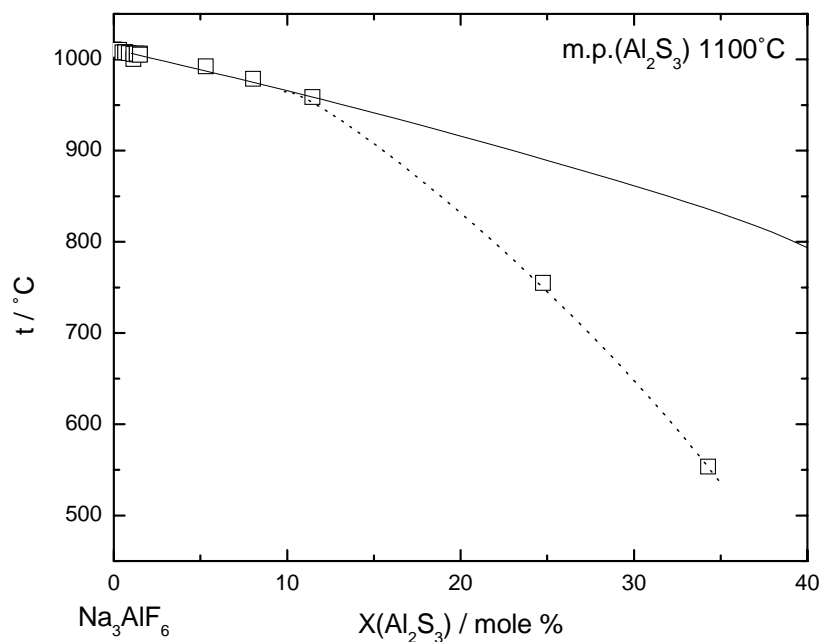


Fig. 3. The cryolite-rich part of the phase diagram of the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$. Open squares: primary crystallisation of Na_3AlF_6 . Full line: calculated (formation of AlF_3 was taken into account).

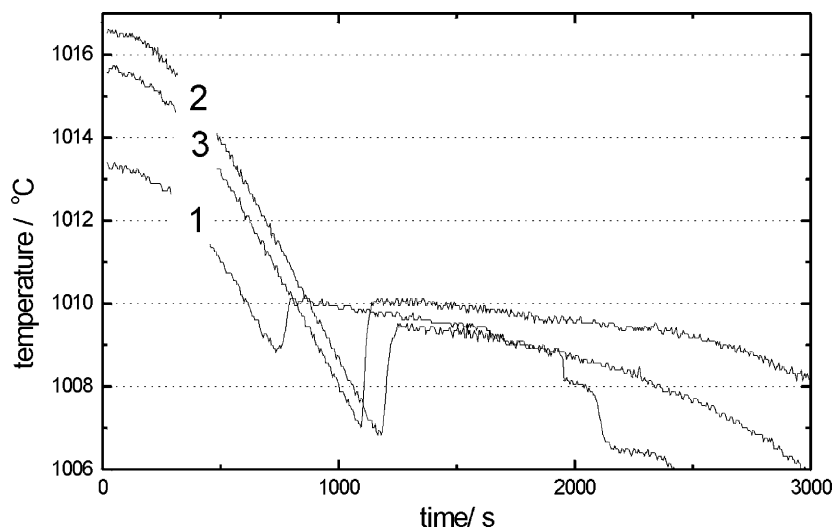


Fig. 4. Cooling curves in the system $\text{Na}_3\text{AlF}_6\text{--FeS}$: (1) pure Na_3AlF_6 ; (2) $\text{Na}_3\text{AlF}_6 + 0.3 \text{ wt.}\% \text{ FeS}$; (3) $\text{Na}_3\text{AlF}_6 + 0.5 \text{ wt.}\% \text{ FeS}$.

10 mol% Al_2S_3 up to 6.0 wt.% for the addition of 30 mol% Al_2S_3 , while it remained constant by higher additions of Al_2S_3 .

This is in accordance with the predictions resulting from a thermodynamic model based on this reaction scheme (Eq. (5)). This model gives only a qualitative explanation of the formation of AlF_3 , since we do not know the activities of Al_2S_3 and Na_2S . The activities of AlF_3 can be estimated on the basis of data published by Solheim and Sterten [14]. The model fails when it is used to calculate the liquidus temperature in the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$ containing more than 15 mol% Al_2S_3 .

The present paper explains the behaviour of sulphide as impurity in cryolite melts. However, further work is needed in order to understand the whole phase diagram for the system $\text{Na}_3\text{AlF}_6\text{--Al}_2\text{S}_3$. This is the reason why a part of the liquidus curve in Fig. 3 is plotted by a dotted line.

In Fig. 4, the cooling curves obtained in the system $\text{Na}_3\text{AlF}_6\text{--FeS}$ are plotted. It follows that within the experimental error FeS has no influence of the temperature of primary crystallisation of cryolite, so it is practically insoluble in this melt. Thus, it was of interest to find out if FeS precipitates when both Fe^{2+} and S^{2-} ions are presents in the melt. According to Jentoftsen et al. [15], up to 15 mol% “FeO” can dissolve in the cryolite melt at 1000 °C (FeO is a non-stoichiometric compound.). We added 5 mol% Al_2S_3 and a corresponding stoichiometric amount of FeO to cryolite and kept the system at the temperature of 1000 °C for 30 min in a BN crucible. When the system was cooled down to ambient temperature, we found a small sphere having diameter of $\sim 5 \text{ mm}$ on the bottom of the crucible. X-ray analysis showed that the sphere consisted of FeS.

A similar experiment was carried out with the admixture of NiO. In this case, a ball of NiS was found on the bottom of the BN crucible. This indicates that NiS does not dissolve

in cryolite melts. These observations may contribute to the understanding of the influence of investigated impurities on the current efficiency in aluminium electrolysis.

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