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The study of the system Na_3AlF_6–FeF_3

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ABSTRACT

Different techniques are used to understand the Na_3AlF_6–FeF_3 system behavior. Rietveld's structure refinement analysis is successfully applied to determine the lattice parameters as well as relative phase abundance of individual phases in the system Na_3AlF_6–FeF_3. The results confirm the presence of $Na_3(Al_xFe_y)F_6$ and $Na_5(Al_xFe_y)_3F_{14}$ ($x + y = 1$) solid solutions, depending on the amount of FeF_3 in the system. The system with 25 mol% FeF_3 contains crystalline phases in weight ratio: 64.8 ± 2.8% of $Na_3(Al_xFe_y)F_6$ and 35.2 ± 2.7% of $Na_5(Al_xFe_y)_3F_{14}$, respectively. In the first mentioned solution, the molar ratio of Al/Fe is 92.8/7.2 and 77.4/22.6 in second one. Weight loss measurements suggest that some new volatile products are emitted from the melt. MAS NMR investigations of the condensate exclude the presence of iron containing fluorides in the condensed sample and confirm that $NaAlF_4$ is the only vapor species, generating in the melted system.

1. Introduction

Iron belongs to predominant impurities that negatively influence the commercial production of aluminum, the Hall–Héroult process. In this process, liquid aluminum is produced by electrolytic reduction of alumina (Al_2O_3) which is dissolved in an electrolyte mainly containing cryolite (Na_3AlF_6) [1]. Iron compounds dissolved in the electrolyte may have a negative influence on the current efficiency of the process and on the resulting metal quality. They can participate in reactions with components of the electrolyte and change the electrolyte's chemical composition [2–4]. Thus, the classification of the mechanism of redox reactions of iron compounds with electrolyte components is needed. The present study is focused on the reactions taking place between FeF_3, and Na_3AlF_6. The traditional view implies that iron(III) compounds, like Fe_2O_3 or FeF_3 react in the electrolyte forming FeF_6^{3-} species [5–7]. Diep studied the solubility of Fe_2O_3 as a function NaF/AlF_3 molar ratio with and without additions of alumina. The obtained data were used to interpret the ionic structure of iron compounds. The presence of a series considered iron-containing compounds that can be written in the general form as $Na_xFe_yF_z$ and $Na_xAl_qFe_yO_wF_z$ was suggested. Up to now, the system Na_3AlF_6–FeF_3 was examined only by Johansen [8]. There are indications that a eutectic is present at approximately 60 mol% FeF_3 at 694 °C. However, complementary analyses are necessary to pinpoint the curves defining phase boundaries [1].

The present paper studies the FeF_3 behavior in cryolite. The intention is to suggest possible processes that take place and to identify reaction products. However, it must be noted that it is impossible to investigate such a system in situ by usual techniques. The reasons are, e.g.: (i) XRD in melt lost its essential purpose (even some averaged structural information could be obtained, but this is out of the scope of this paper); (ii) NMR spectroscopy is useless when paramagnetic species are present. Thus, the following combination of techniques was used: (i) thermal analysis – as a basic method used to investigate molten salts; (ii) XRD and powder neutron diffraction of the quenched samples – in order to characterize reaction products; (iii) MAS NMR spectroscopy of condensed vapors in order to exclude the presence of iron and in order to confirm the suggested chemical reaction, where some of the products are volatile species. The presence of volatile products arises from TG measurements. The mosaic of particular results coming from different techniques can suggest some insight into the processes taking place in melts in spite of the fact that these indices are not direct proves that cannot be obtained (such a direct proofing would require, e.g. femtosecond spectroscopy).

2. Results and discussion

Thermal analysis with cryoscopy calculations was realized in order to study chemical reactions between components taking place in melts. Cryoscopy is a useful experimental method frequently applied for such investigations. For the lowering of

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the temperature of fusion of the solvent A, $\Delta_{\text{fus}}T(\text{A})$, caused by the addition of the solute B the following equation holds

$$\Delta_{\text{fus}}T(\text{A}) = \frac{RT^2_{\text{fus,A}}}{\Delta_{\text{fus}}H_{\text{A}}} x_{\text{B}} k_{\text{St}} \tag{1}$$

where R is the gas constant, $T_{\text{fus,A}}$ and $\Delta_{\text{fus}}H_{\text{A}}$ is the temperature and enthalpy of fusion of the solvent A, respectively, x_{B} is the mole fraction of the solute B, and k_{St} is the semi-empirical correction factor introduced by Stortenbeker [13] representing the number of foreign particles, which introduces the solute B into the solvent A. Differentiating (Eq. (1)) according to x_{A} and setting for $x_{\text{A}} \rightarrow 1$ we get the relation for the tangent to the liquidus curve of the solvent A, k_0, at the temperature of fusion of the solvent A

$$\lim_{x_{\text{A}} \rightarrow 1} \frac{d(\Delta_{\text{fus}}T(\text{A}))}{dx_{\text{A}}} = \frac{RT^2_{\text{fus,A}}}{\Delta_{\text{fus}}H_{\text{A}}} k_{\text{St}} = k_0 \tag{2}$$

Knowing $T_{\text{fus,A}}$ and $\Delta_{\text{fus}}H_{\text{A}}$, from the tangent k_0 we can then calculate k_{St}, which enables one to elucidate the possible chemical reactions between components.

The experimentally determined values of temperature of primary crystallization of individual samples in the investigated system are given in Table 1.

The value of the Stortenbeker's correction factor was calculated from the tangent of the experimental liquidus curve of cryolite at the melting point of pure cryolite according to (Eq. (2)). For the enthalpy of fusion of cryolite the calorimetrically determined value was used [14]. The dependence of temperature of primary crystallization (T_{pc}) on $x_{\text{Na}_3\text{AlF}_6}$ was expressed in the form

$$\Delta T_{\text{PC}} = (190.4 \pm 1.7) - (190.4 \pm 1.8) \cdot x_{\text{Na}_3\text{AlF}_6} \tag{3}$$

The results of cryoscopic measurements for investigated system are shown in Fig. 2. For k_0 and k_{St} the values $k_0 = 58.5$ K and $k_{\text{St}} = 0.46$ were obtained, which indicate the introduction of approximately 0.5 new substances when 1 mol FeF_3 is dissolved in an infinite amount of cryolite (excluding the dissociation products of pure cryolite) [15]. This means that dissolving FeF_3 in cryolite half new particle is formed.

One can suggest the formation of a solid solution because the substitution of Fe^{3+} by Al^{3+} is known not to cause drastic crystallographic changes [16] and also because of similar crystallographic structure of Na_3FeF_6 and Na_3AlF_6. Both compounds posses monoclinic structure with similar space group (*P*1 21 1 for Na_3FeF_6, *P*1 21/n1 for Na_3AlF_6) [10,17] and dimensions of ionic radii of cations placed in the center of $\{FeF_6\}$ and $\{AlF_6\}$ octahedra (0.55 Å for Fe^{3+}, 0.54 Å for Al^{3+}) [18]. Therefore, iron has been shown to partially substitute aluminum in the cryolite structure and the substitution mechanism in the reaction process can be described as follows:

$$\begin{aligned}(3+2x)\ \ Na_3AlF_6(l) + (2+2y)\ \ FeF_3(l) \\ = 2Na_3(Al_xFe_y)F_6(l) + 3\ \ NaAlF_4(g)\end{aligned} \tag{4}$$

where $x + y = 1$.

Table 1
Temperatures of primary crystallization in melts of the system Na_3AlF_6–FeF_3.

x (FeF_3)	t_{pc} (Na_3AlF_6) [°C]
0.000	1007.2
0.000	1007.1
0.010	1005.8
0.010	1006.2
0.020	1005.4
0.020	1005.9
0.030	1005.4
0.030	1005.2
0.050	1005.0
0.050	1004.3
0.075	1002.3
0.075	1002.6
0.100	1001.1
0.100	1000.9

Table 2
The weight-losses in the system Na_3AlF_6–*x* mol% FeF_3 ($x = 0$, 5, 25 and 40).

Weight [mg]	Sample	Δm (1020 °C), 1 h	
		[mg]	%
300	Empty run	−2.0	0.7
300	Pure Na_3AlF_6	−29.0	9.7
300	5 mol% FeF_3	−28.0	9.3
300	25 mol% FeF_3	−41.3	13.8
300	40 mol% FeF_3	−90.9	30.3

The weight losses of investigated mixtures measured 1 h at 10–20 °C up to temperatures of its primary crystallization are summarized in Table 2.

The weight-loss of pure cryolite at 1020 °C was found to be 9.67%. It is well known that cryolite undergoes substantial thermal dissociation at melting under the formation of volatile $NaAlF_4$ and solid NaF, which remains in the bulk [19]. But in other samples 1 h weight-looses of melts further sharply increase with an increasing content of FeF_3 in comparison to pure cryolite. This effect can be caused by direct reaction of FeF_3 with cryolite in the melts. The result of such a process is that some volatile products are generated. This observation confirms the presence of volatile decomposition products originating from reactions in the system.

In order to confirm the above-mentioned suggestions, the capture of eventual gaseous reaction product(s) was realized by means of the developed apparatus (Fig. 1). According to realization of procedure described above the condensate product was obtained. It was placed in a Pt gatherer in the temperature region 700–800 °C (Fig. 1). The sum of weights of residue sample in Pt crucible and condensate product has shown that other volatile products cannot accrue (Fig. 2).

In the next steps, the condensate was homogenized and analyzed by solid state multinuclear (^{27}Al, ^{23}Na and ^{19}F) magnetic resonance spectroscopy with respect to higher sensitivity of this method compared to classical analytical methods (as for example X-ray diffraction analysis). The room temperature ^{27}Al MAS spectrum shows a peak about 1 kHz wide cantered at −13.5 ppm (Fig. 3, peak **A1**) (Table 3).

This signal belongs to a six-fold coordinated aluminum in $\{AlF_6\}$ octahedral site of AlF_3 [20,21]. Moreover, the spectrum reveals two overlapping quadrupolar doublets. Booths represent two types of aluminum isotopes in structure of chiolite, $Na_5Al_3F_{14}$. The structure consists of alternating layers of corner-sharing $\{AlF_6\}$ octahedral and distorted edge-sharing $\{NaF_6\}$ octahedral. In all layers each fourth octahedron, having 2/m or 4/m symmetry, is replaced by a sodium atom. Two sodium atoms are coordinated by eight fluorine atoms and next eight sodium atoms by six fluorines. One $\{AlF_6\}$ octahedron shares corners with four octahedra and next octahedron with two octahedra [11,20,22]. In the spectra the broader doublet (Fig. 3, peak **B1**) represents the Al site in $\{AlF_6\}$ octahedron, which shares corners with two next-nearest-neighboring octahedral or with four next-nearest-neighboring octahedra (with δ_{iso}(**B1**) = −2.1 ppm and δ_{iso}(**A1**) = −3.2 ppm) [22] (Fig. 3, peak **C1**).

The ^{23}Na spectra contain only two broad overlapping quadrupolar doublets at $\delta_{\text{iso}} = -7.4$ ppm and $\delta_{\text{iso}} = -20.7$ ppm (Fig. 4, peaks **A2** and **B2**, respectively). They belong to two different Na sites in chiolite structure.