Investigation of the liquidus curve of chiolite in the system Na_3AlF_6—AlF_3

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The liquidus curve of chiolite in the system Na_3AlF_6—AlF_3 was determined by means of thermal analysis in an open system. The experimental results were submitted to the thermodynamic analysis.

The composition and temperature of the peritectic and eutectic points were found to be (in coordinates NaF—AlF_3): $x_p = 41.1$ mole % AlF_3, $T_p = 1006$ K, $x_E = 46.8$ mole % AlF_3, $T_E = 958$ K. The experimental results obtained in an open system indicate the existence of the compound $NaAlF_4$ in the melts, decomposing at 945 K by a eutectoid reaction into chiolite and AlF_3.

The existence of $NaAlF_4$ has also been confirmed indirectly by a thermodynamic analysis of the experimental and calculated liquidus curves. The determination of the degree of thermal dissociation of the chiolite anion by means of an indirect method showed that the chiolite anion dissociates only to a minor extent, most probably according to the scheme

$$Al_3F_{14}^{5-} \rightleftarrows AlF_6^{3-} + 2AlF_4^-$$

Методом термического анализа в открытой атмосфере была определена кривая ликвидуса хиолита в системе Na_3AlF_6—AlF_3. Результаты были анализированы термодинамически.

Были определены температура и состав перитектики и эвтектики (для координат NaF—AlF_3): $x_p = 41{,}1$ мол. % AlF_3, $T_p = 1006$ K, $x_E = 46{,}8$ мол. % AlF_3, $T_E = 958$ K. Кроме того было доказано существование соединения $NaAlF_4$, которое при 945 K разлагается с образованием хиолита и AlF_3.

Существование $NaAlF_4$ косвенно подтверждено и при термодинамическом рассмотрении экспериментальной и рассчитанной кривой ликвидуса. Косвенное определение степени термической диссоциации аниона хиолита показало, что он диссоциирует в очень незначительной степени, вероятно по схеме

$$Al_3F_{14}^{5-} \rightleftarrows AlF_6^{3-} + 2AlF_4^-$$

The phase equilibria in the system Na_3AlF_6—AlF_3 have been repeatedly investigated owing to the prime importance of this system with respect to the electrodeposition of aluminium. This system, first studied in 1912 by *Fedotiev et al.* [1], was reinvestigated at least 15 times, mostly with respect to the liquidus curve of cryolite. On the other hand, the liquidus curve of chiolite has not been investigated so thoroughly.

For a better understanding of processes which occur in the electrolyte, it is, however, inevitable to dispose with reliable data on the liquidus curve and on the scheme of dissociation of chiolite. The attention will be paid mainly to papers describing the existence of sodium tetrafluoroaluminate, $NaAlF_4$.

Review of the literature data

According to the different authors [2—16], the system Na_3AlF_6—AlF_3 involves the compounds $Na_5Al_3F_{14}$, $NaAlF_4$ and, probably, also $NaAl_2F_7$ [9]. Chiolite melts incongruently at a temperature reported within the range 725—745°C, the composition coordinate of the peritectic point being reported within 39.4—41.0 mole % AlF_3. Chiolite forms with another constituent of the melt a simple eutectic system, the coordinates of the eutecticum being reported within 45—47 mole % AlF_3 and 685—700°C. It should be pointed out that there is not a consent as to the composition of the "another constituent" in the system Na_3AlF_6—AlF_3 which is supposed to be either $NaAlF_4$ or AlF_3.

The presence of the compound $NaAlF_4$ in the system Na_3AlF_6—AlF_3 was first mentioned in 1933 by *Hardouin* [2]. The existence of this compound was further assumed by *Piontelli* [3], *Grünert* [4], and *Boner* [5].

On the other hand, no maximum corresponding to the melting point of $NaAlF_4$ was observed in the investigations of an open system which were carried out by *Abramov et al.* [6] and *Holm* [7].

The direct confirmation of the existence of the compound $NaAlF_4$ was first given in 1954 by *Howard* [8] who identified it by the X-ray analysis in the condensed vapours of the NaF and AlF_3 mixtures close to the composition of this compound. This finding has been confirmed shortly afterwards by *Ginsberg* and *Böhm* [9] and by *Mashovets et al.* [10].

Thus far, the existence of $NaAlF_4$ in the investigated system was confirmed only in the investigation of a closed system. Using the closed-cell method of thermal analysis, *Ginsberg* and *Wefers* [11] concluded that $NaAlF_4$ is formed by a peritectic reaction at 710°C and decomposes at 680°C according to the scheme

$$5NaAlF_4 \rightarrow Na_5Al_3F_{14} + 2AlF_3$$

The existence of $NaAlF_4$ as well as the narrow interval of its thermal stability was later confirmed by *Mesrobian et al.* [12] who worked under argon at $\leq 225 \times 10^5$ Pa.

Thus it may be concluded that the existence of $NaAlF_4$ has been proved, though the course of liquidus of the system Na_3AlF_6—AlF_3 does not indicate its existence if investigated in an open system. Generally, it has been assumed that the existence of this compound can be determined only by thermal analysis in a closed system.

The reported coordinates of the invariant points in the system Na_3AlF_6—AlF_3 [1, 6, 7, 11—23] range within 39.4—41.0 mole % AlF_3 and 998—1018 K for the peritectic and 43.1—47.2 mole % AlF_3 and 957—973 K for the eutectic point. The temperature of the eutectoid reaction was found to be 953 K [11].

Experimental

The liquidus curve of chiolite in the system Na_3AlF_6—AlF_3 was investigated by means of thermal analysis. This investigation was carried out in an open system with samples synthesized of NaF and AlF_3. The experimental procedure was described in the previous papers [24, 25].

In total, 25 mixtures were investigated. The critical temperatures of the individual samples were determined with a reproducibility of ±2°C. The AlF_3 losses owing to sublimation did not surpass the value of 0.15 wt %.

On the cooling curves within the range of the primary crystallization of chiolite three deviations from a monotonous course indicating three different phase transitions have been determined. The first (highest) transition corresponds to the equilibrium solidus—liquidus, accompanied by the separation of the chiolite crystals. The second deviation corresponds to the invariant eutectic crystallization of the couple "chiolite + another constituent of the system".

Finally, at 945 K = 672°C a third deviation was observed, which corresponds to an invariant process again. The proof of the existence of this second invariant process which was not observed on the cooling curves by other investigators thus far, is considered to be the main contribution of this work. This third deviation may be attributed to the following processes:

a) Polymorphous modification of chiolite or AlF_3;

b) Crystallization of the ternary eutectic mixture $Na_5Al_3F_{14} + AlF_3$ + ? (in the case if AlF_3 contained minor quantities of Al_2O_3 or if a third — unknown — component entered into the system);

c) Eutectoid decomposition of $NaAlF_4$ according to the scheme

$$NaAlF_4 \rightleftarrows Na_5Al_3F_{14} + 2AlF_3$$

The most probable appears to be the last possibility as there were no polymorphous modifications of $Na_5Al_3F_{14}$ or AlF_3 observed at the given temperature (672°C) and the cooling curves of pure cryolite and chiolite did not indicate the presence of Al_2O_3 or another impurity.

It should be mentioned that at a heating rate of 0.5°C/min the heating curve did not give any evidence of this eutectoid reaction. It can be assumed that the formation of $NaAlF_4$ by the reaction

$$2AlF_3 + Na_5Al_3F_{14} \rightarrow 5NaAlF_4$$

in the solid state is slowed down to such an extent that it cannot be registered even at low heating rates.

The values obtained by a graphical interpretation of the cooling curves are shown in Fig. 1.

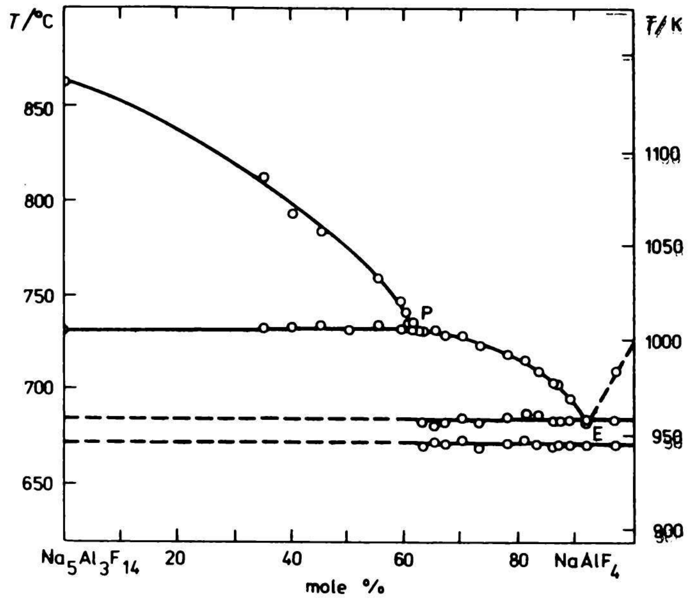

Fig. 1. Phase diagram of the system $Na_5Al_3F_{14}$—$NaAlF_4$.

The existence of the compound $NaAlF_4$ in the melts thus has been confirmed also in an open system, hence in the description of the investigated system in Fig. 1 the composition coordinates "chiolite—$NaAlF_4$" are used.

Indirect determination of the degree of the thermal dissociation of the chiolite anion

The methods for a direct determination of the degree of thermal dissociation of a molten compound [26] are inaccessible to the authors thus far, therefore, an indirect method was applied, similar to the determination of the dissociation of the complex anion in the incongruently melting compound $CaAlF_5$ [25]. This method is based on the comparison of the calculated and experimental courses of the liquidus curve and, as described, *e.g.* by *Glasstone* [27], it has been applied successfully by *Grjotheim* [13] to the determination of the degree of thermal dissociation of the cryolite anion in molten cryolite.

The course of the liquidus of chiolite between the peritectic and the eutectic points can be described by the Le Chatelier—Shreder equation only in the case when the transformation of coordinates leads to an independent system chiolite—second constituent without solid solutions when the investigated system is close to an ideal one.

As the second constituent in the system investigated both AlF_3 and $NaAlF_4$ have been considered using the corresponding values of ΔH_i^f ($i = Na_5Al_3F_{14}$) determined from the slopes of tangents to the experimental liquidus curves. Owing to the narrow temperature interval, in both cases ΔH_i^f was considered to be independent of temperature.

Altogether, three potentially possible schemes of dissociation of chiolite, both pure and in a mixture with the second component (AlF_3 in the first scheme and $NaAlF_4$ in the second and third scheme) were considered.

1. a) Pure chiolite

$$Na_5Al_3F_{14} \rightarrow 5Na^+ + Al_3F_{14}^{5-} \quad \text{(electrolytic dissociation)}$$

$$(1-b)\ Al_3F_{14}^{5-} \rightleftarrows b\ AlF_6^{3-} + 2b\ AlF_4^- \quad \text{(thermal dissociation)}$$

where b is the degree of dissociation of the chiolite anion in pure molten chiolite.

b) Mixture of x moles of chiolite and (1 − x) moles of AlF_3

$$x\ Na_5Al_3F_{14} \rightarrow 5x\ Na^+ + x\ Al_3F_{14}^{5-}$$

$$x(1-c)\ Al_3F_{14}^{5-} \rightleftarrows xc\ AlF_6^{3-} + 2xc\ AlF_4^-$$

$$(1-x)\ AlF_3 + \frac{1-x}{2}\ AlF_6^{3-} \rightarrow \frac{3}{2}(1-x)\ AlF_4^-$$

where c is the degree of dissociation of the chiolite anion in the mixture.

2. a) Dissociation of pure chiolite is considered to be the same as in 1.

b) Mixture of x moles of chiolite and (1 − x) moles of $NaAlF_4$

$$x\ Na_5Al_3F_{14} \rightarrow 5x\ Na^+ + x\ Al_3F_{14}^{5-}$$

$$x(1-c)\ Al_3F_{14}^{5-} \rightleftarrows xc\ AlF_6^{3-} + 2xc\ AlF_4^-$$

$$(1-x)\ NaAlF_4 \rightarrow (1-x)\ Na^+ + (1-x)\ AlF_4^-$$

3. a) Dissociation of the chiolite anion in pure chiolite

$$Na_5Al_3F_{14} \rightarrow 5Na^+ + Al_3F_{14}^{5-}$$

$$(1-b)\ Al_3F_{14}^{5-} \rightleftarrows 3b\ AlF_4^- + 2b\ F^-$$

b) Mixture of x moles of chiolite and (1 − x) moles of $NaAlF_4$

$$x\ Na_5Al_3F_{14} \rightarrow 5x\ Na^+ + x\ Al_3F_{14}^{5-}$$

$$x(1-c)\ Al_3F_{14}^{5-} \rightleftarrows 3xc\ AlF_4^- + 2xc\ F^-$$

$$(1-x)\ NaAlF_4 \rightarrow (1-x)\ Na^+ + (1-x)\ AlF_4^-$$

The degree of dissociation of the chiolite anion, c, in the system was calculated from the equality of dissociation constants of this anion in pure chiolite and in a mixture of chiolite with the second component

$$K^{dis}_{Al_3F_{14}^{5-}} = K^{dis}_{Al_3F_{14}^{5-}/AlF_3} \qquad [T] \qquad (1)$$

or

$$K^{dis}_{Al_3F_{14}^{5-}} = K^{dis}_{Al_3F_{14}^{5-}/NaAlF_4} \qquad [T] \qquad (2)$$

After expressing the activities of the corresponding ions by means of the products of ionic ratios of cations and anions, and introducing into eqn (*1*) or eqn (*2*), the following equations were obtained:

For model *1*

$$\frac{x(1-c)}{1+2xc} = \frac{(2xc+x-1)(4xc-3x+3)^2}{8x(1-c)(2xc+1)^2} \qquad (3)$$

For model *2*

$$\frac{x(1-c)}{1+2xc} = \frac{c(2xc+1-x)^2}{(1-c)(2xc+1)^2} \qquad (4)$$

For model *3*

$$\frac{x(1-c)}{1+4xc} = \frac{(3xc+1-x)^3\, 4xc^2}{(1-c)(4xc+1)^4} \qquad (5)$$

For the first and second model a series of equations of the third degree and for the third model a series of equations of the fifth degree with respect to the unknown quantity c were obtained; the values of b and x were chosen sequentially within the interval $\langle 0, 1 \rangle$. These equations have been solved using the iteration method. In all cases, the solution gave a single root within the interval $\langle 0, 1 \rangle$, which is in agreement with the physical reality. It should be mentioned, however, that with the first model assuming chiolite and AlF_3 as components the solution does not cover the entire concentration interval of x_i corresponding to the liquidus curve. This indicates indirectly the inadequacy of the composition coordinates corresponding to the system chiolite—AlF_3 and supports the assumption on $NaAlF_4$ being the second component.

The liquidus curves calculated by means of a method described elsewhere [27, 28] were compared with the experimental curve. The best fitting was assumed to be criterion for the correctness of the model considered.

The value of ΔH_i^f were obtained from the slopes of tangents, which means that the ΔH_i^f values might imply also the respective values of the enthalpy of dissociation. In the determination of the degree of thermal dissociation of Na_3AlF_6 and Li_3AlF_6 it was found, however, that this does not affect the results in a significant way, at least at a degree of dissociation of *ca.* 30% [28].

The results of this investigation can be documented graphically. The best consent between the experimental and calculated values was obtained with the second

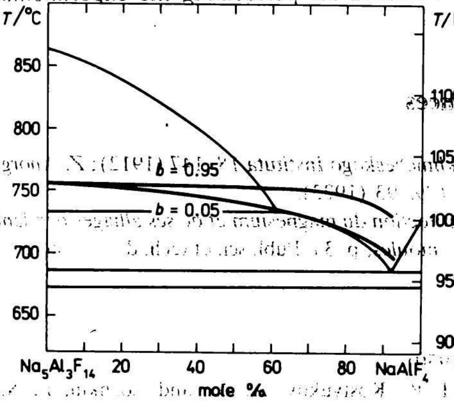

Fig. 2. Comparison of the experimental and calculated liquidus curve for the second model of dissociation.

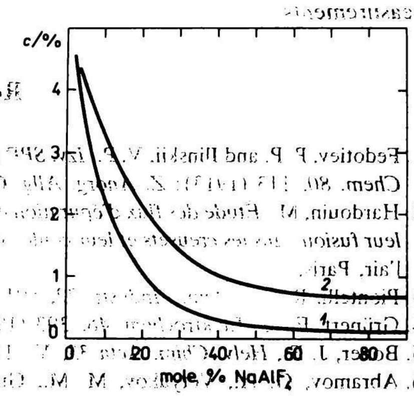

Fig. 3. Change of the degree of dissociation *c* with increasing concentration of the second component for the second and third model.

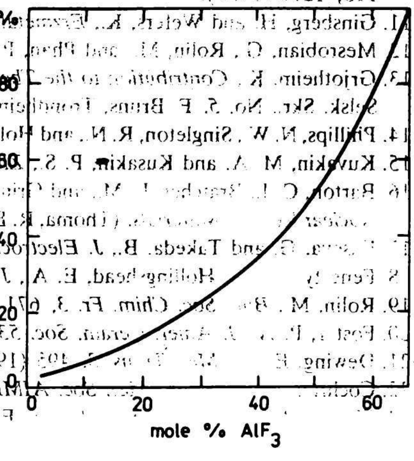

Fig. 4. Change of the degree of dissociation *c* with increasing concentration of the second component for the first model.

model for the degree of dissociation of the chiolite anion in pure chiolite $b = 0.05$ (Fig. 2); in a mixture this value further decreases with increasing concentration of the second component (Fig. 3).

The incorrectness of the first model was confirmed as none of the calculated curves could be fitted to the experimental liquidus curve and, besides, with this model the degree of dissociation c extremely increases with increasing concentration of AlF_3 in the mixture, though it is highly improbable that the degree of thermal dissociation might increase from a value close to 0 up to 100% within the narrow concentration and temperature interval investigated (Fig. 4).

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