# Solubility of $AlPO_4$ and $NaVO_3$ in $NaF-AlF_3$ Melts

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The temperatures of primary crystallization of cryolite in systems $NaF-AlF_3-AlPO_4$ and $NaF-AlF_3-NaVO_3$ were determined by thermal analysis. The measurements were performed at cryolite ratios (CR) equal to 2.5 and 2 [CR = $n(NaF)/n(AlF_3)$]. It is evident that $AlPO_4$ decreases the temperature of primary crystallization of cryolite more than $NaVO_3$ at both selected cryolite ratios.

## Introduction

The industrial electrolyte of aluminum production (Hall–Héroult process) contains impurities, like iron, silicon, sulfur, phosphorus, vanadium, etc.[1] They are introduced to the electrolyte mainly through the raw materials (alumina and fluoride salts) and through anodes.[2] A small amount of vanadium or phosphorus impurities causes a significant decrease of current efficiency in the aluminum cell.[3]

Phosphorus can exist in different oxidation states, starting from −3 up to +5 and can form different compounds containing oxygen and fluorine. Therefore, the chemistry of phosphorus is very complex. A small amount of phosphorus in produced aluminum influences the quality of the metal. The phosphorus lowers the corrosion resistance and increases the brittleness of the metal.[1]

Del Campo[4] determined a phase diagram for the system $Na_3AlF_6-Na_4P_2O_7$ (CR = 3). Bratland et al.[5] on the basis of del Campo's results considered reactions of the pyrophosphate anion ($P_2O_7^{2-}$) with the anions ($AlF_6^{3-}$, $F^-$) that form the $PO_4^{3-}$, $PO_3F^{2-}$, and $PO_3^-$ anions. The $AlF_6^{3-}$ and $F^-$ anions are products of dissociation of molten cryolite.

The $Na_2P_4O_7$ compound was detected in solidified samples of the $Na_3AlF_6-Na_3PO_4$ molten system.[6] When $Al(PO_3)_3$ was added to a cryolite melt, the formation of $AlPO_4$ and gaseous $POF_3$ was recorded by XRD and IR analysis.[7]

Thisted et al.[8] measured a part of the phase diagram of the $Na_3AlF_6-AlPO_4$ system. The eutectic point was determined to be at 57.2 mol % $AlPO_4$ and (696 ± 1) °C. They suggested that in molten cryolite the orthophosphate anion $PO_4^{3-}$ dissociates partly into metaphosphate $PO_3^-$ and oxide ion $O^{2-}$.

Keppert et al.[9] presented a new approach to the structure of the $Na_3AlF_6-AlPO_4$ molten system. They measured in situ high-temperature NMR spectra using a wide range of different nuclei involved in the $Na_3AlF_6-AlPO_4$ system: $^{19}F$, $^{27}Al$, $^{23}Na$, $^{31}P$, and $^{17}O$. The $PO_4$ tetrahedron was found to be a stable structure in the cryolite-based melts. The chemical shift evolutions seemed to indicate the existence of the $PO_4^{3-}$ and $(AlF_4-O-PO_3)^{4-}$ anions with an Al–O–P bond. The $^{19}F$ NMR spectra excluded the presence of a P–F bond (i.e., $PO_3F^{2-}$ group) in $Na_3AlF_6-AlPO_4$ melts.

The solubility of vanadium pentoxide in pure cryolite and in cryolite–alumina melts was measured by Bratland et al.[10] They used a visual method, and the determined solubility of $V_2O_5$ in pure molten cryolite was 1.1 wt. % at 1030 °C. This result is in accordance with the older measurements of Rolin et al.[11] and Belyaev et al.[12] Bratland et al.[10] also found that the solubility of $V_2O_5$ decreases linearly with increasing alumina content in molten cryolite.

Goodes and Algie[13] investigated the distribution of vanadium impurities between the bath and aluminum and between the bath and gaseous phases, respectively. They detected residual vanadium in the bath, during the vanadium transfer across the bath/aluminum interface. Moreover, the content of vanadium in the bath was higher than reported by Bratland et al.[10] The condensate from the fumes above the melt contained vanadium, particularly during the first (2 to 4) h of the runs, and then the volatilization seemed to cease. The reported differences can arise from the fact that different experimental conditions were considered.

Chrenková et al.[14] studied the $Na_3AlF_6-V_2O_5$ system by thermal analysis. The authors concluded that the solubility of vanadium pentoxide in pure cryolite is higher than data reported in refs 10 to 12

Kucharík et al.[15] measured the phase diagram of the $Na_3AlF_6-NaVO_3$ system. The system is a simple eutectic one. The eutectic point was estimated to be 97.5 mol % $NaVO_3$ and 617 °C. The XRD analysis of samples after thermal analysis revealed the presence of cryolite and $NaVO_3$ that supports the above assumption of a simple eutectic binary system. The thermodynamic calculation suggests that some reaction between molten cryolite and sodium metavanadate occurred.

Besides the lowering of the current efficiency, the vanadium impurities introduced into the bath have a negative influence on the quality of produced metal in a manner similar to phosphorus.[1]

In this paper, we will present data on the primary crystallization in the $NaF-AlF_3-AlPO_4$ and $NaF-AlF_3-NaVO_3$ systems.

## Experimental Section

For the preparation of samples, the following chemicals were used: natural hand-picked $Na_3AlF_6$ from Greenland (melting point: (1009 to 1011) °C), $AlF_3$ sublimated in a platinum crucible, NaF (Merck, 99.9 %), $NaVO_3$ (Aldrich, anhydrous, 99.9 %), $AlPO_4$ (Aldrich, 99.99 %), NaCl (Fluka, 99.9 %), and KCl (Fluka, 99.9 %). All chemicals were dried under vacuum at 150 °C for 5 h and handled in a glovebox under a dry nitrogen atmosphere (Messer, 99.99 %). The measurements of cooling

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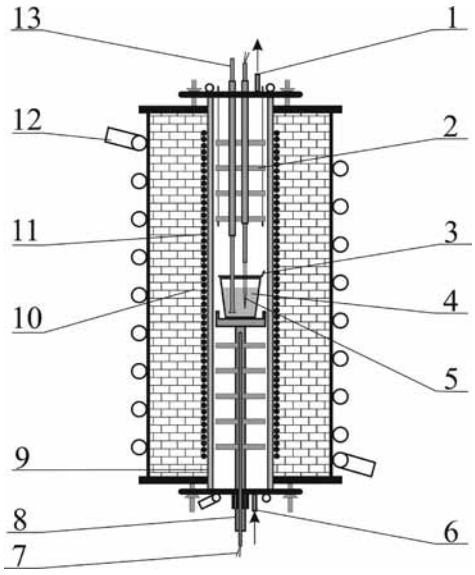


**Figure 1.** Cross section of the resistance furnace. 1, gas outlet; 2, corundum radiation shields; 3, platinum lid; 4, platinum crucible with melt; 5, Pt-PtRh10 measuring thermocouple; 6, gas inlet; 7, Pt-PtRh10 control thermocouple; 8, corundum sheath; 9, corundum tube (Alsint, 99.7 % $Al_2O_3$); 10, insulating material; 11, Kanthal heating element; 12, water cooling pipes; 13, platinum stirrer in corundum sheath.

**Table 1. Compositions and Temperatures of Primary Crystallization ($t$/°C) in the System $NaF-AlF_3-AlPO_4$**[a]

| | $x$(NaF) | $x$($AlF_3$) | $x$($AlPO_4$) | $t$/°C |
|---|---|---|---|---|
| CR = 3 | 0.7500 | 0.2500 | 0 | 1011.0 |
| | 0.7481 | 0.2494 | 0.0025 | 1009.2 |
| | 0.7445 | 0.2482 | 0.0073 | 1005.2 |
| | 0.7403 | 0.2468 | 0.0129 | 1002.3 |
| | 0.7297 | 0.2432 | 0.0271 | 994.4 |
| | 0.7184 | 0.2395 | 0.0422 | 981.4 |
| | 0.7059 | 0.2353 | 0.0588 | 964.5 |
| | 0.6774 | 0.2258 | 0.0968 | 918.4 |
| CR = 2.5 | 0.7143 | 0.2857 | 0 | 1003.0 |
| | 0.7107 | 0.2843 | 0.0050 | 995.8 |
| | 0.7072 | 0.2828 | 0.0100 | 990.2 |
| | 0.7000 | 0.2800 | 0.0200 | 979.0 |
| | 0.6929 | 0.2771 | 0.0300 | 967.6 |
| | 0.6786 | 0.2714 | 0.0500 | 945.7 |
| | 0.6607 | 0.2643 | 0.0750 | 905.0 |
| | 0.6429 | 0.2571 | 0.1000 | 862.6 |
| CR = 2 | 0.6667 | 0.3333 | 0 | 954.0 |
| | 0.6634 | 0.3316 | 0.0050 | 940.0 |
| | 0.6600 | 0.3300 | 0.0100 | 941.1 |
| | 0.6534 | 0.3266 | 0.0200 | 925.0 |
| | 0.6467 | 0.3233 | 0.0300 | 890.0 |
| | 0.6334 | 0.3166 | 0.0500 | 878.8 |
| | 0.6167 | 0.3083 | 0.0750 | 827.0 |
| | 0.6000 | 0.3000 | 0.1000 | 783.3 |

[a] Data for CR = 3 are from Thisted et al.[8]

curves were performed in a closed vertical resistance furnace with water-cooling and under an argon atmosphere (Messer, 99.996 %) (Figure 1). Mixtures of (10.000 ± 0.001) g with known composition were homogenized and transferred into a Pt crucible and placed in the furnace. The temperature was measured using a Pt-PtRh10 thermocouple calibrated with respect to the melting points of known compounds (NaCl, KCl, NaF, and $Na_3AlF_6$). The reproducibility of the measured temperatures was within ± 2 °C. The cooling rate was 1.2 °C·min$^{-1}$. Each sample was kept for 12 h under an argon atmosphere in the furnace at 200 °C before the experiment. After the melting, the sample was homogenized by stirring with a platinum rod mounted on a corundum tube for 15 min.

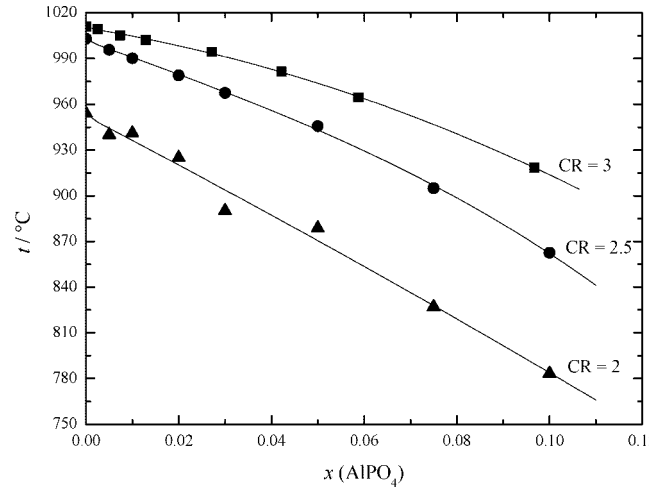


**Figure 2.** Temperatures of primary crystallization in the $NaF-AlF_3-AlPO_4$ system at different cryolite ratios, CR = $n$(NaF)/$n$($AlF_3$). ■, CR = 3; ●, CR = 2.5; ▲, CR = 2. Data for CR = 3 are from Thisted et al.[8]

**Table 2. Compositions and Temperatures of Primary Crystallization ($t$/°C) in the System $NaF-AlF_3-NaVO_3$**[a]

| | $x$(NaF) | $x$($AlF_3$) | $x$($NaVO_3$) | $t$/°C |
|---|---|---|---|---|
| CR = 3 | 0.75 | 0.25 | 0 | 1011 |
| | 0.7472 | 0.2491 | 0.0038 | 1007.1 |
| | 0.7423 | 0.2474 | 0.0103 | 1002.5 |
| | 0.7403 | 0.2468 | 0.0129 | 1001.3 |
| | 0.7297 | 0.2432 | 0.0271 | 996.6 |
| | 0.7183 | 0.2394 | 0.0423 | 991.5 |
| | 0.6923 | 0.2308 | 0.0769 | 982.2 |
| CR = 2.5 | 0.7143 | 0.2857 | 0.0000 | 1003.0 |
| | 0.7107 | 0.2843 | 0.0050 | 998.0 |
| | 0.7072 | 0.2828 | 0.0100 | 996.2 |
| | 0.7000 | 0.2800 | 0.0200 | 992.4 |
| | 0.6929 | 0.2771 | 0.0300 | 987.9 |
| | 0.6786 | 0.2714 | 0.0500 | 982.0 |
| | 0.6607 | 0.2643 | 0.0750 | 974.9 |
| CR = 2 | 0.6667 | 0.3333 | 0.0000 | 954.8 |
| | 0.6634 | 0.3316 | 0.0050 | 951.5 |
| | 0.6600 | 0.3300 | 0.0100 | 941.5 |
| | 0.6534 | 0.3266 | 0.0200 | 935.0 |
| | 0.6467 | 0.3233 | 0.0300 | 930.0 |
| | 0.6400 | 0.3200 | 0.0400 | 926.7 |
| | 0.6334 | 0.3166 | 0.0500 | 924.3 |

[a] Data for CR = 3 are from Kucharík et al.[15]

## Results and Discussion

The experimentally determined data for the $NaF-AlF_3-AlPO_4$ system are presented in Table 1 and for the $NaF-AlF_3-NaVO_3$ system are summarized in Table 2.

The graphical illustrations of primary crystallization temperatures versus composition are shown in Figure 2 ($NaF-AlF_3-AlPO_4$ system) and in Figure 3 ($NaF-AlF_3-NaVO_3$ system). It is evident that $AlPO_4$ decreases the temperature of primary crystallization more than $NaVO_3$ at identical compositions.

From results measured at CR = 2.5 and 2, it is not possible to conclude something about the structure of both molten systems, but it can be assumed that the obtained results (measurements and thermodynamic calculations) in the $Na_3AlF_6-AlPO_4$ system (CR = 3)[8] or $Na_3AlF_6-NaVO_3$ system (CR = 3),[15] respectively, will be approximately valid for cryolite ratios of 2.5 and 2.

Because high-temperature $^{19}F$ NMR measurements[9] excluded the presence of the P−F bond in the $Na_3AlF_6-AlPO_4$ molten system, it can be assumed that the change of the cryolite ratios to lower values did not influence the product of $AlPO_4$

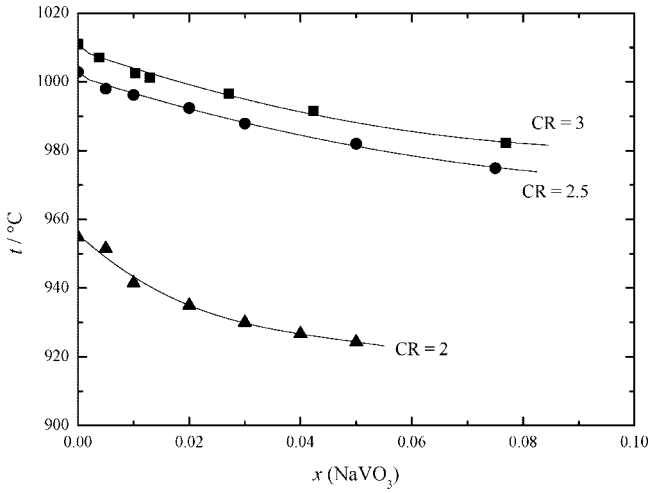


**Figure 3.** Temperatures of primary crystallization in the $NaF-AlF_3-NaVO_3$ system at different cryolite ratios, CR = $n$(NaF)/$n$($AlF_3$). ■, CR = 3; ●, CR = 2.5; ▲, CR = 2. Data for CR = 3 are from Kucharík et al.[15]

dissolution in $NaF-AlF_3$ melts which should have been different phosphate anions.

In the case of the $NaVO_3$ in the $NaF-AlF_3$ molten system, an additional work, e.g., high-temperature NMR and Raman spectroscopy, should be performed as the next step for better understanding of dissolution process.

Generally, the measured data of primary crystallization temperatures are necessary for further physicochemical (density, viscosity, electrical conductivity, surface tension, etc.), electrochemical, and spectroscopic (HT NMR, HT Raman) measurements. Volume properties from density, electrochemical, and spectroscopic measurements are especially important for further study of the structure and also chemical and electrochemical reactions in these systems. Nowadays, cells in the aluminum industry work at cryolite ratios between 2 and 2.5, and therefore the measured data are interesting from a technological point of view.

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