EXECUTIVE SUMMARY OF FINAL SCIENTIFIC/TECHNICAL REPORT

Project Title: DEVELOPMENT OF A NOVEL NON-CONSUMABLE ANODE FOR ELECTROWINNING PRIMARY ALUMINUM

Covering Period: October 1, 1999 through September 30, 2003

Date of Report: December 4, 2003

Recipient: The Ohio State University Research Foundation, OSU, Columbus, OH 43210

Award Number: DOE-OIT PROJECT DE-FC07-99ID13813

Contact: Principal Investigator Robert A. Rapp, (614) 292-6178, rapp.4@osu.edu

Project Team: DOE HQ: Thomas Robinson; Project Manager: John Yankeelov

Collaborating Subcontractors (until 3-31-2001): Gas Technology Institute, Kaiser Aluminum Corporation, Siemens-Westinghouse Corporation

The principal goal of the project was to determine through theoretical considerations and from chemical and electrochemical laboratory studies the technical and economic feasibility for the substitution and retrofitting of an SOFC-type anode for today's carbon anode in a cell for electrowinning primary Al. However, solubility measurements showed that no value of cryolite ratio can exist where the solubilities of the solid electrolyte components (zirconia and especially yttria) would be small relative to the alumina solubility. Therefore, the utilization of the proposed SOFC-type anode cannot be realized for any cell involving a cryolite-base solvent. However, the project suggested that the SOFC-type anode scheme might be successful if the solvent/electrolyte for electrowinning Al could be changed to a fused sulfate melt.

During the solubility experiments, electrochemical probes were developed, and a bath characterization was defined, to measure quantitatively the acid-base character of cryolite melts. The measured acid-base behavior was then used to correlate the alumina solubility in cryolite over a wide range of cryolite ratio at 1300K. A mathematical modeling of the alumina solubility as a function of basicity identified three solutes of Al_2O_3 in cryolite-base melts: $\text{Na}_2\text{Al}_2\text{OF}_6$, $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$, and $\text{Na}_4\text{Al}_2\text{O}_2\text{F}_6$ as acidic, neutral and basic solutes, respectively. For the first time, the stereochemistry (geometries) of these complex solutes was clarified. For the non-oxygen containing Al-F complex anions, Na_3AlF_6 and NaAlF_4 were also considered as solutes, and some NaF (but no AlF_3) could remain in the melts. The previously suggested solute Na_2AlF_5 was found to be unstable. The strong complexing in the cryolite/alumina system means that the bath is highly buffered so that a significant shift in basicity is not possible and therefore the alumina solubility does not vary greatly. The maximum solubility for alumina occurs at a cryolite ratio of about four.

The method used for theoretical modeling of the alumina solubility in the NaF- AlF_3 system involved the simultaneous solution of all possible equilibria in the bath coupled with element balances, similar to the software program SOLGASMIX. Such an analysis identified the dominant complex oxyfluoride solutes in the system and provided a quantitative evaluation for their stabilities. With these new values added to the thermodynamic data bank, the solubilities of other oxides in cryolite could be analyzed. Thus new papers by other authors on the solubilities of $\text{NiO}/\text{NiAl}_2\text{O}_4$, $\text{FeO}/\text{FeAl}_2\text{O}_4$, and

TiO₂ in cryolite were interpreted differently than the original authors to identify the solute ions and provide quantitative data for their stabilities in these systems: Na₂NiF₄, Na₄NiF₆, Na₂FeF₄, Na₄FeF₆, FeF₂, Na₄TiO₂F₄, NaTiOF₃, and Na₃TiO₃F. Again the stereochemistry for these solutes was described by simple geometric (octahedral and tetrahedral) arrangements of large anions about a smaller cation. In the case of the solubilities for the oxides of iron and nickel, the data and explanations would be useful in understanding the dissolution of the proposed Fe,Ni oxide composite for the oxygen-evolving inert anode. The research on this project has demonstrated the correct method to analyze the complicated equilibria in such a complex solution, and exposed as inadequate (incorrect) the existing (log-log) method of treating only one or two equilibria in isolation.

In response to a high priority from the 2002 Aluminum Roadmapping report, two sensors were proposed to measure the dissolved alumina content in cryolite. Because of the high cost of the necessary BN hardware, however, confirming experiments were not undertaken. Hole-in-tube type sensors were designed and demonstrated for the measurement of Mg activity/concentration in binary Al-Mg melts and for Li activity/concentration in binary Al-Li melts. In each case, these probes provided accurate and reproducible data over the commercial ranges of temperature and composition. The probes were tested and performed well in industrial shop conditions, and the sensors are considered suitable for industrial commercialization and in-line service at this time.

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Project Objectives:

This project entitled "Development of a Novel Non-Consumable Anode for Electrowinning Primary Aluminum", was initiated on October 1, 1999 with subcontractors Siemens-Westinghouse, Kaiser Aluminum and GRI/GTI. The principal goal of the project was to determine through theoretical considerations and from chemical and electrochemical laboratory studies the technical and economic feasibility for the substitution and retrofitting of an SOFC-type anode for today's carbon anode in a cell for electrowinning primary Al. However, as described in detail later in this report, solubility measurements made at OSU showed that no value of cryolite ratio can exist where the solubilities of the solid electrolyte components (zirconia and especially yttria) would be small relative to the alumina solubility. Therefore, the utilization of the proposed SOFC-type anode cannot be realized for any cell involving a cryolite-base solvent. Based on the failure to realize the original Project objectives, the roles of the original collaborating subcontractors became superfluous, and they were deleted from further participation and funding after the initial 18 months.

Following discussions with the Project Monitors, the project was redirected, starting April 1, 2001, to fundamental studies of cryolite chemistry and the development of robust probes to measure alumina concentration in undersaturated cryolite melts and to indicate specific alloying element concentrations in Al alloy melts. For the remaining 2.5 years of the project, all of the activities and finances were confined to the OSU laboratories of Professor Rapp. This recent research involved theoretical studies of the thermodynamic modeling of oxide solubilities for cryolite bath compositions relevant to the current Hall cell practice. Where solubility data were lacking or uncertain, new measurements were made. To assist in understanding cryolite melt chemistry, sensors were developed to measure and quantify the acid/base property of melts, and to correlate this factor to the cryolite ratio. This modeling provided a general procedure for understanding all oxide solubilities in cryolite baths, and for further clarification of the melt acid/base property and its measurement. The research has led to a software program and database for the general analysis of multi-component equilibria in cryolite melts for the industrial range of bath compositions and temperature. Specifically, the identities and stabilities for solutes for the oxides $\text{NiO/NiAl}_2\text{O}_4$, $\text{FeO/FeAl}_2\text{O}_4$, and TiO_2 were determined.

Likewise, the effects of the common cryolite additives LiF, CaF₂ and MgF₂ on the thermodynamic activities and the alumina solubility were established as a function of temperature. Two novel sensors were developed and successfully tested: 1. a sensor to measure the concentration (activity) of Mg in liquid Al-Mg alloys, and 2. A sensor to measure the concentration (activity) of lithium in Al-Li melts.

In the following text, the highlights of the research accomplished throughout this project are presented, in chronological order. Almost all of the detailed results of this research have been published in readily available open literature, and also previously provided as attached files in previous Quarterly and Annual reports for this project. Nevertheless, the most important results will be presented and interpreted in the text of this Final Report, while the cited publications are understood to contain all the details.

Studies of Cryolite Chemistry

Thermodynamic Activity Probes

In order to quantify the acid-base property of the experimental cryolite melts, two electrochemical reference electrodes were developed, as depicted in Fig. 1. These thermodynamic activity probes for Al and Na had “hole-in-tube” configurations, and contained, respectively, either pure Al or a Sn-0.5 wt% Na alloy ($a_{Na} = 3.7 \times 10^{-6}$ for 1300K, as measured against an Al-0.1 wt% Na alloy as the reference) in the bottoms of the alumina tubes. The composition of the bath over the pure Al and the Na-Sn alloy in the alumina tubes was exactly the same as that for the bulk bath in the alumina or graphite crucible because of bath entry and mass transport through the holes (~ 1 mm diameter). Tungsten wires contacting the pure Al or the Na-Sn alloy served as the electrical leads for the reference probes. Another tungsten wire touching the bath in the alumina or graphite crucible was used as the working electrode for both reference probes. The lengths of these tungsten wires exposed to air were minimized by their sealed enclosure in alumina tubes, with only the tips of the wires touching the bath or the liquid metal. For any given state of the molten salt, this dual sensor arrangement provided values for the Al activity and for the Na activity in the cryolite-base melt. For the NaF-AlF₃-Al₂O₃ ternary system, these activity values for Al and Na were then converted by calculation to provide values for the thermodynamic activities for the NaF and AlF₃ components in these melts. For ternary NaF-AlF₃-Al₂O₃ melts, the following reaction was considered:

for which we have

$$\Delta G^0(2) = 3\Delta G_f^0(NaF) - \Delta G_f^0(AlF_3) = RT \ln \frac{a_{Na}^3 a_{AlF_3}}{a_{NaF}^3 a_{Al}} \quad [2]$$

$$\ln a_{AlF_3} - 3 \ln a_{NaF} = \frac{3\Delta G_f^0(NaF) - \Delta G_f^0(AlF_3)}{RT} - 3 \ln a_{Na} + \ln a_{Al} \quad [3]$$

Thermodynamic data in JANAF tables were used to calculate the first term on the right side of Eq. [3], and the expressions of Sterten and Maeland⁽²⁾ for the activities of NaF and AlF₃ as a function of cryolite ratio r in Al₂O₃-saturated NaF-AlF₃ melt were used to evaluate the two terms on the left side of Eq. [3]. With known values

Fig. 1 Schematic illustration of the two reference probes to monitor the melt chemistry (1).

of activities for Al and Na obtained from measurements by the two thermodynamic activity probes, the equilibrium cryolite ratio r value was calculated using the equation:

$$\left\{ \frac{F}{RT} \left[1.361 \ln \left(\frac{3+r}{0.3+0.9r} \right) - 1.493 \right] - 3.029 \right\} - 3 \left\{ \frac{F}{RT} [3.63 \ln r + 0.454 \ln(3+r) - 4.084 \ln(0.3+0.9r) - 0.423] - 0.106 \right\} = -11.225 - 3 \ln a_{Na} + \ln a_{Al} \quad [4]$$

It is important to point out that the development of these electrochemical reference probes to indicate quantitatively the acid-base property of a cryolite melt, and indeed the definitions of “bath basicity = $-\log a_{NaF}$ ” and “bath acidity = $\log a_{AlF_3}$ ” are significant and novel contributions of this research project. These quantitative parameters are readily correlated to the more empirical designation of cryolite ratio $r = \text{mol NaF} / \text{mol AlF}_3$ using Eqs. [1 – 4], as is demonstrated in the plot of Fig. 2. The validity and importance of these concepts were presented in the publication by Y. Zhang and R.A. Rapp, “Complex Cryolite Chemistry” in *Aluminum Now*, **3**, May/June, (2001) p. 31. A paper by R. A. Rapp, “Some Generalities in the Analyses of Equilibria in Ionic Solutions”, The 2000 TMS Institute of Metals Lecture, *Metall. Mater. Trans.* **31A**, (2000) pp. 2105-2118, explained the importance of electrochemical reference probes and thermodynamically defined acid-base parameters in analyzing the solubilities of many oxides in a variety of ionic solutions.

Cryolite salt chemistry

Fig. 2 Salt basicity for cryolite base melts vs. salt composition at 1200 K

Solubility Measurements of Al_2O_3 , ZrO_2 and Y_2O_3 in Na_3AlF_6 -NaF- CaF_2 -LiF Melts

The purpose of these experiments was to ascertain whether the acid-base property of a cryolite-base melt could be manipulated to provide adequate alumina solubility and (at the same time) minimal solubilities for the required SOFC components ZrO_2 and Y_2O_3 . Twelve experiments were conducted involving measurements of solubilities for Al_2O_3 , ZrO_2 and Y_2O_3 in Na_3AlF_6 -NaF- CaF_2 -LiF melts. Three different compositions of electrolytes were tested to relate the oxide solubility to the melt chemistry (basicity or acidity). The tested electrolytes and experimental conditions for the oxide solubility measurements are listed in Table 1.

For each experiment, 50 or 60 g of the salt mixture was charged into an alumina crucible with ~5 g of alumina powder plus a number of segments of high purity alumina tubes, or else with a similar amount of this alumina source, along with ~10 g of porous disks of ZrO_2 - Y_2O_3 mixture (1:1 by weight). The porous disks were prepared by sintering pressed powder mixtures of the two oxides at 1500°C for 8 hours. The crucible with its contents was placed in the center of a vertical furnace, and dried overnight before being heated to the desired test temperature. To stir the melt, air bubbles were introduced to the melt at a rate of 50-60 bubbles a minute. The bubbling was stopped at least 3 hours before sampling. Salt samples were taken by quenching a small amount of liquid salt onto a cool alumina rod, and the samples were then ground. The thermodynamic activities of Al and Na were measured to quantify the melt basicity for each solubility measurement. Inductively coupled plasma emission analyses (ICPE) were

employed to determine the solubilities of Al_2O_3 , ZrO_2 and Y_2O_3 in the fluoride melts, and neutron activation analyses (NAA) were also used for the Al_2O_3 solubility measurements.

Table 1 Tested electrolytes and experimental conditions for solubility measurements

Electrolyte No.	Composition wt %	Estimated liquidus, °C	Test temperature °C	Oxide(s) charged
1	65 Na_3AlF_6 - 25 NaF- 5 CaF_2 - 5 LiF	895-900	960	Al_2O_3 only
				$\text{Al}_2\text{O}_3 + \text{ZrO}_2/\text{Y}_2\text{O}_3$
			927	Al_2O_3 only
				$\text{Al}_2\text{O}_3 + \text{ZrO}_2/\text{Y}_2\text{O}_3$
2	75 Na_3AlF_6 - 15 NaF- 5 CaF_2 - 5 LiF	915-920	960	Al_2O_3 only
				$\text{Al}_2\text{O}_3 + \text{ZrO}_2/\text{Y}_2\text{O}_3$
			927	Al_2O_3 only
				$\text{Al}_2\text{O}_3 + \text{ZrO}_2/\text{Y}_2\text{O}_3$
3	85 Na_3AlF_6 - 5 NaF- 5 CaF_2 - 5 LiF	930-935	960	Al_2O_3 only
				$\text{Al}_2\text{O}_3 + \text{ZrO}_2/\text{Y}_2\text{O}_3$
			940	Al_2O_3 only
				$\text{Al}_2\text{O}_3 + \text{ZrO}_2/\text{Y}_2\text{O}_3$

For both analysis techniques, calibration was first made with standard samples. The total contents for Al, or for Al, Zr and Y in the salt samples were then determined, and, finally, the solubilities of the oxides were calculated. Table 2 lists the Al_2O_3 solubility data obtained from NAA results, while Table 3 shows the solubility values for Al_2O_3 , ZrO_2 and Y_2O_3 derived from ICPE analyses. In Tables 2 and 3, the absolute values for Al_2O_3 solubility determined from the two analysis techniques are somewhat different, but the trend is the same. When only Al_2O_3 was dissolved, the oxide exhibited the highest solubility in the bath of 75 Na_3AlF_6 -15 NaF-5 CaF_2 -5 wt% LiF. When the three oxides were charged at the same time, the available Y_2O_3 was almost totally dissolved in the melt of 85 Na_3AlF_6 -5 NaF-5 CaF_2 -5 wt% LiF, and Y_2O_3 had a very high solubility in the fused salt of 75 Na_3AlF_6 -15 NaF-5 CaF_2 -5 wt% LiF. Upon the excessive dissolution of ZrO_2 and Y_2O_3 , almost no Al_2O_3 solubility was detected for either melt. This acidic dissolution of Y_2O_3 is described by the reaction:

Table 2 Al_2O_3 solubility data obtained from NAA analysis results

Electrolyte composition wt %	Test temperature °C	Al_2O_3 solubility wt %	
		Charged with Al_2O_3 only	Charged with $\text{Al}_2\text{O}_3 + \text{ZrO}_2/\text{Y}_2\text{O}_3$
65 Na_3AlF_6 -25NaF - 5 CaF_2 -5LiF	960	6.19	~0
	927	2.79	~0
75 Na_3AlF_6 -15NaF - 5 CaF_2 -5LiF	960	7.21	~ 0
	927	4.08	~ 0
85 Na_3AlF_6 -5NaF - 5 CaF_2 -5LiF	960	6.36	~ 0
	940	3.68	~ 0

Table 3 Solubilities of three oxides derived from plasma emission analysis results

Electrolyte composition wt %	Test temperature °C	Charged with Al ₂ O ₃ only	Charged with Al ₂ O ₃ + ZrO ₂ /Y ₂ O ₃		
		solubility for Al ₂ O ₃ wt%	For Al ₂ O ₃ wt%	For ZrO ₂ wt%	For Y ₂ O ₃ wt%
65Na ₃ AlF ₆ -25NaF - 5CaF ₂ -5LiF	960	6.37	~0	0.20	6.35
	927	4.35	~0	0.14	5.71
75Na ₃ AlF ₆ -15NaF - 5CaF ₂ -5LiF	960	8.22	1.06	0.28	6.86
	927	4.53	~ 0	0.16	6.09
85Na ₃ AlF ₆ -5NaF - 5CaF ₂ -5LiF	960	6.67	~ 0	0.28	8.38
	940	4.45	~ 0	0.19	8.13

This reaction of Y₂O₃ with AlF₃ in the cryolite has minimized the dissolution of Al₂O₃. Because AlF₃ is an intrinsic component of cryolite, this reaction leading to excessive Y₂O₃ dissolution, as well as minimal Al₂O₃ solubility, cannot be avoided for any composition (acid-base property) of cryolite-base bath.

Table 4 shows the salt basicity and acidity values which were monitored with the two probes providing the independent measurements of the thermodynamic activities for Na and Al. The melts became a little more basic when the three oxides were charged at the same time. This may be attributed to the acidic dissolution reaction of Y₂O₃ which consumed AlF₃. Table 4 shows only minor differences in basicity for large composition differences, evidence for the "buffering" action of forming several oxyfluoride anions.

These results clearly show that these three basic melt compositions have adequate solubilities for alumina in the absence of ZrO₂ and Y₂O₃, but when all three oxides are present, the ZrO₂ solubility is too high (about 0.2 wt%), and the Y₂O₃ has an even higher solubility (several wt%). In the presence of the solid electrolyte oxides, the alumina solubility drops to essentially zero. Therefore, we can conclude that there is no "chemical window of opportunity" for application of the proposed SOFC-type anode

Table 4 Recorded salt chemistry for the oxide solubility measurement experiments

Electrolyte composition wt %	Test temperature °C	Charged with Al ₂ O ₃ only		Charged with Al ₂ O ₃ + ZrO ₂ /Y ₂ O ₃	
65Na ₃ AlF ₆ -25NaF- 5CaF ₂ -5LiF	960	0.567	3.87 x 10 ⁻⁵	0.595	3.36 x 10 ⁻⁵
	927	0.560	3.76 x 10 ⁻⁵	0.586	3.28 x 10 ⁻⁵
75Na ₃ AlF ₆ -15NaF- 5CaF ₂ -5LiF	960	0.462	9.49 x 10 ⁻⁵	0.472	8.87 x 10 ⁻⁵
	927	0.460	9.14 x 10 ⁻⁵	0.474	8.37 x 10 ⁻⁵
85Na ₃ AlF ₆ -5NaF- 5CaF ₂ -5LiF	960	0.365	2.26 x 10 ⁻⁴	0.431	1.37 x 10 ⁻⁴
	940	0.362	2.20 x 10 ⁻⁴	0.448	1.19 x 10 ⁻⁴

in a cryolite-base fluoride melt. For this reason, the project was redirected in April 2001 to involve only fundamental studies of cryolite melt thermodynamics and chemistry, including

a successful effort for modeling and interpreting the solubility of any oxide in cryolite melts, even those containing the additive components MgF_2 , CaF_2 , and Li.

Based on these solubility results, the impossibility to use zirconia-yttria solid electrolyte tubes in contact with cryolite to electrochemically titrate oxide ions from the bath and to effect the oxidation of reformed natural gas internal to these "inert anodes" was painfully realized. These detailed arguments were published by Yunshu Zhang and Robert A. Rapp, "Fate of the SOFC-Type Inert Anode for Production of Primary Aluminum", *Light Metals* 2002, TMS, pp.463-8.

Because of the unfavorable solubilities for the SOFC tubes, the testing of the experimental electrolysis cell shown schematically in Fig. 3 was not initiated. However, the intention of that study was to demonstrate that indeed dissolved oxide ions could be driven electrically from the cryolite, through the SOFC tube, to react on the metallic anode surface to effect the oxidation of hydrogen passing internally. For these proposed experiments, the use of hydrogen was simpler than the more complicated use of reformed methane, the ultimately intended reductant for industrial application. In principal, a comparison of the hydrogen to water ratio of the gas exiting the anode to that calculated by using Faraday's Law applied to the cell current could confirm the validity of the concept. Our collaborating industry Siemens-Westinghouse (S-W), the world's leading developer of SOFC equipment spent their efforts to fabricate the necessary nickel porous layer on the inside of closed-end SOFC tubes. In today's S-W SOFC technology, the porous Ni anode is external to the tubes, although much earlier, S-W had used an internal porous Ni geometry. At the end of the initial 18 month period, S-W was able to supply one appropriate closed-end tube. However, because of the solubility results, the experiment illustrated in Fig. 3 was not attempted. The role of our collaborator GRI/GTI on the project at that time was to evaluate the relative cost of electrical energy and of natural gas to understand better the potential savings promised by the ultimate application of the SOFC anode in electrorefining primary aluminum. They also were involved with an analysis of the specific sort of methane reforming that would be most favorable for cell operation. The results of the energy cost considerations and the reforming reactions were reported in our DOE Quarterly reports. However, during that particular time period, 1999-2001, energy costs and supplies were unusually uncertain, so this information probably lacks importance generally, and considerations of the reforming reaction were no longer required when the SOFC concept was shown to be infeasible.

Fig. 3 Schematic drawing of the arrangement for electrolysis experiments

An Alternate Fused Electrolyte/Solvent Suited to the SOFC-Type Anode for Electrowinning Aluminum

Unlike cryolite-base melts where the acid-base range is greatly restricted by the formation of complex oxyfluoride anions, oxides dissolve in fused sodium sulfate melts to

form uncomplexed oxide anions, and such melts enjoy a wide acid-base range. Extensive previous measurements of oxide solubilities in fused sodium sulfate at 1200K show that in a very basic melt (where NaAlO_2 becomes stable) the solubility of alumina is about 10 mol %, while the solubilities for zirconia and yttria would be very much lower. Therefore, at a temperature suited to use of the YSZ electrolyte, the chemical conditions required for the SOFC-type inert anode should be satisfied.

As detailed in Fig. 4, a significant difference in basicity exists between the solubility minima for Al_2O_3 and CeO_2 in fused Na_2SO_4 at 1200K. (Actually, the solubility for ZrO_2 in fused Na_2SO_4 has not been determined, but its plot must lie quite close to that for CeO_2 .) Indeed, the solubility of Y_2O_3 in pure fused Na_2SO_4 was not measured directly, but the plot is known from related measurements in a sulfate-vanadate melt. (According to Fig. 4, if the basicity of a Na_2SO_4 melt could be fixed at the equilibrium between Al_2O_3 and NaAlO_2 (a value of $-\log a_{\text{Na}_2\text{O}}$ of about 8.7), then at 1200K the alumina solubility would be about 8 mole% while the CeO_2 (or ZrO_2) solubility would be only about 0.1 mole%, and the Y_2O_3 solubility about 0.006 mole%. Such large

Fig. 4 Measured solubilities at 1200K for CeO_2 , Y_2O_3 and Al_2O_3 in fused Na_2SO_4

differences (and low magnitudes for CeO_2 and Y_2O_3) could be sufficient to permit the use of zirconia-yttria electrolyte tubes for the SOFC-type anode if Na_2SO_4 could be used as the fused salt solvent (instead of cryolite) for a cell electrowinning primary aluminum.

Despite the apparent promise for using the SOFC anode in fused Na_2SO_4 arising from Fig. 4, the Na-Al-S-O phase stability diagram shown in Fig. 5 indicates that liquid Al (representing a very low oxygen activity) is not compatible with fused sodium sulfate, but should react to form a sodium-aluminum sulfide. However, a preliminary experiment

immersing a liquid Al droplet in fused Na_2SO_4 for 24 hours at 900C indicated only very slow reaction between the Al and sodium sulfate resulting in a hardly visible product film. Zhang has also previously held YSZ electrolyte tubes in fused Na_2SO_4 and performed coulometric titration (as needed for the anode application) for days without severe attack of these tubes. Therefore, the application of a SOFC-type inert anode might be realized upon a change in the solvent for alumina from fused cryolite to sodium sulfate. At the moment, with much confirming experimentation yet needed, there seems to be no “chemical showstopper”, but significant promise, in the use of a Na_2SO_4 fused electrolyte in combination with the SOFC-type electrode for electrowinning primary aluminum. A temperature of about 900-950C is needed to ensure that the zirconia electrolyte tubes have sufficient ionic conductivity.

Fig. 5 Na-Al-S-O phase stability diagram at 1200K

One must then ask why Hall, Heroult and their successors in the Al industry did not think to use the Na_2SO_4 solvent instead of cryolite, and the answer is obvious. The anodes available to the Al industry (then and now) have been either a consumable carbon anode (evolving CO_2), or (in the laboratory today) an oxygen-evolving cermet anode. In the latter case, if such an “inert” anode (operating at high oxidation potentials) were used for a Na_2SO_4 melt, SO_2 and SO_3 would be the primary gaseous products evolved, an impossible situation. For the use of a carbon anode, the CO_2 and CO gases evolved could react with the sulfate bath, perhaps forming CS_2 or SO_2 or some other undesirable product. However, if the proposed SOFC anode were used in a sulfate melt, operating at a much more reducing potential than that for oxygen evolution, then oxide ions could be electrically driven from the bath through the solid electrolyte tubes to the internal anode without any SO_2 or SO_3 evolution. In fact, the internal Ni anode, supplied with a fuel such as reformed methane, would make no physical contact with the fused salt bath. In other words, such a change to the SOFC-type anode would permit such a change in the salt bath solvent, a prospect previously unavailable.

Then one must ask whether the potential substitution of a fused sodium sulfate melt (for cryolite) would introduce any new or different problems, and several matters arise for consideration. First, the sulfate at about 950°C must exhibit about the same electrical conductivity (or higher) and a similar density (or lower) as the fused cryolite composition. These conditions are satisfied. At 1200 K (927°C), the density of fused Na_2SO_4 is 2.05 g/cm³, and its conductivity is 2.40 S/cm. For 1000°C, the density of $\text{Na}_3\text{AlF}_6\text{-AlF}_3$ (CR=2.4) is 2.04 g/cm³; its conductivity is 2.60 S/cm, and its viscosity is 2.5×10^{-3} Ns/m². The ultimate purpose for considering fused sulfates instead of fused fluoride (cryolite) as the solvent for alumina in an Al electrowinning cell is that the sulfate chemistry seems better suited (greater acid/base variability) to differentiate between the solubility magnitudes for alumina and YSZ, thereby supporting the use of the SOFC-type anode.

A Modular Vertical SOFC-Type Anode

The original project proposal and the referenced patents^(3,4) have suggested the introduction of a multiplicity of tubular horizontal SOFC-type anodes retrofitted into the HHC for electrowinning primary aluminum. In brief, an electrocatalytic anode (e.g. porous nickel) would be separated from the molten salt electrolyte (solvent for alumina) by a thin dense tube of an oxygen-ion conducting solid electrolyte, e.g. YSZ. A multiplicity of such horizontal tubes comprised each anode assembly would be manifolded to an incoming fuel gas (e.g. reformed natural gas) with the provision to collect, reprocess, and dispose of the product gases resulting from the electrochemical oxidation of the fuel. A DC voltage applied between the internal metallic anode (positive polarity) and the negative cathode (either the liquid Al pad or else a wettable inert cathode) would electrically drive the oxide ions dissolved in the fused salt solvent through the solid electrolyte tubes. At the internal anode, the electrochemical combustion/oxidation of the fuel would occur, and at the cathode, liquid Al would be electrodeposited. Significant reductions in processing costs, in electrical energy consumption, and in the release of polluting greenhouse gases would be expected if use of such an SOFC anode were feasible. The preceding discussion explains that the solid YSZ tubes would suffer excessive dissolution into any cryolite-base fused fluoride salt, but the current section suggests a suitable chemical compatibility between YSZ and Na_2SO_4 .

The previously suggested cell geometry of a multiplicity of submerged horizontal tubes (positioned parallel to the liquid Al pad) represents an arrangement which would be both difficult to fabricate and highly sensitive to a flaw or fracture which would disable a significant and expensive part of a cell and disrupt cell operation. For example, if about 10 such tubes were connected as a unit to a common inlet fuel manifold and to a common exit manifold, then even a small hole or crack in any part of the submerged system would require disruptive replacement of the entire expensive structure, probably with little hope for refurbishment. (The YSZ solid electrolyte has a high thermal expansion coefficient and low fracture toughness, so that it is particularly susceptible to thermal and mechanical shocks, especially for complex geometries.)

Likewise, the active area for a tubular “horizontal anode” could not exceed that for the Al pad (in common with the present carbon anode). The maximum rate of Al production is proportional to the anode area, since a rate-limiting anodic current density (multiplied by the anode area) decides the maximum cell current. What is needed to replace the suggested multiple “horizontal” tubes parallel to the Al pad is some sort of simpler anode geometry in a modular unit, so that any flaw or failure is less likely, and such a flaw would not lead to such an expensive and disruptive replacement. In addition, an alternative cell

geometry involving a modular “vertical” anode, in combination with a “vertical” inert cathode, could offer the advantage to greatly increase the active anode area and therefore the maximum Al production rate.

Fig. 6 Schematic drawing of the SOFC-type anode module.

Figure 6 is a schematic drawing of the SOFC-type anode module proposed to meet these requirements. A closed-end tube of a suitable solid electrolyte, e.g. a thin dense YSZ tube, has its internal surface coated with a porous, electrocatalytic anode material (e.g. Ni-Y₂O₃ as used in the SOFC today). Inside this solid electrolyte tube, a metal pipe of smaller diameter supplies a flow of fuel, e.g. reformed natural gas, to the inside bottom of the closed-end solid electrolyte tube, while at the same time serving to conduct the electrical current to the metallic coated anode. A low-resistance connection can be made between the central fuel pipe and the coated anode by provision of a mutually contacting metal screen (perhaps made of Cu). Above the cell, both the fuel pipe and the annulus between the fuel pipe and the solid electrolyte tube are fitted via gas-tight connectors to manifolds. The fuel gas is delivered to the inside closed-end of the solid electrolyte tube, and is thereafter electrochemically oxidized at the anode surface upon its return flow in the annulus, and ultimately collected in the exit-gas manifold. (The exothermic oxidation of the fuel in the annulus, and the countercurrent flow of the inlet fuel and the exiting product gas, provide an advantageous heat exchange to warm the fuel and to cool the combustion product gases. The I²R Joule heating of the central fuel rod would also contribute to the heat exchange.) The

connectors necessary to supply the fuel and collect the annulus gas can be fabricated from existing commercial hardware.

The retrofit of such “vertical” anode modules, as illustrated in Fig. 7, offers definite advantages over the “horizontal” multiple tube arrangement. First, if the module should crack, leak or break, its fuel supply could be interrupted by some pressure-sensitive switch, and the single module might be withdrawn and replaced without the loss of a much larger and more expensive arrangement, and without interrupting the production of Al. Secondly, as explained in the following paragraphs, a geometric arrangement of such vertical anode modules in a cell could offer the further advantage of greatly increasing the productivity of the primary Al electrowinning cell. For today’s HHC, the carbon anodes provide an anode area equal to about 0.85 of the Al pad cathode area.

Figure 7 provides a schematic top view for one possible (hexagonal) arrangement of the SOFC-type anode modules retrofitted above a HHC hearth. (To simplify the illustration, the manifolds and connectors necessary for the fuel and combustion product gases are not shown.) A hexagonal array is known to provide close-packing in a plane, along with the largest vacant spaces for feeding (if the inert cathodes are provided in only some fraction of the hexagons). These large spaces for feeding alumina to the cell could also be useful for the removal and replacement of some failed anode without interrupting cell operation. For example, a tube of 6 cm diameter can surely be extracted through a hole with 8 cm diameter. Table 5 provides some sample calculations for the hexagonal anode arrangement of Fig. 7. The diagonal spacing S (chosen here as 8 cm) represents the summation of the inert cathode diameter (if cylindrical) plus two times the nearest anode to cathode spacing (ACS). This latter term is paramount in establishing the IR drop contribution to the applied cell voltage, and therefore contributes importantly to the electrical cost of producing Al. Other dimensions are defined in Fig. 7; N is the number of anodes and NA is the total anode area per square meter of Al pad for immersion depths L of 20 and 40 cm.

Fig. 7 Proposed Cell Geometry for Vertical Modular SOFC-Type Anodes in Al Electrowinning Cell

Table 5: Calculated Values for Total Anode Area NA per Unit Area of Al Pad; $S = 8$ cm in Hexagonal Array for immersion depths L of 20 and 40 cm.

D (m)	X (m)	(X - D)	N	$NA(m^2)$ (L = 0.2m)	$NA(m^2)$ (L = 0.4m)
0.03	0.055	0.025	220	4.46	8.60
0.04	0.06	0.02	185	5.11	9.76
0.05	0.065	0.015	158	5.58	10.5
0.06	0.07	0.01	136	5.90	11.0
0.07	0.075	0.005	119	6.15	11.4

Some of the calculated results presented in Table 5 for a hexagonal array are quite unexpected. First, such an arrangement of anodes involves very large numbers of tubes/m² of Al pad. When one considers the required tube connections and manifolding, such dense tube stacking could probably not be handled. The second surprise is the comparatively weak dependence of the total anode area NA (for either 20 cm or 40 cm immersion depth) on the tube diameter or number of tubes. (In the interest of minimal expense and easier connections, fewer but bigger tubes would be preferred.) The third favorable surprise is the large values (between 4.5 and 11) for the active anode area/mm² of Al pad even for immersion depths of only 20 or 40 cm.; these far exceed the value of 0.85 for today's HHC. Again, the large volume available for feeding the cell might be used for the exchange of anodes without excessive disturbance of the cell operation. Interestingly, this hexagonal array offers various arrangements providing different ratios of cathodes to feed-ports: 1:1 (as drawn), 2:1, 1:2, etc. so that the arrangement of anodes, cathodes, and feed-ports could be chosen to optimize the process operation. The illustrated cell arrangement assumes that a wettable, electronically-conducting, "inert" cathode which is chemically resistant to both liquid Al and to the fused salt solvent can be fabricated to any desired shape to provide a vertical surface for the electrodeposition of liquid Al. (The inert cathode is supported by the hearth floor, making electrical contact with the surrounding Al pad, and therefore sharing its electrical potential.) Liquid Al electroplated onto the inert cathode surface flows down and adds to the Al pad that is periodically tapped. Such inert cathodes are being developed today and are considered to be feasible, although a fused Na₂SO₄ solvent would require a separate development.

The vertical modular anode arrangement of Fig. 7 shows the possibility to increase the ratio of active anodic area to Al pad area (and therefore the Al production rate) depending upon the submerged depth of the electrodes. The maximum realizable depth for the vertical anodes would probably be decided by the ability to supply (feed) alumina (from above) for the entire tube length. To support this important "feeding" step, alternate squares of the anode arrangement of Fig. 7 have not been provisioned with a vertical inert cathode, but rather would serve as feed-ports for alumina. This arrangement would also be useful in distancing the alumina feed from the Al deposition site, thereby minimizing contamination of the Al. (As a result of local heating at the anode surfaces, convection in the fused salt solvent should cause flow of the salt up the anode surfaces and down in the volumes between the anodes.) The dissolution of alumina and the transport of the dissolved oxide ions to the various anode tube surfaces should be less difficult than in today's HHC where a lateral transport distance of about a half meter is required.

Concluding Remarks for the Alternate Fused Electrolyte/Solvent

The SOFC-type anode in electrowinning Al cannot be used for a cryolite-base fluoride solvent bath because YSZ is highly soluble for any value of melt acidity. However, the chemical compatibility of YSZ with basic fused Na₂SO₄ is known to be much more favorable. However, liquid Al is not thermodynamically stable in contact with fused Na₂SO₄, and a fused (Na,Al)S film should be formed. The consequences of this reaction have not been studied experimentally.

To realize the potential benefits for the SOFC-type anode in electrowinning Al, use of a Na₂SO₄-base electrolyte in combination with modular vertical tubular anodes, supported by vertical inert cathodes, perhaps in a hexagonal array, offers significant promise to increase the Al production rate compared to the HHC.

Measurement and Interpretation of Oxide Solubilities in NaF-AlF₃ Melts at 1300K:

Alumina (Al₂O₃)

Modeling of Al₂O₃ Solubility in Pure Cryolite Melts with a Composition Range of $1.5 \leq r \leq 3$ for 1300K

The experimentally well established solubility⁵ of Al₂O₃ in cryolite was modeled on this project over the range of acidic to neutral cryolite base melts with $1.5 \leq r \leq 3.0$ (r is the molar ratio of NaF/AlF₃). A new approach, using element balances, similar to the software program SOLGASMIX, considers element balances for the reactants and products. This method avoids any confusion in the definition of compound compositions, and provides equilibrium constants which can be compared with existing literature values and be entered into existing data banks for computer analyses.

For a preliminary attempt based on existing literature, Na₂Al₂O₆F₆ (called A), Na₂Al₂O₂F₄ (N) and Na₄Al₂O₂F₆ (B) were assumed as acidic, neutral and basic solutes of Al₂O₃ in cryolite-base melts, respectively. For the non-oxygen containing Al-F complex anions, Na₃AlF₆ (named C), Na₂AlF₅ (D) and NaAlF₄ (E) were considered as the solutes, and some NaF (but no AlF₃) could remain in the melts. The molar fraction for each solute is related to its equilibrium constant and activity data for NaF and AlF₃. If X_1 and X_2 stand for the initial molar fractions of NaF and AlF₃, X_3 for dissolved Al₂O₃, then n_t is the total moles of all the solutes in the melts, so we can write the expressions

$$([A]+2[N]+2[B])n_t = 3X_3$$

$$(2[A]+2[N]+4[B]+3[C]+2[D]+[E]+[NaF])n_t = X_1$$

$$(2[A]+2[N]+2[B]+[C]+[D]+[E])n_t = X_2+2X_3$$

$$(6[A]+4[N]+6[B]+6[C]+5[D]+4[E]+[NaF])n_t = X_1+3X_2$$

for oxygen, sodium, aluminum and fluorine elemental balances, respectively. The following relation indicates that the sum of molar fractions for all the solutes must be unity:

$$[A]+[N]+[B]+[C]+[D]+[E]+[NaF] = 1$$

This set of equations was solved for different compositions (basicity) of melts.

A computer software program was used to evaluate all the unknowns such that they should provide a minimum overall error for all the relations. This new approach has led to an even better agreement between the modeled result and the experimentally determined alumina solubility data. The maximum deviation for all the equations with the melt compositions of $1.5 \leq r \leq 3.0$ is as low as 3%. A comparison of the experimentally determined alumina solubility in the NaF-AlF₃ system is shown in Fig. 8. In fact, the lines from the experimental measurements and data points from the modeling calculations for

alumina solubility overlap each other. The other three lines in Fig. 8 indicate the calculated dissolved alumina contents contributed by the acidic, neutral and basic solutes, $\text{Na}_2\text{Al}_2\text{OF}_6$, $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ and $\text{Na}_4\text{Al}_2\text{O}_2\text{F}_6$, respectively.

Fig. 8. Comparison of solubility of Al_2O_3 in NaF-AlF_3 system at 1300K as a function of melt basicity from experiment (top line) and data points calculated from the present model.

Figure 9 presents the calculated concentrations for all the suggested solutes in this cryolite composition range from the present model. In a very acidic melt, NaAlF_4 and $\text{Na}_2\text{Al}_2\text{OF}_6$ have higher contents while in the neutral melt $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ is the dominant solute. This work has led to the publication: Yunshu Zhang, Sanjeev Gupta, Yogesh Sahai, and Robert A. Rapp, "Modeling of the Solubility of Alumina in the NaF-AlF_3 System at 1300K", *Metallurgical and Materials Transactions B*, **33B**, (2002), pp. 315-19.

Fig. 9. Calculated concentrations of all the solutes for the Al_2O_3 -saturated cryolite melts at 1300K

Al_2O_3 Solubility Measurements in Basic Cryolite Melts and Modeling of Al_2O_3 Solubility in Cryolite Melts with a Wide Composition Range of $1.5 \leq r \leq 12.5$

The several existing studies for alumina solubility in very basic cryolite melts have provided scattered data, probably resulting from questionable experimentation. Likewise, the literature has debated whether additional oxyfluoride species are needed to describe very basic melts. To provide a good knowledge of the Al_2O_3 solubility over a wider composition range of cryolite melts, the solubility of Al_2O_3 was measured in basic cryolite melts in the composition range of $3 \leq r \leq 12.5$. α - Al_2O_3 powder and rod segments were used for the solubility measurements in melts with $r = 3$ and 3.5 while in the other melts, β - Al_2O_3 powder was used as the Al_2O_3 source because β - Al_2O_3 , not α - Al_2O_3 , is stable in this basic composition range. Large size (> 0.1 mm in diameter) powders for both types of Al_2O_3 were chosen so that no time for settling was needed before sampling. For each experiment, 30–35g Na_3AlF_6 -NaF salt was charged into an alumina crucible with an excess amount of Al_2O_3 powder. Air bubbles were introduced to stir the melt for 7–8 hours. The two activity probes for Al and Na were again used to monitor the melt chemistry. Samples were taken by quenching a small amount of salt onto an alumina rod. The salt samples were analyzed by inductively coupled plasma emission (ICPE) for total Al contents, and the Al_2O_3 solubility was calculated from the analytical results. The measured solubility results are shown in Table 6, along with the recorded melt chemistry. Each datum is the average of results from two separate experiments.

Table 6 Measured Al_2O_3 solubility data in basic cryolite melts at 1300K

Initial cryolite ratio r	Equil. cryolite ratio r	Melt chemistry		Alumina solubility	
		a_{NaF}	a_{AlF_3}	wt %	mol %
3.0	2.98	0.353	4.43×10^{-4}	13.7	7.6
3.5	3.58	0.459	1.56×10^{-4}	14.7	8.0
4.0	4.10	0.536	8.64×10^{-5}	15.2	8.1
4.5	4.65	0.606	5.17×10^{-5}	15.1	7.9
5.0	5.25	0.664	3.25×10^{-5}	14.8	7.7
6.0	6.42	0.731	1.61×10^{-5}	14.5	7.3
8.0	8.44	0.802	7.11×10^{-6}	12.7	6.2
12.0	12.5	0.879	2.80×10^{-6}	10.2	4.8

The existence of the same solutes as discussed above from the modeling of Al_2O_3 solubility in $1.5 \leq r \leq 3$, and the same equilibrium constants, were assumed to describe this wider composition range of cryolite melts. Figure 10 compares modeled and experimental Al_2O_3 solubility for a wider composition range of $1.5 \leq r \leq 12.5$. From Figure 10, the maximum solubility of Al_2O_3 occurs near the cryolite ratio $r = 4$. In very acidic melts, acidic solute $\text{Na}_2\text{Al}_2\text{OF}_6$ is dominant, while in less acidic melts, the dominant solute is $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$, and in basic melts the basic solute $\text{Na}_4\text{Al}_2\text{O}_2\text{F}_6$ also becomes important. The calculated concentrations of all the solutes in the cryolite melts at 1300K are presented in Figure 11. The fit of the three-oxyfluoride species model to the experimental solubility data is virtually perfect over the entire composition range, indicating the sufficiency for only three complex oxyfluoride anions. The determination of the equilibrium constants and values for ΔG° of formation for the identified solutes permitted the prediction of solute distributions also for undersaturated solutions, a subject of debate in the literature. These new results were incorporated as part of a comprehensive publication: Yunshu Zhang, Xiaoxia Wu and Robert A. Rapp, "Solubility of Alumina in Cryolite Melts: Measurements and Modeling at 1300K", Metallurgical and Materials Transactions B, **34B**, (2003), 235-42.

An important contribution to the description and quantification of cryolite chemistry has resulted from the solubility studies on this project. Specifically, the quantity $\log a_{\text{NaF}}$ has been defined as a quantitative measure of melt basicity (and $\log a_{\text{AlF}_3}$ for melt acidity). For the first time, electrochemical sensors were used to measure these quantities which relate directly to the thermodynamic stabilities of the competing oxyfluoride complexes in cryolite melts. Today, the aluminum industry describes and characterizes the cryolite bath compositions in terms of the Cryolite Ratio (NaF/AlF_3 molar ratio) which has no fundamental significance, no direct relation to the solution thermodynamics, and no simple means for direct measurement for cryolite melts.

Fig. 10 Comparison of Al_2O_3 solubility in $\text{NaF}\text{-}\text{AlF}_3$ system at 1300K as a function of melt basicity from experiments (data points) and calculated from the present model (top line). The other three lines represent the individual Al_2O_3 solubility contributions by acidic ($\text{Na}_2\text{Al}_2\text{OF}_6$), neutral ($\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$) and basic ($\text{Na}_4\text{Al}_2\text{O}_2\text{F}_6$) solutes.

As a single most important conclusion reached by such analysis, because of its propensity to form several complex oxyfluoride ions, the cryolite-base melts are highly "buffered" in their acid-base behavior, similar to ammoniated aqueous solutions. Any tendency to change the acid-base property, e.g. by an increase or decrease in cryolite ratio, is largely compensated by a redistribution among the oxyfluoride complexes. The significance of the new considerations is further described in two publications: Y. Zhang and R. A. Rapp, "Complex" Cryolite Chemistry, *Aluminum Now*, May/June, 2001, p. 31; Y. Zhang and R. A. Rapp, "An Alternative Fused Electrolyte/Solvent Suited to the SOFC-Type Anode for Electrowinning Aluminum", *Light Metals 2002*, W. Schneider, Ed., TMS, Warrendale, PA, pp. 463-8.

Fig. 11 Calculated concentrations of all the solutes in cryolite melts at 1300K for the composition range of $1.5 \leq r \leq 12.5$ at 1300K

Stereochemistry of the Solutes

As presented in the publication: Yunshu Zhang, Xiaoxia Wu, and Robert A. Rapp, "Modeling of the Solubility of Alumina in the NaF-AlF₃ System at 1300K", *Metallurgical and Materials Transactions B*, **34B**, (2003), pp. 235-42, ionic solutes must be expected to satisfy certain logical geometric arrangements based on energy minimization. Specifically, to the extent possible, large anions (oxygen, fluorine) must be arranged symmetrically in a simple polyhedron surrounding smaller cations (Al, Ti, Fe, Ni). Tetrahedral and octahedral arrangements are especially favored energetically. More complex and asymmetric geometries will tend to dissociate into two or more simpler species. The stereochemistry for the three solutes of alumina in cryolite melts is described in Fig. 12. To our knowledge, the stereochemistry for these oxyfluoride solutes of alumina in cryolite has not been previously published.

Acidic solute:

(a)

Neutral solute:

(b)

Basic solute:

Fig. 12 Proposed 3-D geometries for oxyfluoride solutes $\text{Al}_2\text{OF}_6^{2-}$ (a), $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ (b) and $\text{Al}_2\text{O}_2\text{F}_6^{4-}$ (c).

NiO/NiAl₂O₄ and FeO/FeAl₂O₄ Solubilities

The previously reported solubility data experimentally determined by Jentoftsen, Lorentsen, Dewing, Haarberg and Thonstad⁽⁶⁾, were supplemented with new solubility data measured on this project. The resulting solubility data are given in Fig. 13.

The solubility of NiAl₂O₄ in Al₂O₃-saturated cryolite melts at 1300K was modeled thermodynamically in terms of two Ni-containing basic solutes Na₂NiF₄ and Na₄NiF₆ over a wide composition range of $2 \leq \text{cryolite ratio } r \leq 12$. (The previous authors⁽⁶⁾ were not able to correlate their data to specific solutes.) Equilibrium constants and values of ΔG^0 for the formation of these two solute species were thereby estimated. In the plot of Fig. 14 describing the NiO/NiAl₂O₄ solubility in dependence on the alumina concentration, an inflection point occurs at NiO/NiAl₂O₄ equilibrium. The specific location of this inflection point represents a measurement of the ΔG^0 for the formation of NiAl₂O₄ from the binary oxides.

Fig. 13 Comparison of the experimentally determined solubility of Ni from NiAl_2O_4 in Al_2O_3 -saturated cryolite melts at 1300K and that calculated from the present model. The solid line is the modeled NiAl_2O_4 solubility line, and the data points are experimentally determined values.

Jentoftsen, et al.⁽⁶⁾, also measured the solubilities of FeO and FeAl_2O_4 in cryolite melts and again, their data were supplemented by new measurements on this project. The resulting compilation of solubility data shown in Fig. 15 was modeled in terms of three Fe-containing solute complexes, as shown in Fig. 16. (Again, the previous authors⁽⁶⁾ could not interpret their results in terms of identifying solute species.) For the solubility values in the composition range of $3 \leq r \leq 8$, a model involving two Fe-containing solutes (Na_2FeF_4 and Na_4FeF_6) fits the experimental data well. This result is similar to the modeled result for the $\text{NiO}/\text{NiAl}_2\text{O}_4$ solubility. However, to interpret the solubility data for acid melts with $r \leq 3$, the solubility of FeAl_2O_4 requires the existence of a third (an acidic) solute FeF_2 . This three-solute model was used to interpret the dissolution behavior of $\text{FeO}/\text{FeAl}_2\text{O}_4$ in cryolite melts as a function of both dissolved Al_2O_3 content and cryolite ratio. Of course, this study was important in explaining the dissolution in cryolite of any Fe-Ni-base composite, as proposed for the oxygen-evolving inert anode. The stereochemistry for these solutes is given in Fig. 17. As seen there, the solutes identified comprise the simple geometries of a tetrahedron and an octahedron. The results of our research are in press: Yunshu Zhang and Robert A. Rapp, "Modeling of the Solubility of $\text{NiO}/\text{NiAl}_2\text{O}_4$ and $\text{FeO}/\text{FeAl}_2\text{O}_4$ in Cryolite Melts at 1300K", *Metallurgical and Materials Transactions B.*, **35B**, Feb. (2004). The following single reviewer's report was received: "The paper is a good paper, and it is very well written. This paper is of great importance for the new advances (inert anodes) for the aluminum industry. The paper should be published as fast as possible."

Fig. 14 Distributions of Ni-containing solutes as a function of dissolved Al_2O_3 content

Fig. 15 Comparison of experimental data for $FeAl_2O_4$ with theoretical model (line)

Fig. 16 Concentrations of Fe-containing solutes in Al_2O_3 -saturated cryolite melts at 1300K

Titanium Oxide (TiO_2)

The same Trondheim group, Jentoftsen, Lorentsen, Dewing, Haarberg and Thonstad⁽⁷⁾ also published an experimental study of the solubility of titanium oxide (TiO_2) in cryolite with an interpretation of solute identity using the simple log-log method. Figure 18 reproduces their experimentally determined data points, as well as a line 1 plotting their empirical function fitted to the entire data set, namely:

$$[\text{wt}\% \text{Ti}] = \alpha + \frac{\beta [\text{wt}\% \text{O}]^2}{[\text{wt}\% \text{O}] - \gamma}$$

where the constants α , β , and γ were determined by iteration to be 1.8, 0.092, and 1.7, respectively.

The specific (log-log) mode of thermodynamic modeling used by these authors⁽⁷⁾ involves an implicit assumption that one Ti solute species is dominant over all others for a specific range of analysis. If this assumption were valid, the dominant TiO_2 solute in a given concentration range could be identified by a specific dependence of this solute activity upon the activity of another solute in the solution, in this case the dissolved alumina activity. This procedure is commonly called the log-log method of thermodynamic modeling, and in principle, it leads to an identification of both the solute and its stability, i.e. its standard Gibbs formation energy if the underlying single solute assumption is met.

M = Ni or Fe

Fig. 17 3-D geometries (stereochemistry) of Na_2MF_4 and Na_4MF_6 solutes (M stands for Ni or Fe)

Fig. 18 Experimental data and fitted results for TiO₂ solubility in cryolite-alumina melts

More generally, the existence of several competitive solutes in a given composition range requires that a more complex equilibrium must be considered, whereby each of the coexisting solutes must satisfy a set of relevant equilibrium constants. Such a computer-assisted analysis by the current authors^[2] was certainly needed to identify the three competitive solutes responsible for alumina dissolution in NaF-AlF₃ melts: Na₂Al₂O₂F₆, Na₂Al₂O₂F₄, and Na₄Al₂O₂F₆. Likewise, because of the melt buffering provided by the formation of these oxyfluoride solutes, cryolite melts are limited to a narrow range of basicity ($-\log a_{\text{NaF}}$), so that competitive solutes for other oxides should be expected in a given range of melt composition.

Fig. 19 The solubility of Ti from TiO_2 and contributions by the three solutes as a function of dissolved Al_2O_3 content at 1300 K

Accordingly, the log-log method of thermodynamic modeling is only valid when indeed a single solute is dominant over a specific range of melt composition. But inherently highly buffered cryolite solutions would not be expected to fit this format. Likewise, as demonstrated for the three solutes of Al_2O_3 in cryolite, realistic solutes in ionic solutions should exhibit a reasonable stereochemistry, i.e. a specific simple geometry providing local charge balance via large anions surrounding the smaller cation, i.e. tetrahedra or octahedra, etc. The two solutes for TiO_2 identified in ref. 7 using the log-log method of thermodynamic modeling, namely TiOF_2 and Na_2TiO_3 , would seem to exist only as planar triangular solutes, an unrealistic stereochemistry. Therefore, in the current study, the experimental data of ref. 7 were reinterpreted to arrive at different proposed solutes, their Gibbs energies of formation, and their molecular geometries.

Fig. 20 3-D geometries (stereochemistry) of solutes $\text{Na}_4\text{TiO}_2\text{F}_4$, NaTiOF_3 and $\text{Na}_3\text{TiO}_3\text{F}$

Without presenting the detailed calculations here, we have reinterpreted the identification of the solutes by the Trondheim group to reveal three basic solutes: $\text{Na}_4\text{TiO}_2\text{F}_4$, NaTiOF_3 , and $\text{Na}_3\text{TiO}_3\text{F}$, each of these with a reasonable stereochemistry. Curve 3 of Fig. 18 shows the improved fit of these solutes to the experimental data. Fig. 19 provides a plot of the distribution of the three solutes as a function of total oxygen content. Fig. 20 shows their corresponding stereochemistry, a combination of tetrahedral and octahedral geometries. As a result of our modeling of their data, a Note entitled "The Solubility of Titanium Dioxide in Cryolite-Alumina Melts at 1300K" by Yunshu Zhang and Robert A. Rapp has been accepted for publication in *Met. Mater. Trans. B*, **35B**, Feb. (2004) and is now in press.

The Effects of Additives and Temperature on the Alumina Solubility In Cryolite Melts

Because of its industrial importance in primary aluminum production by the Hall-Heroult process, the alumina solubility in cryolite melts has been determined experimentally and modeled thermodynamically in terms of oxyfluoride solute complexes. In our previous work, three oxyfluoride solutes $\text{Na}_2\text{Al}_2\text{OF}_6$ (acidic solute, called A), $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_6$ (neutral solute, called N), and $\text{Na}_4\text{Al}_2\text{O}_2\text{F}_6$ (basic solute, called B) were identified. This model describes perfectly the melt structure of the $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3$ system.⁽¹⁾

Small amounts of LiF , CaF_2 and MgF_2 are common additives to Hall-Heroult cells to improve physiochemical properties of the cryolite electrolyte, e.g., to lower the liquidus temperature of the cryolite electrolyte and increase current efficiency. The effects of these additives on the **alumina solubility** in cryolite melts are of practical significance. The experimentally determined dependencies of alumina solubility on the additions of these fluorides are given as follows:⁽⁵⁾

$$[\text{Al}_2\text{O}_3]_{\text{sat}} = A \left(\frac{t}{1000} \right)^B$$

where

$$A = 11.9 - 0.062[\text{AlF}_3] - 0.0031[\text{AlF}_3]^2 - 0.50[\text{LiF}] - 0.20[\text{CaF}_2] - 0.30[\text{MgF}_2] + \frac{42[\text{LiF}][\text{AlF}_3]}{2000 + [\text{LiF}][\text{AlF}_3]}$$

$$B = 4.8 - 0.048[\text{AlF}_3] + \frac{2.2[\text{LiF}]^{1.5}}{10 + [\text{LiF}] + 0.001[\text{AlF}_3]^3}$$

where the square brackets denote weight percent of components in the system $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3(\text{sat})\text{-AlF}_3\text{-CaF}_2\text{-MgF}_2\text{-LiF}$, and t is the temperature in $^\circ\text{C}$.

On the **thermodynamic front**, from experimental vapor pressures, emf's and/or Raman spectra, some authors have estimated changes in thermodynamic activities of NaF and AlF_3 in the "stoichiometric" cryolite melt (cryolite ratio $r = 3$) with small molar

additions of LiF , CaF_2 and MgF_2 at temperatures close to 1300 K: $\frac{\partial \ln a_{\text{NaF}}}{\partial x_{\text{add}}}$ and $\frac{\partial \ln a_{\text{AlF}_3}}{\partial x_{\text{add}}}$

(called interaction derivatives here).^(6,7)

Table 7 Literature data for interaction derivatives in "stoichiometric" cryolite melt^(6,7)

Addition	LiF	CaF ₂	MgF ₂
$\partial \ln a_{\text{NaF}} / \partial x_{\text{add}}$	-0.7	-2	-4.2
$\partial \ln a_{\text{AlF}_3} / \partial x_{\text{add}}$	-1.9	2	8.1

Our previous solution modeling⁽¹⁾ in the $\text{NaF-AlF}_3\text{-Al}_2\text{O}_3$ system was extended to understand the effects of these additives on the alumina solubility in a "stoichiometric" cryolite melt at 1300K. The interaction derivatives for the binary NaF-AlF_3 system listed in Table 7 were used to calculate the activities of NaF and AlF_3 in the Al_2O_3 -saturated cryolite melt ($r = 3$) in dependence upon the amount of fluoride additive in the melt. For

this purpose, the equilibrium activities for NaF and AlF_3 in the system of NaF- AlF_3 - $\text{Al}_2\text{O}_3(\text{sat.})$ were chosen as the initial activity values. This procedure implies that the effect of the Al_2O_3 content in the binary NaF- AlF_3 system was taken into account before the interaction derivatives of these fluoride additions were applied. The molar fractions of the three oxyfluoride solutes A, N and B in the Al_2O_3 -saturated melt were calculated using the revised activity values. The revised alumina solubility values were calculated for small additions of fluorides LiF, CaF_2 and MgF_2 from the equation:

$$x_{\text{Al}_2\text{O}_3} = \frac{(x_A + 2x_N + 2x_B)n_t}{3}$$

where n_t is the total moles of all the solutes in the melt, which is assumed to be unchanged by these small additions.

A comparison of the calculated alumina solubility values with those determined experimentally is shown in Table 8, with 1 to 5 wt % of fluorides added to the NaF- AlF_3 melt. Table 8 indicates very good agreement between the calculated data and the experimentally determined data. This implies that the estimated interaction derivatives in Table 7 are correct, or at least reasonable.

Table 8 Comparison of alumina solubility values for “stoichiometric” cryolite ($r = 3$) calculated from the interaction derivatives with those determined experimentally upon additions of fluorides

Addition wt %	Alumina solubility, molar fraction	
	From calculation	From experiments
0	0.075	0.074
LiF addition		
1	0.071	0.071
2	0.067	0.068
3	0.064	0.064
4	0.061	0.061
5	0.058	0.058
CaF_2 addition		
1	0.074	0.073
2	0.072	0.072
3	0.071	0.071
4	0.070	0.070
5	0.069	0.069
MgF_2 addition		
1	0.073	0.073
2	0.071	0.071
3	0.070	0.069
4	0.068	0.067
5	0.066	0.065

The alumina solubility was also calculated as a function of temperature (1240 – 1300 K) and melt composition r (1.5 – 3.0). The detailed calculations are described in the publication: Y. Zhang and R. A. Rapp, “Modeling the Dependence of Alumina Solubility on

Temperature and Melt Composition in Cryolite-Based Melts”, Met. Mater. Trans. **35B**, (2004), in press. This paper received comments from two reviewers. Reviewer #1 wrote: “The work and presentation are very high quality, which is expected considering the experience of the authors. The paper is a contribution for the metallurgical archives”.

It is important to point out that in this paper, the solubility of alumina in cryolite melts at 1300 K was remodeled thermodynamically in terms of three oxyfluoride solutes $\text{Na}_2\text{Al}_2\text{OF}_6$ (acidic solute), $\text{Na}_2\text{Al}_2\text{O}_2\text{F}_4$ (neutral solute) and $\text{Na}_4\text{Al}_2\text{O}_2\text{F}_6$ (basic solute), and only two oxygen-free solutes Na_3AlF_6 and NaAlF_4 , excluding the questionable solute Na_2AlF_5 . The remodeling provided an even better fit to the experimental data than the original model assuming three oxygen-free aluminum fluoride anions. The equilibrium constants for the formation of these solutes were recalculated, and the corresponding ΔG_f^0 values were also derived.

SENSORS FOR THE ALUMINUM INDUSTRY

The September 2002 Aluminum Roadmapping meeting in Pittsburgh raised, as important desirable developments for future research, a need for sensors to measure: 1. the concentration of dissolved alumina in undersaturated cryolite melts, and 2. the concentrations of elements (both intentional and deleterious) in liquid Al alloys. As part of this research project, sensors were proposed to accomplish these measurements. Each arrangement employs a “hole-in-tube” type immersion sensor to serve as a potentiometric electrochemical concentration cell.

Sensor for Dissolved Alumina Concentration in Cryolite

Two alternate geometries were suggested for the “alumina sensor” in cryolite. . Figure 21 shows schematically a sensor intended to measure the dissolved alumina activity in the bulk bath contacting the tungsten working electrode. The cryolite bath itself serves as the fused electrolyte required for the cell. The dissolved alumina activity would be calculated from the Nernst expression:

$$E = -RT/6F \ln [a_{\text{Al}_2\text{O}_3} (\text{WE}) / a_{\text{Al}_2\text{O}_3} (\text{RE})]$$

The alumina-saturated Reference Electrode (inside the tube) has an alumina activity of unity. Information is readily available to convert the dissolved alumina activity to its concentration.⁽⁵⁾

Figure 22 shows schematically a sensor intended to measure the “average” dissolved alumina concentration (activity) in the cryolite bath contacting the Al pad. The same Nernst expression applies. Local cell action along the interface between the Al melt and the cryolite bath should insure that the average dissolved alumina activity at the interface is indicated.

While either of the alumina probes should be effective, in principle, their fabrication is dependent upon the chemical resistance to cryolite of insulating BN tubes. Although a preliminary experiment has shown adequate stability for the Carborundum BN material, the cost of such tubes is excessive (\$465 for a closed-end tube of 12” length). For this reason, the experimental fabrication and demonstration of sensors for dissolved alumina were not undertaken on the project. However, the designs shown in Figs. 21 and 22 are available for future studies.

Fig. 21 Schematic illustration of probe to measure dissolved alumina concentration in bulk cryolite bath (Arrangement 1)

Fig. 22 Schematic illustration of probe intended to measure the average dissolved alumina concentration at the melt/bath interface (Arrangement 2)

Sensor for Magnesium Concentration in liquid Al-Mg Alloy

The probe to measure the thermodynamic activity for Mg in liquid Al-Mg alloys is drawn schematically in Fig. 23. Again, this probe involves a hole-in-tube design, with a fused salt electrolyte. The electrolyte chosen comprises a solution of MgCl_2 and KCl, and perhaps other chlorides which are more stable than Al chloride. This condition eliminates the potential problem of a displacement reaction which would lead to an erroneous cell voltage. The schematic diagram for the alloy composition sensor shows its fabrication from less expensive alumina tubes. The Al-Mg reference alloy inside the tube has a known activity for Mg, although any other such reference alloy would also be acceptable. A porous ceramic frit constitutes the "separator, allowing a common salt solution to contact both the Working Electrode (test alloy) and the Reference Electrode.

Fig. 23 Schematic illustration of Mg probe for measurement of Mg content in Al alloys
The cell voltage for the probe illustrated in Fig. 23 is provided by the expression:

$$E = -RT/2F \ln [a_{\text{Mg}} (\text{WE}) / a_{\text{Mg}} (\text{RE})]$$

Figure 24 provides the results of a series of experiments where the temperature and alloy composition were changed in steps. These results are highly reproducible, and this probe is suited for industrial application with binary Al-Mg alloys. However, if the alloy should also contain a sufficient concentration of a component which forms a chloride more stable than MgCl_2 , e.g. Li, Sc, Sr or K, then the cell voltage would be adversely affected by a displacement reaction. Experimentally, we have found that a large Zn addition to an Al-Mg alloy had no important effect (except dilution), while a large Li addition caused probe failure.

This Mg probe indeed is quite similar to one patented by Tiwari and Howe in 1986⁽⁸⁾ and described in the reference (9). For this reason, no effort was made to seek patent coverage.

Fig. 24 Test results of Mg probe for different temperatures

Sensor for Lithium Concentration in liquid Al-Li Alloy

Figure 25 is a schematic drawing of a similar probe to measure directly the thermodynamic activity of Li in a binary Al-Li alloy. The important probe elements are again a reference Al-Li alloy with known activity of Li, a porous alumina frit for separating the reference alloy from the test melt, and a common fused chloride solution ($\text{KCl} + \text{LiCl}$). As

for the Al-Mg probe one problem limiting long-term use industrially is the dissolution of the tungsten lead wire into the test and reference alloy. We found that coating the electrode tips with carbon in a vacuum evaporator chamber greatly extended the life of the probe.

Fig. 25 Schematic illustration of Li probe for measurement of Li content in Al alloys

The results of measurements using this probe are presented in Fig. 26. Again, for a binary Al-Li alloy, these results are highly reproducible. The average uncertainty for each measurement is less than one millivolt, certainly adequate for industrial application.

Fig. 26 Test results of Li-probes in liquid Al-Li alloys

Industrial Demonstration of the Mg and Li probes

These probes were demonstrated in the development shop of KB Alloys in Henderson, KY for rather large alloy melts heated by induction. Both probes behaved acceptably, and KBA may be interested to have such probes fabricated for them, for their marketing. Their decision will be affected by various market factors.

Two engineers from the Pechiney Research Lab in Voiron, France visited our lab at OSU, and again the probes were demonstrated without problems. These engineers will be in contact with KB Alloys to learn about the potential commercial availability for these probes. In principle, such probes could also be produced for the elements Sr, K, Sc, and Ca, but these would seem to offer lesser commercial promise.

We could not find any references to literature or patents for the lithium probe. However, in design and operation, it is identical to the patented Al-Mg probe, and lithium would represent a limited industrial interest compared to magnesium. We have not pursued this patenting prospect further.

CONCLUDING REMARKS OF FINAL PROJECT REPORT

The initial goal of this project, to demonstrate the possibility for the introduction of a SOFC-type anode into an Al electrowinning cell, was not achieved. But in this quest, a quantitative measure of cryolite basicity/acidity was defined, and probes were developed and demonstrated to measure this melt property. Solubility studies showed that the ZrO_2 and Y_2O_3 components of the SOFC tubes were excessively soluble at all values of

cryolite ratio. The impossibility of the desired project goal was discovered, and explained by new scientific knowledge, within 18 months. Indeed, the project suggested that introduction of the proposed SOFC anode might be possible if the cell solvent/electrolyte were changed from cryolite to sodium sulfate.

Thereafter, the project was focussed on the evaluation and understanding of cryolite chemistry at The Ohio State University. Both novel experimental and theoretical methods were demonstrated to provide a quantitative understanding for the dissolution of alumina in cryolite. For the first time, the stereochemistry (molecular geometries) for the solutes was illustrated. This modeling was extended to incorporate the dependencies on alumina solubility of temperature and small bath additions of LiF, CaF₂, or MgF₂. The modeling method of requiring a global equilibrium for all possible reactions and species, coupled with element balances, proved to be highly effective for identifying the dominant solute species in cryolite solutions, and establishing their thermodynamic stabilities. A point was made to explain the deficiency of the usual "log-log" method of analysis, whereby only one or a couple equilibria are considered. Our modeling method was used to reinterpret recent papers describing the solubilities in cryolite of NiO/NiAl₂O₄, FeO/FeAl₂O₄, and TiO₂. Again, the stereochemistry for the solutes in these systems was illustrated.

In response to a priority from the 2002 Aluminum Roadmap, two different versions of a sensor to measure the dissolved alumina activity/concentration in cryolite were proposed, but experimental verification was not attempted. On the other hand, sensors to measure the activity/concentration of Mg in liquid Al-Mg and Li in liquid Al-Li alloys were developed, experimentally validated, and successfully demonstrated in an industrial Al shop. These sensors are considered ready for in-line measurements in the Al processing industry.

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Yunshu Zhang and Robert A. Rapp, "Correlations of Melt Structure and Acid-Base Property for Fused Salts", Thermodynamics of Alloys 2002 meeting in Rome, Italy, September 8-13, 2002

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Yunshu Zhang and Robert A. Rapp, "The Effects of Additives on the Alumina Solubility in Cryolite Melts at 1300K", presented at the 2003 Spring/May meeting of the Electrochemical Soc. in Paris, France.

Awards Received during the Project Period

Graduate student Xiaoxia Wu passed her oral defense of the thesis: "Modeling of the Solubility of Alumina and $\text{NiO/NiAl}_2\text{O}_4$ in Cryolite Melts at 1300K ". The thesis was accepted and she received an MS Degree in MSE.

Robert A. Rapp, at the March 2000 TMS meeting in Nashville, TN presented the TMS Institute of Metals Lecture, "Some Generalities in the Analyses of Equilibria in Ionic Solutions", and received the R. F. Mehl Award.

Robert A. Rapp, at the October 2000 ASM meeting in St. Louis, MO received the ASM Gold Medal.

Robert A. Rapp, at the March 2003 TMS meeting in San Diego, CA received the TMS Educator Award.