

3. INERT ANODES AND WETTABLE CATHODES

The selected papers on inert anodes and wettable cathodes are concentrated on earlier publications that cover the fundamentals of the science and have been built on by later researchers. The 1963 paper by C.E. Ransley titled “The Application of the Refractory Carbides and Borides to Aluminum Reduction Cells” is an important paper that introduces the concept of wettable cathodes. Work in these areas is commercially sensitive and major Western companies are no longer publishing the results. Another gap is the absence of papers on the Drained Cathode program completed by Comalco over many years that was never presented at the TMS Annual Meetings.

For readers with an interest in these topics, it is important to access the review papers and to study the extensive recommended reading list which includes many of the later papers, including those from Moltech and more recent work from China.

SOLUBILITIES OF OXIDES FOR INERT ANODES IN CRYOLITE-BASED MELTS

David H. DeYoung

Aluminum Company of America
Alcoa Laboratories
P. O. Box 772
New Kensington, PA 15068

ABSTRACT

The solubilities of Fe_2O_3 , NiO, and NiFe_2O_4 have been measured in $\text{NaF-AlF}_3\text{-CaF}_2\text{-Al}_2\text{O}_3$ melts as a function of temperature and melt composition. The solubilities of Fe_2O_3 and NiO for melts containing 1.5 to 6.5 wt% Al_2O_3 and for bath ratios ranging from 0.7 to 1.5 are represented by the relationships,

$$\log \text{wt\% Fe} = 4.71 - 7080/T,$$

and

$$\log \text{wt\% Ni} = 6.27 - 9740/T,$$

respectively. The solubilities of both Fe_2O_3 and NiO increased with decreasing concentrations of Al_2O_3 in the melt, particularly at <1 wt% Al_2O_3 . The solubility of Fe_2O_3 decreased moderately with decreasing bath ratio (wt NaF/wt AlF_3), while no change occurred for NiO. The solubility of NiFe_2O_4 was less than the solubilities of Fe_2O_3 and NiO, and there was good agreement between the free energy of formation of NiFe_2O_4 calculated from the measured solubilities of Fe_2O_3 , NiO, and NiFe_2O_4 and the free energy of formation reported in the literature.

INTRODUCTION

A primary criterion of an inert anode material for aluminum electrolysis is that it must be relatively insoluble in the cryolite-based electrolyte. The most promising inert anode materials are oxides which have small but finite solubilities in the electrolyte. Nickel ferrite-based materials have been identified by Ray (1, 2) as reasonably good anode materials. The life of these anodes and the purity of aluminum produced from them are directly related to the rate at which the anode dissolves in the electrolyte. Therefore, solubilities of nickel ferrite and its component oxides Fe_2O_3 and NiO directly affect the performance of the anode. Metals such as nickel (2) or copper (3) have been added to the nickel ferrite materials to improve the electrical conductivity. Since oxides form on the surface of these metallic constituents during operation, the dissolution of the nickel ferrite will still control the anode life and aluminum purity.

As part of Alcoa's inert anode development program, a study of the dissolution rates of inert anode materials was undertaken. The goals of this study were to define the mechanisms for dissolution,

identify the rate-limiting step, and reduce the dissolution rates of the inert anodes. The first part of the study, the subject of this paper, was to measure the solubilities as a function of electrolyte composition and temperature. The objectives were to identify conditions that minimized solubilities and to obtain the thermodynamic information needed to interpret kinetic data.

Some data are reported in the literature for the solubilities of these oxides in Na_3AlF_6 and in $\text{Na}_3\text{AlF}_6\text{-5\% Al}_2\text{O}_3$ melts, but there has been no systematic study of the solubilities over temperature and electrolyte composition ranges for which Hall cells can be operated. Additionally, there are significant differences between the results from different investigators. Belyaev et al (4) measured the solubilities of NiO and Fe_2O_3 in Na_3AlF_6 and $\text{Na}_3\text{AlF}_6\text{-5 wt\% Al}_2\text{O}_3$ melts. Rolin and Bernard (5) reported solubilities of Fe_2O_3 and NiO in Na_3AlF_6 . Johansen (6) measured a portion of the $\text{Na}_3\text{AlF}_6\text{-Fe}_2\text{O}_3$ phase diagram using the DTA technique. Recently, Horinouchi et al (7) reported measurements of solubilities of NiO, Fe_2O_3 , and NiFe_2O_4 in $\text{Na}_3\text{AlF}_6\text{-10 wt\% Al}_2\text{O}_3$ melts. With the exception of Johansen's phase diagram, all of these measurements were made at approximately 1000°C.

The scope of this work was to determine solubilities from 1025°C down to the liquidus temperature of the electrolyte, from bath ratios (wt NaF/wt AlF_3) of 0.7 to 1.3, and for electrolytes containing 0.5 to 6.5 wt% Al_2O_3 . Several measurements were also made at bath ratios of 1.5 and 2.8. The effects of CaF_2 , MgF_2 , ZrO_2 , and SiO_2 additions to certain electrolyte compositions on the solubilities of NiO and Fe_2O_3 were also determined, but will not be covered in this paper.

EXPERIMENTAL METHOD

Solubility measurements were made using an equilibration technique. Pellets of the oxides were equilibrated with the melt, and samples of the melt were periodically withdrawn and chemically analyzed for the oxide components.

The experimental apparatus is shown in Figure 1. Approximately 250 g of melt was contained in a 125 ml platinum crucible. This crucible was nestled in an alumina crucible, which in turn was supported on bubble alumina in a closed-end alumina tube. To minimize thermal convection in the furnace, a baffle

constructed of three alumina plates was placed on top of the alumina crucible. The entire assembly was inserted in a Kanthal wound resistance furnace. The top of the tube was sealed with a water-cooled copper cap using a teflon gasket. Ports in this cap with sealable fittings provided access for a thermocouple, gas inlet and exit tubes, and a sampling tube. The temperature of the melt was monitored using a type S thermocouple, protected from the melt by a platinum sleeve.

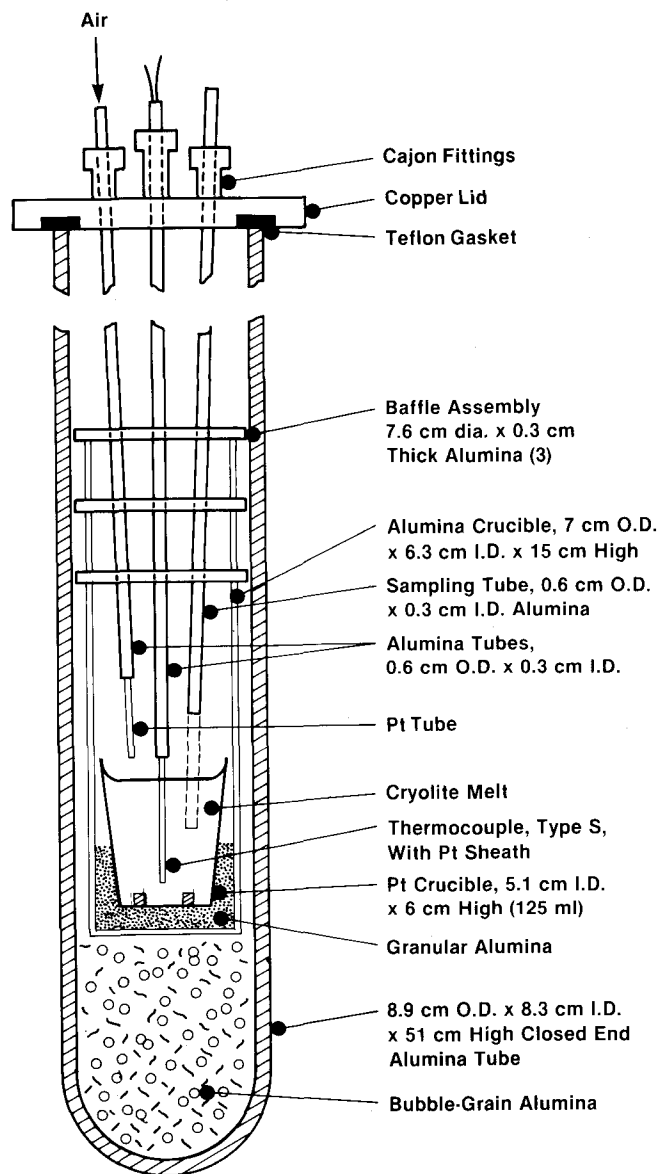


Figure 1. Experimental apparatus for solubility measurements.

Crushed Greenland cryolite, Alcoa-produced AlF_3 , reagent grade CaF_2 , and calcined $Al(OH)_3$ were used to prepare the melts. The cryolite and the AlF_3 were chemically analyzed prior to use, and melt compositions were based upon these analyses and the charge weights.

Samples of the melt were withdrawn into an alumina tube by a syringe assembly attached to the top of the tube. The samples were crushed, mixed, and analyzed for impurities by either the inductively coupled plasma technique (ICP) or by atomic absorption. The precision of the analyses is approximately $\pm 5\%$ of the total quantity present. Prior to the analyses the samples were dissolved in either HCl or HNO_3 .

Reagent grade NiO (Fisher N-69) and Fe_2O_3 (Fisher I-116) were used to prepare oxide pellets without further purification. The raw materials were mixed, uniaxially pressed into 0.95 cm diameter x 1.59 cm high cylinders at 25,000 psi, and sintered in air at $1350^\circ C$ for 16 hours. Samples of the resulting pellets were analyzed by X-ray diffraction to confirm the phase of the material. The densities of the pellets were: $NiO - 5.72 \text{ g/cm}^3$; $Fe_2O_3 - 5.13 \text{ g/cm}^3$; $NiFe_2O_4 - 4.64 \text{ g/cm}^3$. For each experiment, approximately 2 to 3 g of oxide were added to the melt. Each pellet was broken into 3 to 5 pieces before adding it to the melt.

Air was circulated over the bath surface during the experiment and was periodically bubbled into the melt to provide stirring and to equilibrate the melt with air. The air was dried by passing it through a column of calcium sulfate (Drierite). After bubbling, the melt was allowed to settle for at least 25 minutes before sampling.

The duration of an experiment was typically 80 to 100 hours, during which the melt was cycled through 3 or 4 temperatures. After initial experiments, in which the equilibration time was determined, two melt samples from the end of each time period at a given temperature were analyzed to determine the solubility. For some experiments, several melt samples were analyzed for bath ratio (wt NaF /wt AlF_3) and Al_2O_3 . The bath ratio was determined by pyrotitration and the Al_2O_3 concentration was determined from the weight of insolubles in an aqueous $AlCl_3$ solution.

Figures 2 and 3 show the approach to equilibrium for Fe_2O_3 and NiO , respectively. Steady-state concentrations, which were taken to be the solubilities, were reached approximately 8 hours after the oxide pellets were dropped into the melt. The melt was allowed to equilibrate for approximately 24 hours at each temperature.

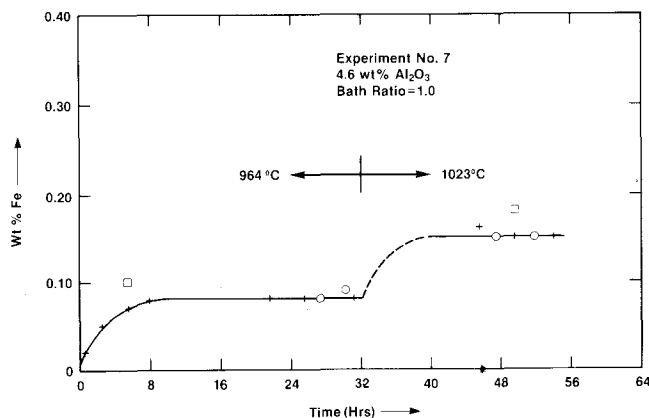


Figure 2. Bath analyses illustrating time needed for equilibration of Fe_2O_3 with the melt.

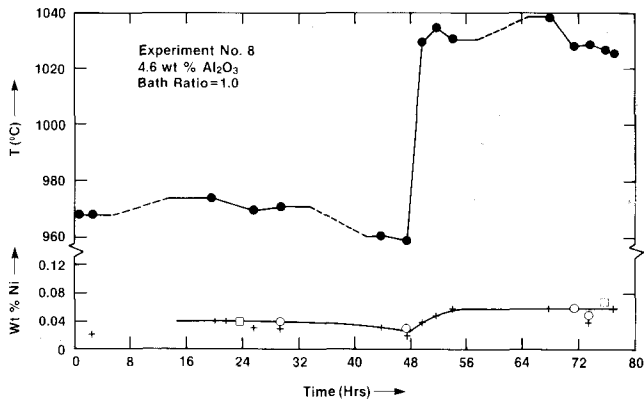


Figure 3. Bath analyses illustrating time needed for equilibration of NiO with the melt.

To assure that the steady-state, plateau concentrations were true equilibrium solubilities, equilibrium was approached from both directions during several experiments. Figure 4 gives an example. The initially measured solubility (melt changing from a lower temperature to a higher temperature and dissolving NiO) agrees with the result obtained later (melt changing from a higher temperature to a lower one and precipitating out NiO).

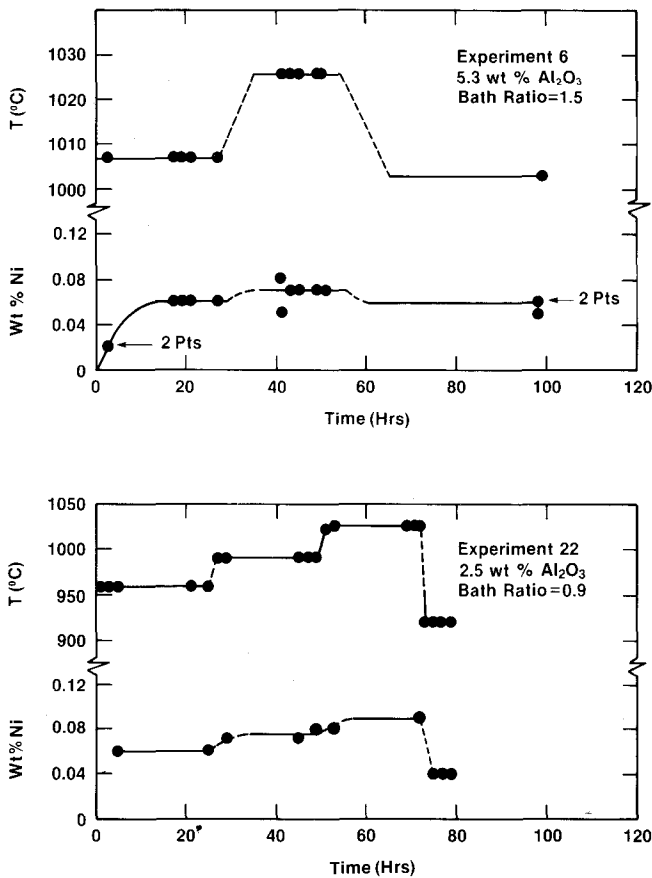


Figure 4. Approach to solubilities from lower and higher temperatures.

In general, the solubility for most experiments was measured at a higher temperature and then at a lower temperature, followed by at least one measurement at an intervening temperature. In this way equilibrium was approached from both directions, and the consistency of the results from a given experiment was evidence for equilibrium. Occasionally results were not consistent; these experiments were repeated.

The bath ratio changed somewhat during the experiments, particularly for those with initially low bath ratios and of long duration. The maximum increase in bath ratio due to vaporization of NaAlF₄ was approximately 0.1, though it was usually about 0.05. As will be shown later in the paper, this change had a small effect on the solubilities. In Figure 5, bath ratio and percent Al₂O₃ are plotted versus time for several experiments. Nominal starting ratios and Al₂O₃ concentrations are indicated in parentheses for the respective runs. The uncertainties in bath composition are estimated to be ±0.5% in Al₂O₃ and +0.1, -0 in bath ratio.

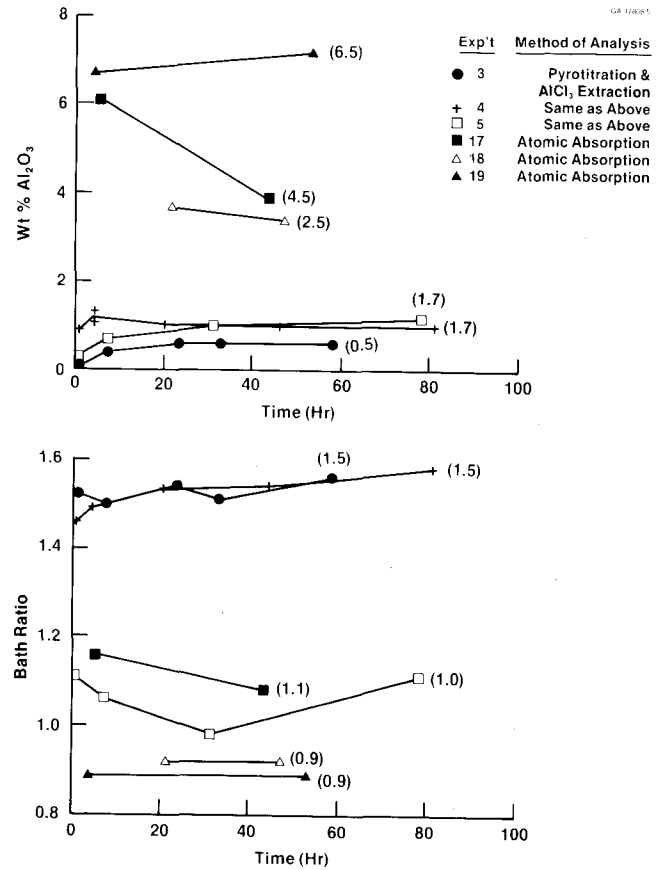


Figure 5. Analyses of melts from selected experiments for bath ratio (wt NaF/wt AlF₃) and Al₂O₃.

RESULTS AND DISCUSSION

Solubilities

Figures 6 through 8 show the solubilities of Fe₂O₃, NiO, and NiFe₂O₄, respectively, as a function of temperature. Measurements were made to the

liquidus temperature for each bath composition. Lines connecting the data points for each experiment are not meant to indicate that the solubilities vary linearly with temperature; rather, they group the data from each experiment. The solubilities of Fe₂O₃ are approximately twice those for NiO. The solubilities for Fe₂O₃ and NiO from NiFe₂O₄ are less than the solubilities of Fe₂O₃ and NiO, respectively; this is expected because of the added thermodynamic stability of the ferrite over the simple oxides.

composition of 2.5% Al₂O₃, 0.9 bath ratio. Likewise, it is demonstrated in Figure 7 by the NiO results for melt compositions of 2.5% Al₂O₃, 0.9 bath ratio, and 4.5% Al₂O₃, 1.1 bath ratio.

The NiFe₂O₄ data indicate that it did not dissolve stoichiometrically. The weight ratio Fe/Ni ranges from approximately 3 to 8. However, the bath contains a background level of approximately 0.02 wt% Fe, so that stoichiometric dissolution of NiFe₂O₄ into bath already containing Fe would result in Fe/Ni ratios of those reported and would result in a bath composition saturated with NiFe₂O₄.

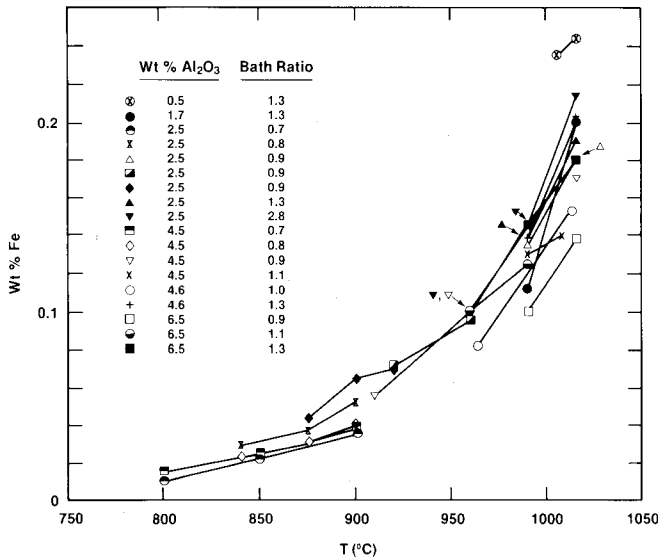


Figure 6. Solubility of Fe₂O₃ in NaF-AlF₃-CaF₂-Al₂O₃ melts.

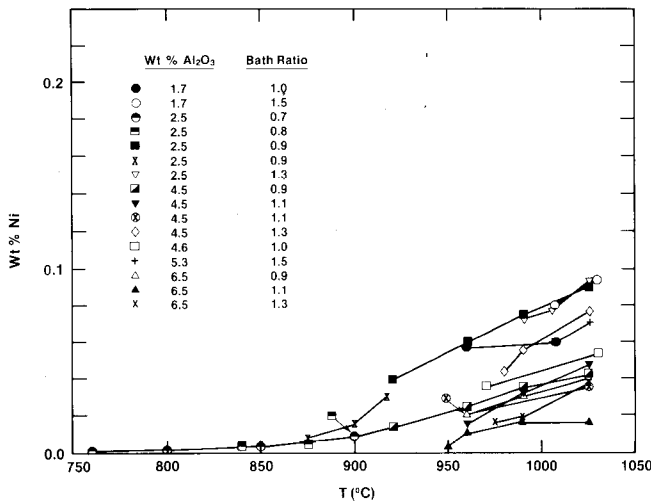


Figure 7. Solubility of NiO in NaF-AlF₃-CaF₂-Al₂O₃ melts.

The uncertainty in the sample analyses is ±5% of the amount of Fe or Ni present, which corresponds to ±0.01 to ±0.001% Fe and ±0.005% to ±0.0005% Ni. Experimental results for identical bath compositions are within these uncertainties. This is illustrated in Figure 6 by results for Fe₂O₃ for a melt

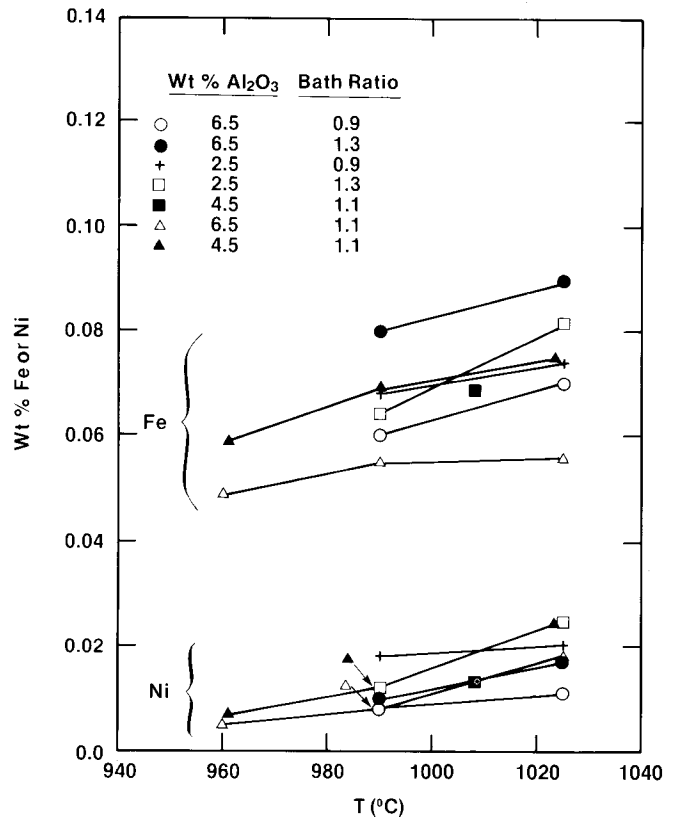
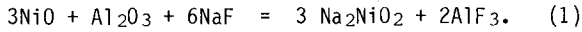


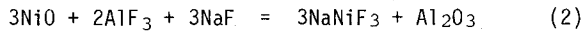
Figure 8. Solubility of NiFe₂O₄ in NaF-AlF₃-CaF₂-Al₂O₃ melts.

Figures 9 and 10 show the variation in solubilities with Al₂O₃. These are crossplots of some of the data in Figures 6 and 7; each point shown is an experimentally measured point. The solubilities decrease with Al₂O₃, and the effect is stronger for NiO than for Fe₂O₃. For Fe₂O₃, the solubility is approximately constant for melts with more than 2.5% Al₂O₃. For both oxides, the biggest change occurs at less than 2% Al₂O₃. The behavior seems to follow a solubility product-type relationship so that as the activity of Al₂O₃ decreases the solubility of the iron or nickel oxide increases. It certainly does not simply substitute for Al₂O₃ as a source of oxide ion to dissolve in the melt. Because of this effect of Al₂O₃, it appears that neither iron nor nickel oxides are dissolving as metal-oxide anions such as a nickelate ion, NiO₂²⁻. If they were, it would be expected that Al₂O₃ would increase the solubility of

these ions. For example, a possible dissolution reaction would be



An increase in the activity of Al_2O_3 would drive the reaction to the right and increase the solubility of the NiO . The dissolving species are more likely metal cations, metal fluoride anions, or metal oxy-fluoride anions, for which a decrease in the Al_2O_3 activity would increase their solubility. For example, the dissolution of NiO to form a nickel fluoride anion would proceed by the overall reaction,



in which the activity of the dissolved compound would be inversely proportional to the activity of Al_2O_3 to the one-third power.

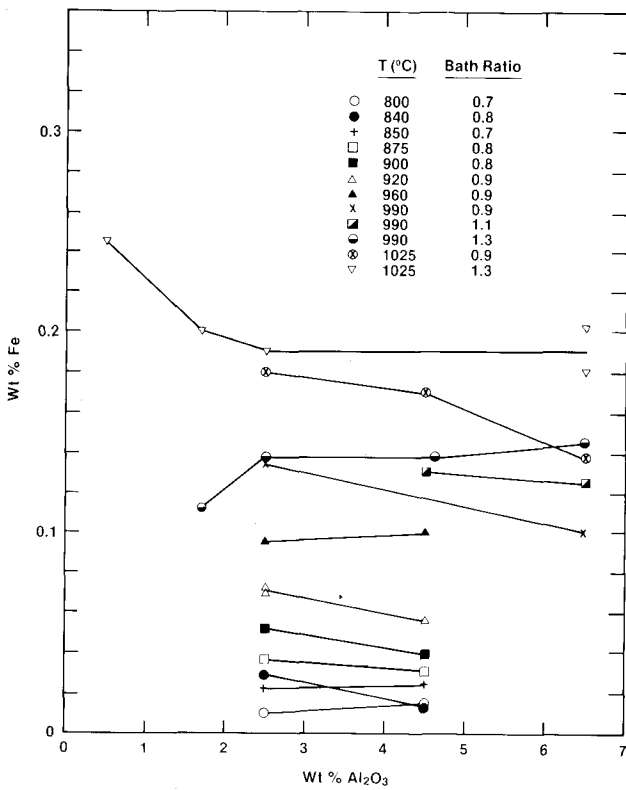


Figure 9. Effect of Al_2O_3 concentration in the melt on the solubility of Fe_2O_3 .

Figures 11 and 12 show the solubilities plotted as a function of bath ratio. The solubility of Fe_2O_3 decreases moderately with decreasing bath ratio, while there does not appear to be any change in the solubility of NiO within the uncertainty of the measurements. It is difficult to infer any information on the ionic species for Fe and Ni that form on dissolution of the oxides, other than discussed above, because of the limited basicity range over which data was obtained. In the NaF-AlF_3 system, the activity of AlF_3 changes by one order of magnitude from a bath ratio of 0.9 to 1.3, while the activity of NaF changes by a factor of three over the same compositional range (8). Measurements over several

orders of magnitude would be needed to infer any further structural information.

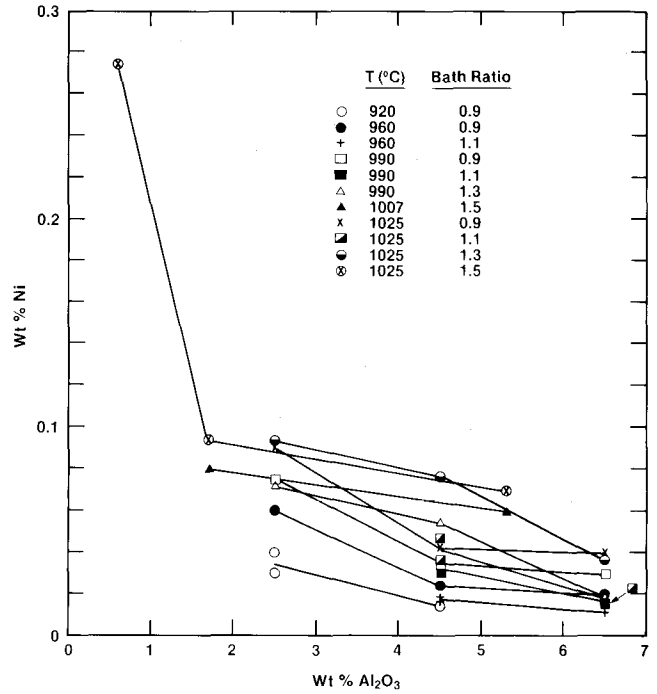


Figure 10. Effect of Al_2O_3 concentration in the melt on the solubility of NiO .

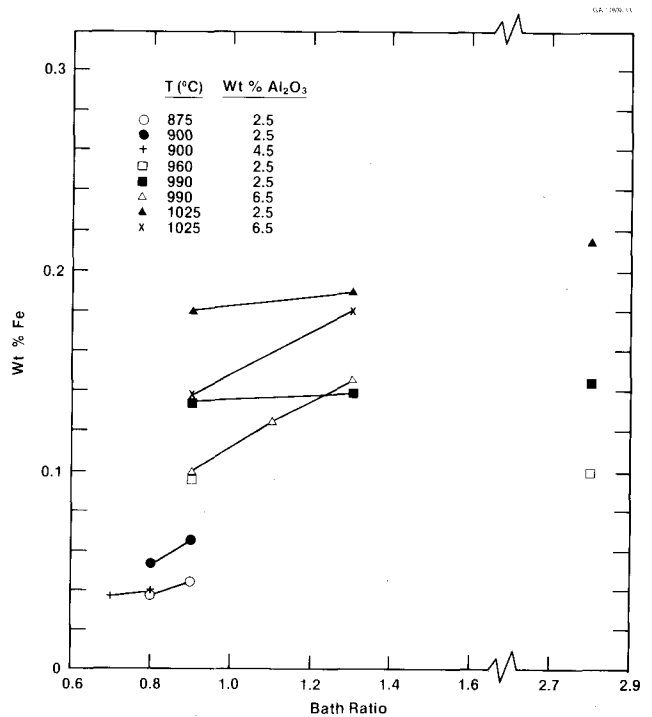


Figure 11. Effect of bath ratio (wt NaF /wt AlF_3) on the solubility of Fe_2O_3 .

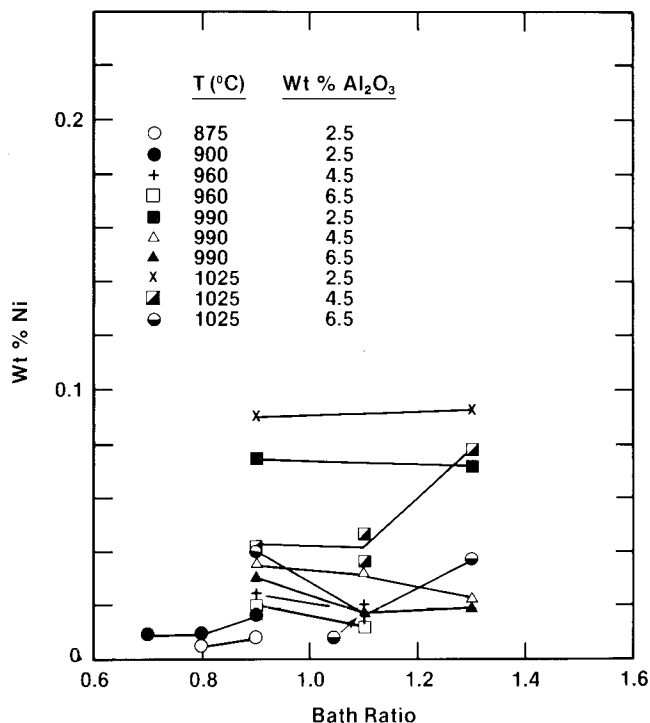


Figure 12. Effect of bath ratio (wt NaF/wt AlF₃) on the solubility of NiO.

Enthalpy of Dissolution

The enthalpy of dissolution of the oxides in the melts can be obtained from the solubility data. Since all solubilities that were measured were relatively small, the assumption of Henrian behavior in the solution may be reasonable. The activities of the dissolved species can be represented by

$$a_{NiO} = \gamma_{NiO} X_{NiO} \tag{3}$$

and

$$a_{Fe_2O_3} = \gamma_{Fe_2O_3} X_{Fe_2O_3} \tag{4}$$

At saturation with respect to the solid, a_{NiO} and $a_{Fe_2O_3} = 1$; therefore

$$\gamma_{NiO}^{\circ} = 1/X_{NiO}^{sat} \tag{5}$$

and

$$\gamma_{Fe_2O_3}^{\circ} = 1/X_{Fe_2O_3}^{sat} \tag{6}$$

From the Gibbs-Helmholtz equation,

$$\partial (2.303R \log \gamma_i) / \partial (1/T) = \Delta H_i^M \tag{7}$$

Therefore, $\log (X_i^{sat})$ or $\log (wt\% i)$ should vary linearly with $1/T$ provided the assumption of Henrian behavior holds and ΔH_i^M is constant with temperature.

Figures 13 and 14 show the data for Fe₂O₃ and NiO plotted in this manner. The correlation for Fe₂O₃ is

quite good, even though data for all melt compositions are included. This indicates that the changes with Al₂O₃ concentration and bath ratio are relatively small compared to changes in solubility with temperature. Data for melts with less than 1.5% Al₂O₃ were not included. The correlation for NiO is not as good, but this is expected since the Al₂O₃ concentration in the melt had a larger influence than for Fe₂O₃. Attempts at fitting the data to the proposed model at constant Al₂O₃ concentration gave a better correlation for melts with 2.5% Al₂O₃, but poorer correlation for melts with higher concentrations. This is true because data in melts with higher concentrations of Al₂O₃ were obtained over a limited temperature range. Therefore, the best overall correlation is obtained by using all compositions. The least squares equations are

$$\log wt\% Fe = 4.71 - 7080/T \tag{8}$$

and

$$\log wt\% Ni = 6.27 - 9740/T \tag{9}$$

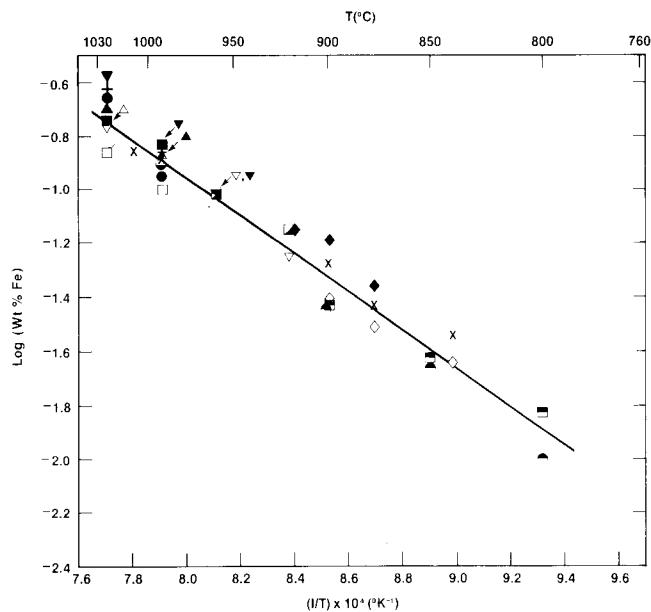


Figure 13. Least-squares fit of the Fe₂O₃ solubility data.

The partial molar enthalpies of dissolution of the oxides, ΔH_i^M , calculated from the slopes of these equations are +33.1 and +44.6 kcal/mole for Fe₂O₃ and NiO, respectively.

Figure 15 shows the solubility data from NiFe₂O₄ plotted as a function of inverse temperature. Least squares lines were calculated, although the temperature range for the data was limited and the correlation coefficients were poor. The least squares lines are

$$\log wt\% Fe = 1.26 - 3100/T \tag{10}$$

and

$$\log \text{wt\% Ni} = 7.25 - 11700/T. \quad (11)$$

$$\Delta G_f^\circ(\text{NiFe}_2\text{O}_4) = -4750 - 0.9 T \text{ cal/mole} \quad (13)$$

(855 < T < 1700°K)

with an uncertainty of ± 1000 cal/mole; at 1000°C the free energy of formation is -5900 ± 1000 cal/mole. The results of this study are, therefore, in agreement with this independent thermodynamic data, which was obtained by an emf cell method.

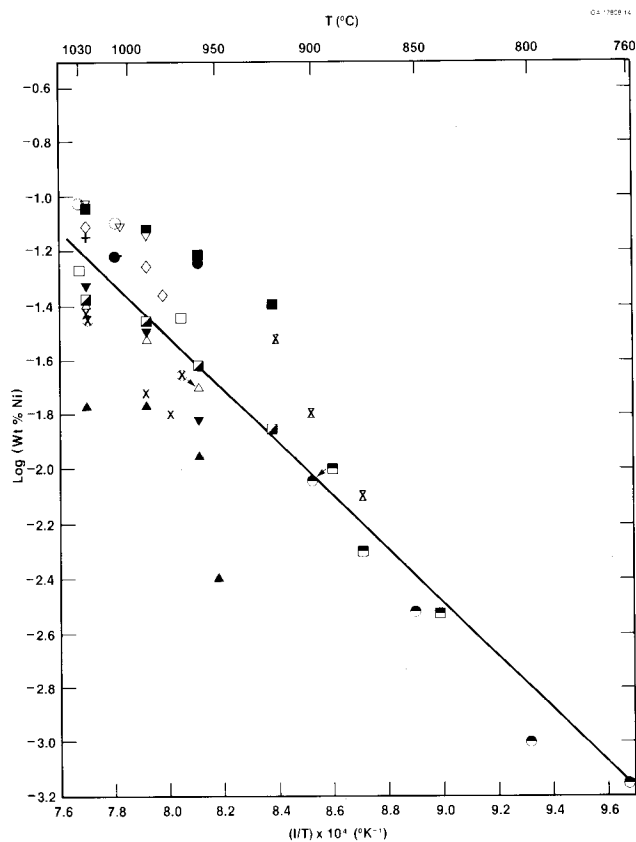


Figure 14. Least-squares fit of the NiO solubility data.

Comparison to Other Thermodynamic Data

To assess whether the measured data agree with other thermodynamic data found in the literature, the standard free energy of formation of NiFe₂O₄ was calculated from the above Henrian activity coefficients and the measured solubility of NiFe₂O₄. For the formation of stoichiometric NiFe₂O₄, ΔG_f° can be calculated from the relationship,

$$\Delta G_f^\circ(\text{NiFe}_2\text{O}_4) = - 2.303 RT \log [1/(\gamma_{\text{NiO}} \cdot X_{\text{NiO}} \cdot \gamma_{\text{Fe}_2\text{O}_3} \cdot X_{\text{Fe}_2\text{O}_3})] \quad (12)$$

where $X_{\text{Fe}_2\text{O}_3}$ and X_{NiO} are the mole fractions of Fe₂O₃ and NiO in the melt which is saturated with NiFe₂O₄. Substituting the activity coefficients calculated from Equations 5, 6, 8, and 9, and saturation concentrations from Equations 10 and 11 into this equation gives a free energy of formation of -4920 cal/mole at 1000°C. Kubaschewski (9) reported the free energy of formation from the simple oxides to be

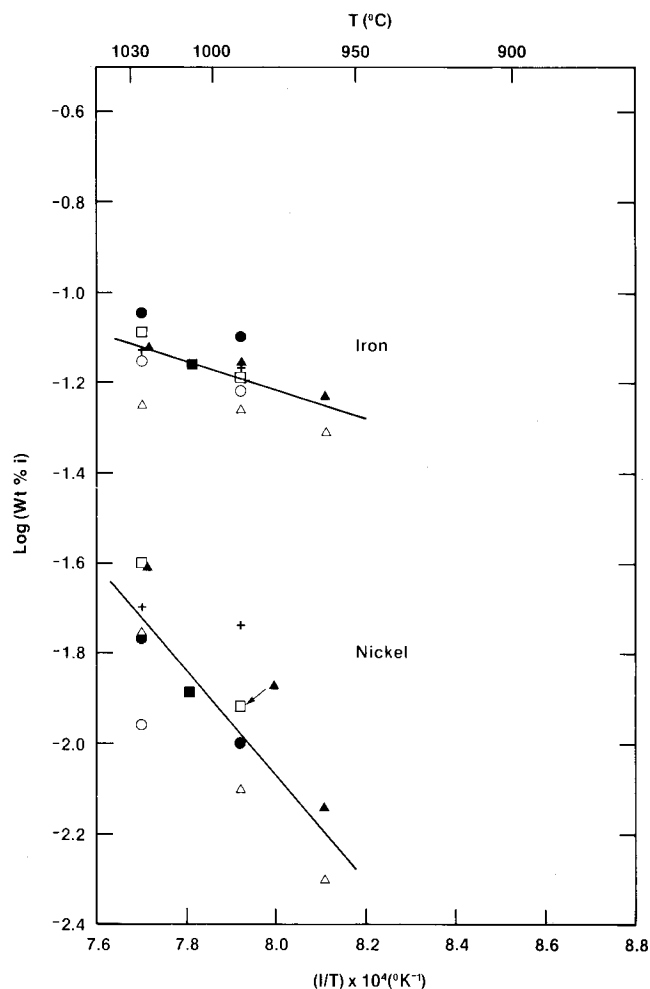


Figure 15. Least-squares fit to the solubility data for NiFe₂O₄.

There are several measurements of the solubilities of Fe₂O₃, NiO, and NiFe₂O₄ in Na₃AlF₆-Al₂O₃ melts reported in the literature. Table I compares available data for Fe₂O₃ to that from this study. There is an order of magnitude discrepancy for the literature data, and the result of this study lies between them. Actually, no measurements were made in pure Na₃AlF₆; the cryolite contained 0.5% Al₂O₃. Considering the rather large effect Al₂O₃ has on the solubilities at low concentrations of Al₂O₃, the agreement between this study and Belayeav (4) and Rolin (5) seems reasonable. The value measured by Johansen (6) seems high, but if the cryolite was extremely pure this value would be plausible. The agreement between this study and Horinouchi (7) for the melt containing 10% Al₂O₃ seems reasonable. The

major disagreement is between Belyaev and this study for the melt with 5% Al₂O₃. In defense of this study, it should be noted that concentrations greater than 0.02% are always found in bath (saturated with Al₂O₃) in Hall cells operated with NiFe₂O₄-based inert anodes. This would make the Belyaev data at least an order of magnitude too low.

Table I. Solubility of Fe₂O₃ in Na₃AlF₆-Al₂O₃ Melts at 1000°C

Investigator	Solvent		
	0% Al ₂ O ₃	5% Al ₂ O ₃	10% Al ₂ O ₃
Belyaev (4)	0.18	0.003	
Rolin (5)	0.14*		
Johansen (6)	1.07		
Horinouchi (7)			0.14
Present Study	>0.27**	>0.22**	<0.22***

*Value for 1030°C
 **Value for bath ratio = 1.3, 0.5 wt% Al₂O₃
 ***Value for bath ratio = 1.3, 4.6 wt% Al₂O₃

Table II gives a comparison of data for NiO. The agreement for Na₃AlF₆ is reasonable. In the melt with 5% Al₂O₃, Belyaev's measured solubility is greater than found in the present study, though the difference is not nearly as great as for Fe₂O₃.

Table II. Solubility of NiO in Na₃AlF₆-Al₂O₃ Melts at 1000°C

Investigator	Solvent		
	0% Al ₂ O ₃	5% Al ₂ O ₃	10% Al ₂ O ₃
Belyaev (4)	0.32	0.18	
Rolin (5)	0.15*		
Horinouchi (7)			0.18
Present Study	0.25**	0.07***	<0.07***

*Value for 1030°C
 **Value for melt with 0.6 wt% Al₂O₃
 ***Value for melt with 5.3 wt% Al₂O₃

Table III compares results for NiFe₂O₄. The agreement between this study and Horinouchi's measurement is good, and the two sets of data are probably within the combined uncertainties of the measurements. Both sets of data give free energies of formation of NiFe₂O₄ that are within the ±1000 cal/mole uncertainty for the literature data for ΔG^o(NiFe₂O₄).

Table III. Solubility of NiFe₂O₄ in Na₃AlF₆-10% Al₂O₃ Melt at 1000°C

Investigator	Fe	Ni
Horinouchi (7)	0.05	0.02
Present Study	0.058*	0.009*

*Value for melt with 6.5 wt% Al₂O₃, bath ratio 1.1

Implications to Hall Cell Operation

These solubility data have several implications regarding Hall cell operation with nickel ferrite-based inert anodes. First, the electrolyte should have as high a concentration of Al₂O₃ as possible to minimize the solubilities of the anode materials. This is not standard operating practice for commercial Hall cells and, therefore, may require some developmental effort to achieve this type of operation.

Second, because the solubility of Fe₂O₃ is greater than that for NiO, a NiFe₂O₄-based anode should be composed of NiO-rich NiFe₂O₄. The solubility of Fe and Ni from NiFe₂O₄ are inversely related to each other as follows (for stoichiometric NiFe₂O₄),

$$K = 1/[X_{Fe_2O_3} X_{NiO}] (\gamma_{Fe_2O_3} \gamma_{NiO}) \quad (14)$$

The solubility of Fe from NiFe₂O₄ will be a maximum at the Fe₂O₃-NiFe₂O₄ phase boundary, and it will be equal to the solubility of Fe₂O₃. The solubility of Ni from NiFe₂O₄ will be a maximum at the NiO-NiFe₂O₄ phase boundary, and it will be equal to the solubility of NiO. Since the solubility of NiO is less than the solubility of Fe₂O₃, the overall solubility of NiFe₂O₄ (X_{Fe₂O₃}² X_{NiO}) will be a minimum at the NiO-NiFe₂O₄ phase boundary. A slight excess of NiO added to the anode composition would accomplish this.

Third, the cell should be operated at as low a temperature as possible to minimize the anode solubility. This is true as long as the oxides are the stable solid phase in equilibrium with cryolite.

CONCLUSIONS

The solubilities of Fe₂O₃, NiO, and NiFe₂O₄ have been measured in NaF-AlF₃-CaF₂-Al₂O₃ melts. The solubilities of these oxides increase with decreasing concentration of Al₂O₃ in the melt. The solubility of Fe₂O₃ decreases with decreasing bath ratio, while the solubility of NiO does not change with bath ratio, within the uncertainty of the measurements. The partial molar enthalpies of dissolution of Fe₂O₃ and NiO in the cryolite-based melt were determined to be 33.1 and 44.6 kcal/mole, respectively. The solubility of NiFe₂O₄ is lower than the solubilities of the simple oxides. The free energy of formation of NiFe₂O₄ calculated from the solubilities of the simple oxides and the ferrite is in good agreement

with data reported in the literature, which had been determined by an independent technique. This agreement permits the solubility of the ferrite to be predicted for the entire range of melt composition and temperature for which the solubilities of simple oxides were measured. The results of this study show that a Hall cell using nickel ferrite-based inert anodes should be operated at low temperatures, the electrolyte should contain high concentrations of Al_2O_3 , and the anode should be formulated with excess NiO .

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