Aluminum - tin (Al-Sn), sodium - tin (Na-Sn), and lithium - tin (Li-Sn) alloys were prepared and used in equilibrium with the cryolitic melt to study replacement reactions. Tin was used as a noble phase to retain the equilibrated concentrations of Al, Na, and Li. The activity of the aluminum was decreased so that the Na and Li activity (concentration) could be determined. The Na and Li concentrations increased proportionally with the aluminum concentration in Sn. The results of this study provide an understanding of the Na and Li concentration and activity in the complicated aluminum - cryolitic melt system.

INTRODUCTION

Replacement reactions occur in almost every multi-component chemical system. There is no exception for aluminum - cryolitic molten salt system. Aluminum is produced commercially by electrolytic reduction of aluminum oxide dissolved in the molten cryolitic electrolyte in Hall cells. Due to the nature of the aluminum fluoride (AlF₃) - sodium fluoride (NaF) cryolitic electrolyte used, replacement reactions occur and metallic Na exists as one of the major light metal impurities in aluminum metal produced during the cell electrolysis. The Na activity and concentration in the produced aluminum have been a subject of studies by investigators for the past decades (1-6). These studies provide understandings of the stability of the aluminum/cryolite system and offer fairly accurate data in estimating thermodynamic parameters of cryolitic components. The Na concentration in molten aluminum can be predicted given a specific cryolitic melt composition (7).

Bath electrolyte components other than AlF₃ and NaF are also present in the cryolitic melt. This is due to either intentional or unintentional modification of the Hall cell bath chemistry in order to improve the current efficiency and energy consumption. Intentional addition of lithium fluoride (LiF) to the cryolitic bath -- so called “lithium
modified bath chemistry" -- is an example (8,9). The primary benefits in adding LiF to the cryolitic melt include decreased bath freezing point and increased electrical conductivity. However, LiF behaves much like NaF. The presence of LiF in the cryolitic melt also brings Li into the metal pad as an impurity. The Li concentration in aluminum is a subject of study by several investigators (7, 10).

Though different measurement techniques were used, the prior studies had a common experimental approach: measuring the Na or/and Li concentrations while varying the cryolitic melt composition and maintaining the aluminum phase at unity. Additionally, accurate determination of the sodium and lithium content of aluminum in equilibrium with the cryolite melts proves to be difficult. Different from the literature reported measurement technique for the Na and Li contents of aluminum, this study used aluminum - tin (Al-Sn), sodium - tin (Na-Sn) and lithium - tin (Li-Sn) alloys in equilibrium with the cryolitic melt. Tin was used as a noble phase to retain the equilibrated concentrations of Al, Na and Li. The activity of aluminum in the system was varied so that the Na concentration could be measured. Replacement reactions of aluminum metal with cryolitic components were studied. The relationships among the Al, Na and Li concentrations were obtained.

EXPERIMENTAL

The major pieces of equipment used in this study included a vertical electrically-powered furnace, a specially-designed and manufactured boron nitride (BN) crucible assembly, and a sample quenching apparatus. The equipment was described in detail elsewhere (11). Only a brief explanation relevant to this study is given below.

BN Crucible

A schematic view of the BN crucible used in this study is shown in Figure 1. The crucible with its lid was placed in a graphite holder and fastened with three Inconel bolts so that neither melt nor vapors of metallic species could escape from inside the crucible. The crucible assembly (with loaded samples) was hung inside the furnace tube during the test. As shown in Figure 1, during equilibration of the cryolitic melt with the metal alloy, replacement reactions occur at the metal/electrolyte interface. Reaction products are retained in the metal phase. Once an equilibrium is established, the molten sample is quenched to ambient temperature.

Sample Quenching Apparatus

A rapid quenching rate is critical for studying the "real equilibrium state" of the cryolitic melts with the Al alloys. The faster the quenching rate, the closer the quenched sample remains to the equilibrium state of the testing condition. A water-cooled fluidized
bed of Cu particles (-40 to + 80 mesh) was selected and used for quenching the BN crucible loaded with equilibrated melt samples.

Chemicals
All chemicals used were analytical grade. Cryolite (Na₃AlF₆) and aluminum fluoride (AlF₃), from CERAC, Inc., and sodium fluoride (NaF) and lithium fluoride (LiF), from Fisher Scientific, were pre-dried at 110°C for at least 24 hours before use. A typically 99.9% pure tin as 0.27 cm (1/8 inch) shot was obtained from CERAC, Inc. A grade of 99.95% pure aluminum in 1.27 cm (1/2) inch pieces was purchased from ASAR, Inc. The metal samples were used without any further treatment.

Experimental Procedures
Na-Sn, Li-Sn, and Al-Sn alloys were first prepared in a series of different compositions. They were then used to equilibrate with the cryolitic melts. The following experimental procedures were used: Once the furnace was stabilized at the temperature of interest, the BN crucible which was loaded with the initial alloy and cryolitic samples, was mounted in the crucible holder, and then manually loaded into the furnace. For each test, a total of 35 - 40 grams of metal alloy and cryolitic sample were loaded together in the crucible. Once the alloy and cryolitic melt equilibrated in the furnace for a predetermined period, the crucible was taken out and immediately immersed into the fluidized bed and quenched to ambient temperature. After quenching, the alloy and electrolyte were manually separated for chemical analysis. The content of the Na, Li, and Al in the recovered Sn phase was analyzed by inductively coupled plasma spectrometry (ICP).

RESULTS AND DISCUSSION

1. Pure Cryolite
Pure cryolite melt with no additives was studied at 1030°C. Al-Sn and Na-Sn alloys with varying concentrations were equilibrated with the pure cryolite melt. Figure 2 shows the results of the Na concentration as a function of Al concentration in the Sn phase when in equilibrium with the pure cryolite melt. In the logarithmic domain, the [Na] is a linear function of [Al] in Sn: when [Al] increased from 0.05 to 1 wt.%, the [Na] correspondingly increased from less than 1 wt.% to over 3 wt.%. The concentration of the Na is about one hundred times higher than that (0.02 wt.%) of Na in the pure Al in equilibrium with the cryolite. The aluminum concentration is about one hundred times lower than the pure aluminum phase.

The results shown in Figure 2 indicate that the Na concentration can be very high without the presence of the pure aluminum. When Al-Sn or Na-Sn alloy is equilibrated with the cryolite melt, replacement reactions occur at the metal/cryolite interface:
or

\[
\text{Na}_3\text{AlF}_6|_{\text{melt}} + \text{Al}|_{\text{Sn}} \Leftrightarrow 2\text{AlF}_3|_{\text{melt}} + 3\text{Na}|_{\text{Sn}}
\] (1)

\[
3\text{NaF}|_{\text{melt}} + \text{Al}|_{\text{Sn}} \Leftrightarrow \text{AlF}_3|_{\text{melt}} + 3\text{Na}|_{\text{Sn}}
\] (2)

For the pure cryolite composition at a constant temperature, the activity of Na is only a function of the activity of Al in Sn. The activity coefficients of Al and Na in Sn were calculated according to thermodynamic data (12). The activity of Na in the Sn phase containing Al may be expressed as (13):

\[
\ln (\gamma_{\text{Na}})|_{\text{Sn-Al}} = \ln (\gamma)|_{\text{Sn}} + N_{\text{Na}}\varepsilon_{\text{Al}}^{\text{Na}}
\] (3)

If the molar fraction of Na, \(N_{\text{Na}}\), is small, the Al - Na interaction term, \(N_{\text{Na}}\varepsilon_{\text{Al}}^{\text{Na}}\), is not significant and can be neglected when the Al content in Sn is below 1.0 wt.%, and therefore:

\[
\ln (\gamma_{\text{Na}})|_{\text{Sn-Al}} = \ln (\gamma)|_{\text{Sn}}
\] (4)

The activity of Al in Sn was calculated in a similar manner. The activity of Na in pure Al (when no Sn phase is used) was calculated according to the thermodynamic data available from the literature (14).

Figure 3 shows the relationship of Na activity as a function of aluminum activity in the cryolite/aluminum system. The activity of Na in pure Al (activity of Al is unity) using the literature data is also included. As shown in Figure 3, the activity of Na linearly increases with the activity of aluminum. The activity of Na increased from about 0.001 to 0.03 as the Al activity increased from 0.001 to 1. The linear relationship confirms that the interaction between Al and Na can be disregarded when [Al] is below 1 wt.% in the Sn phase.

2. Cryolite Ratio Effect

Cryolitic melts containing 5.0 wt.% \(\text{Al}_2\text{O}_3\) and 1.0 wt.% LiF were equilibrated with Al-Sn and Na-Sn alloys at 995°C. Cryolite molar ratio varied from 2.0 to 3.5.

Figure 4 shows the dependence of the Na concentration on that of Al in Sn. The results were obtained from a series of tests when varying the Al-Sn and Na-Sn alloys compositions and cryolite ratios. For cryolitic melts with a constant cryolite ratio, the Na concentration increased with the increase of the Al concentration in Sn. Even though a significant amount of scattering existed, a linear relationship was generally observed in the logarithm domain when the Al concentration fell below a certain value. Beyond this...
value, the Na concentration no longer increased but decreased with the increase of the Al concentration in the Sn phase.

The Na concentration is also a function of the cryolite ratio. For a fixed Al concentration, higher cryolite ratio resulted in higher Na concentration. For example, at \([\text{Al}]_{\text{Sn}} = 0.1\) wt.\%, the Na concentration, \([\text{Na}]_{\text{Sn}}\) increased from 0.05 to 2 wt.\% when the cryolite ratio varied from 2.0 to 3.5.

It is very interesting to note that there exist critical Al concentrations in the Sn phase, beyond which the concentration of Na is no longer increasing but decreasing with the increase of the Al concentration. This behavior may be related to the thermodynamics of Na and Al coexistence in Sn and the fact that Na and Al are not miscible in the liquid state.

Figure 5 shows the Na concentration when varying cryolite ratio. The Na content of pure aluminum from the literature is also presented. A non-linear relationship was obtained. An increase of the cryolite ratio (higher NaF in the cryolitic melt) resulted in a higher Na concentration in Sn. For example, when \([\text{Al}]_{\text{Sn}}\) was maintained at 0.1 wt.\%, the Na concentration, \([\text{Na}]_{\text{Sn}}\) increased from just below 0.1 wt.\% to over 1.0 wt.\% when the cryolite ratio was changed from 2.0 to 3.5. The Na content of aluminum increased from below 0.01 wt.\% to just 0.025 wt.\% when the cryolite ratio changed from 2.0 to 3.5.

For an Al - Na replacement reaction (2) at equilibrium:

\[
3\text{NaF}_{\text{melt}} + \text{Al}_{\text{Sn}} \leftrightarrow \text{AlF}_3_{\text{melt}} + 3\text{Na}_{\text{Sn}} \tag{2}
\]

The equilibrium constant, \(K\), may be expressed as:

\[
K = \frac{(\alpha_{\text{Na}}^3 \cdot \alpha_{\text{AlF}3})}{(\alpha_{\text{Al}} \cdot \alpha_{\text{NaF}3}^3)} \tag{5}
\]

and the Na activity can be expressed by:

\[
\ln \alpha_{\text{Na}} = \frac{1}{3} \ln K + \ln(\alpha_{\text{NaF}} \cdot \alpha_{\text{AlF}3}^{-1/3}) \quad + \frac{1}{3} \ln \alpha_{\text{Al}} \tag{6}
\]

The equilibrium constant, \(K\), will not change at a constant temperature and can be calculated by using the Gibbs free energy of the reaction (15). Thermodynamic data are available for calculation of the activities of NaF and AlF\(_3\) in cryolitic melts.(14, 16). The term \(\ln(\alpha_{\text{NaF}} \cdot \alpha_{\text{AlF}3}^{-1/3})\) can be expressed by an empirical equation as a function of cryolite ratio or mole fraction of the AlF\(_3\) component:

\[
(\alpha_{\text{NaF}} \cdot \alpha_{\text{AlF}3}^{-1/3}) = 6.247 - 19.207N_{\text{AlF3}} \tag{7}
\]
And the final expression of the Na activity as a function of Al activity and cryolite ratio may be expressed as:

$$\log a_{\text{Na}} = C - 19.207N_{\text{AlF}_3} + 1/3 \log a_{\text{Al}}$$ (8)

where C is constant and is only a function of temperature. Equation (8) indicates that in logarithmic domain, the Na activity linearly decreases with the AlF₃ mole fraction (increase with NaF mole fraction) and increases logarithmically with the Al activity.

Figure 6 shows the dependence of the Na activity on the Al activity in equilibrium with the cryolitic melts. A linear relationship was observed for all cases. When the Al activity, $\alpha_{\text{Al}}$, increased from 0.001 to 1, the Na activity corresponding increased from 0.0001 to about 0.1 depending on the cryolite ratio.

When the Al concentration in Sn exceeded a certain amount, the Al - Na interaction cannot be neglected. Due to the increased interaction, the Na concentration in Sn no longer increased but decreased as the Al concentration increased when in equilibrium with the cryolitic melts. The Al - Na interaction coefficient in Sn can be calculated using equation (2) and the results in Figures 4 to 6.

The cryolitic melt also contained 1.0 wt.% LiF. The replacement reaction of Al or Na with the LiF exists:

$$3\text{LiF}_{\text{melt}} + \text{Al} \leftrightarrow 3\text{Li}_{\text{Sn}} + \text{AlF}_3$$ (9)

and

$$\text{LiF}_{\text{melt}} + \text{Na}_{\text{Sn}} \leftrightarrow \text{Li}_{\text{Sn}} + \text{NaF}_{\text{melt}}$$ (10)

The relationship between the Na and Li concentrations was examined only. Figure 7 shows the [Li] as a function of [Na] in Sn when varying cryolite ratios of the cryolitic melt. Overall, [Li] linearly increased in the logarithm domain with the increase of [Na]. For an example, when [Na] increased from 0.01 to 1.0 wt.%, the [Li] correspondingly increased from 0.0001 to 0.01 wt.%. The cryolite ratio effect was not significant though higher ratio tended to decrease the concentration of Li. When the cryolite ratio increased from 2.0 to 3.5, the LiF molar fraction decreased from 0.022 to 0.020 even though the cryolitic melt contained a constant 1.0 wt.% LiF.

3. LiF Effect

Cryolitic melt containing CR=2.5 and Al₂O₃=5.0 wt.% was used to equilibrate with Na-Sn, Al-Sn, and Li-Sn alloys at 995°C. LiF concentration varied from 1.0 to 10 wt.% in the cryolitic melt. Figure 8 shows the [Li] as a function of [Na] in Sn. The [Li]
increased with [Na] in the logarithm domain. As an example, for the melt containing 2.5 wt.% LiF, the [Li] increased from 0.003 to 0.01 wt.% when the [Na] increased from 0.01 to 1.0 wt.%. Higher LiF in the melt also resulted in higher [Li]. When LiF increased from 1.0 to 10 wt.% (mole fraction from 0.02 to 0.19), an increase of a decade in the [Li] was observed.

The relationship between the Li and Na activity was also estimated in the similar way as for the Na and Al activity. Figure 9 shows the dependence of Li activity on that of the Na in Sn. A linear relationship was observed for all the cases. However, the Li activity was about 100 times lower than that of Na. For a constant Na activity, higher LiF resulted in higher Li activity in the system.

4. Discussion

The Na activity/concentration changes when the Al activity/concentration varies in the cryolitic melts. Metallic Li also exists when the cryolitic melt contains LiF. The results of these replacement reactions may be applied to understand a dynamic (non-equilibrium) Al - cryolitic system where the Al activity and cryolitic melt composition may be locally different inside the operating cells (17,18). Compositional gradients exist at the interfaces of anode gas/cryolitic melt, cryolitic melt/metal pad, and metal pad/cathode block material. The localized Na and Al content/activity in industrial cells should also follow the thermodynamic law and they are a function of cryolite ratio (excess of AlF3) and bath temperature (19). As demonstrated in this study, the Na content could be very high given a proper thermodynamic condition.

The results may also help in understanding the important role of the Na in changing the bath electrolyte and metal flow pattern and rate by influencing the interfacial phenomena (20). The change of the bath and metal flow pattern and rate would affect:

• The metal dissolution rate, which would positively or adversely affect the current efficiency of the cell. The Na content in the metal pad was used as an indicator for the current efficiency in industrial cells (21).

• The material performance of reduction cells (22). During cell electrolysis, the increased Na content in the metal pad results from the enriched Na+ at the melt/metal interface for the cell with less vigorous liquid movements. High Na content may result in higher diffusion rate of the Na into the cathode block material. For certain types of reduction cells, the activity/concentration of Na therefore plays a dominant role in the performance and life span of cathode block materials.

• The Li concentration was 10 to 100 times lower than the Na concentration even when
the cryolitic melt contained as high as 20 mole% (10 wt.%). The benefit of the LiF addition in the Hall bath electrolyte needs to be further studied.

SUMMARY

Replacement reactions of aluminum with the cryolitic melts were studied using Al-Sn, Na-Sn, and Li-Sn alloys. The relationship among the Al, Na, and Li concentrations in Sn were obtained. The following conclusions were drawn:

1. The aluminum activity/concentration was reduced from unity and varied in a reasonable range from 0.01 up to 5.0 wt.% using a Sn metal phase. The Na reactivity/concentration was measured to be from 0.001 up to 5.0 wt.% depending on the cryolitic melt composition.

2. Metallic Li exists when a LiF-modified bath chemistry is used. However, the Li magnitude was determined to be 10 to 100 times lower than Na even for the cryolitic melt containing as high as 20 mole% LiF.

3. The results demonstrate that the Na concentration can be much higher than the value of 0.025 wt.% reported in the literature given a proper condition in the cryolitic system. The Sn phase used to retain the reaction products decreases the Na activity coefficient from 10^2 in pure Al down to less than one in metal Sn. The Na activity increased with the Al activity in the Al - cryolitic melt system.

4. The results may be used to understand dynamic (non-equilibrium) operating cells where only localized equilibrium exists. The Na activity and concentration could be very high locally which may change the melt/metal flow pattern and metal dissolution rate, and therefore could positively or adversely influence the current efficiency.

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Figures:

Figure 1  A schematic view of a BN crucible loaded with equilibrated melts.

Figure 2  Relationship of Na and Al concentration in Sn when in equilibrium with pure cryolite melt at 1030°C.
Figure 3  Activity of Na as a function of Al in Sn when equilibrated with pure cryolite at 1030°C.

Figure 4  [Na] as a function of [Al] in Sn equilibrated with the cryolitic melt: CR=2.5, 5.0 wt.% Al₂O₃, and 1.0 wt.% LiF at 995°C.
Figure 5  The dependence of Na activity on the cryolite ratio at varied levels of [Al] in Sn.

Figure 6  Relationship of Na activity and Al activity when in equilibrium with the cryolitic melts at 995°C.
Figure 7  [Li] as a function of [Na] in Sn equilibrated with the cryolitic melt containing 5.0 wt.% Al₂O₃ and 1.0 wt.% LiF at 995°C.

Figure 8  [Li] as a function of [Na] in Sn equilibrated with the cryolitic melt CR=2.5, 5.0 wt.% Al₂O₃ at 995°C.
Figure 9  Li activity as a function of the Na activity in Sn in equilibrium with the cryolitic melt at 995°C.