THERMODYNAMICS OF Li₂O - LiF - CaF₂ MELTS

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ABSTRACT

Processing of aluminum-lithium alloys by electrochemical method was investigated. Thermodynamics of solubility of lithium oxide in Li₂O-LiF-CaF₂ melts was studied as a function of temperature and it was found to increase from 10.6 wt% at 1058 K to 14.8 wt% at 1133 K. The liquidus temperature of 4LiF.CaF₂ + Li₂O (saturated) melt was determined to be 1004.5 ± 2.5 K. The equilibrium phase and activity of Li₂O in the melts as a function of temperature was determined. The calculated activity coefficients of Li₂O in the melts exhibited a negative deviation from Raoult’s law.

INTRODUCTION

There is an evergrowing demand for the use of aluminum-lithium alloys in the aerospace industry, because of their light-weight and improved modulus. The increase in demand was due to rapid escalation of fuel costs; higher thrust for more fuel efficient aircraft and improved overall structural properties for Al-Li alloys over the existing aerospace structural Al-alloys of AA 2xxx and 7xxx series. Reduction in aircraft weight is one means of decreasing fuel consumption. Since majority of aircraft frames are made out of aluminum alloys, development of low-density structural aluminum alloys is of paramount interest. Each weight percent lithium added to an alloy reduces the density 3 percent and increases the elastic modulus by 6 percent(1). Addition of lithium to aluminum also improves the corrosion resistance(2). Presently two types of Al-Li alloys viz., AA 2090 and 8090 are commercially available. The present commercial method for production
of Al-Li alloys is by powder metallurgy or melting and casting methods involving the use of pure metallic lithium which is added to the molten aluminum(3). Production of Al-Li alloys by mixing the pure metal is an energy intensive and expensive process. The principal objective of the described research is to develop physico-chemical information that can be applied to the direct production of Al-Li alloys by electrochemical method.

To study the viability of a process for obtaining a metal from its oxide, it is necessary to obtain sufficient information on the solubility characteristics of the oxide in the fluoride melt. While extensive studies have been done for Al2O3 - cryolite system (4-7), very little work has been done for other oxide-halide systems. Belyayev (8) found that mixed fluorides, particularly cryolite (Na3AlF6) are good solvents for metal oxides while Stern (9) found that molten chlorides have a very limited solubility for metal oxides. Haupin (10) studied the solubility of Al2O3 in AlCl3 - LiCl melts and predicted a simple model for the reaction between the oxide and chloride to form the dissolved species. He predicted the dissolved species to be AlOCl and found that the Al2O3 solubility increases with the cube root of activity of AlCl3. Wai and Blander (11) studied the solubility of Al2O3 in eutectic LiCl - KCl containing dissolved AlCl3 using a proton activation technique. The presence of AlO+ complex species in the melt was identified and a formation constant for the AlO+ was deduced. From the solubility data, they obtained a value of 300 KJ/mole for the specific bond free energy for the Al3+ and O2- ions.

In the present study, a systematic investigation was undertaken to measure the solubilities of Li2O in LiF - CaF2 melts at different temperatures and also to find the liquidus temperature of 4LiF.CaF2 + Li2O (saturated). The solubility of Li2O in LiF - CaF2 electrolytes must be significant because it is the only dissolved oxide in the complex oxyfluoride form which is available for reduction at the anode during electrolysis. Also, it is necessary to find the liquidus temperature of 4LiF.CaF2 + Li2O (saturated) in order to determine the optimum temperature for electrolysis of Li2O in 4LiF.CaF2 melts.
EXPERIMENTAL

The solubility of Li$_2$O was investigated as a function of temperature in the range of 1058 to 1133 K in 4LiF.CaF$_2$ electrolyte. The liquidus freezing temperature of ternary Li$_2$O-LiF-CaF$_2$ melt was measured. The experimental set-up and procedure were described elsewhere (12,13) and only a brief description is given here.

Materials :

Calcium fluoride of 99.9% purity and lithium fluoride of 99.9% purity were weighed and mixed in stoichiometric proportions of 4:1 to form 75 grams of CaF$_2$ - LiF mixture. Lithium oxide of 99.8% purity was used.

Apparatus and Procedure :

The apparatus used for the solubility studies consisted of a 11.5 cm diameter stainless steel chamber with ports for evacuation, argon gas outlet and oxide additions. The chamber was heated by a 10 cm diameter kanthal wire-wound cylindrical resistance furnace. A schematic diagram of the set up used is shown in Figure 1. The CaF$_2$ - LiF mixture in 4:1 ratio was dried in dynamic vacuum at 423 K for 6 hours and then melted at 1073 K under a dry argon atmosphere for one hour in a graphite crucible. The solidified mixture was crushed and remelted under dry argon atmosphere at the required temperature till a homogeneous melt was obtained. Li$_2$O, 20% by weight of electrolyte mixture (15 g) was added to the melt. The molybdenum tube containing purified argon gas was passed at a rate of 60 to 80 cm$^3$/min by immersing it into the melt to provide a stirring effect. Samples were withdrawn through a graphite tube at selected time intervals after the addition of oxide. The solidified samples were grounded to less than 100 mesh size in an alundum vial to obtain a homogenized mixture and the powder was analyzed for the constituent elements viz., Ca, Li, F and O.

Liquidus Temperature of 4LiF.CaF$_2$ + Li$_2$O :

In order to determine the optimum temperature for electrolysis of Li$_2$O in 4LiF.CaF$_2$ melts, the liquidus temperature of 4LiF.CaF$_2$ + Li$_2$O (saturated) melt was determined. For this, the melt was held at 1093 K for
6 hours after the addition of excess Li$_2$O, using same set up discussed in the preceding section, and then cooled at the rate of 0.5 K/minute. Three sets of heating and cooling cycles were performed. A liquidus temperature of 1004.5 ± 2.5 K was obtained with a thermal arrest time of 3.5 to 4.6 minutes as shown in Table 1. The cooling curve of the sample showing a thermal arrest temperature of 1006 K and a thermal arrest time of 4.6 minutes is shown in Figure 2.

RESULTS AND DISCUSSION

**Solubility of Li$_2$O in Li$_2$O-LiF-CaF$_2$ Melts**:

The experimental data on the solubility of Li$_2$O as a function of temperature are presented in Table 2. It can be seen that the solubility of Li$_2$O increases with increase in temperature of the melt. For example, the solubility of Li$_2$O increased from 10.6 wt% at 1058 K to 14.8 wt% at 1133 K. The calculated mole fraction of Li$_2$O in the melt as a function of temperature is plotted in Figure 3. A linear relationship between ln mole fraction of Li$_2$O and temperature was obtained and given by:

\[
\ln X_{Li_2O} = 2.411 - \frac{4567.8}{T}
\]  

with a correlation coefficient of 0.98.

**Activity of Li$_2$O in the Melt**:

The liquidus freezing temperature of 4LiF.CaF$_2$ + Li$_2$O (saturated) melt is 1004.5 ± 2.5 K at 11.77 mole % of Li$_2$O. At any temperature above 1004 K, for 4LiF.CaF$_2$ + Li$_2$O (saturated) melt, solid Li$_2$O is in equilibrium with the liquid electrolyte. In other words,

\[
Li_2O \text{ (liquid, electrolyte)} = Li_2O \text{ (pure, solid)}
\]  

The partial molar free energy of Li$_2$O in the liquid electrolyte, $\Delta G_{Li_2O(l)}$, should be equal to the molar free energy of the pure solid Li$_2$O, $\Delta G_{Li_2O(s)}$. Hence,
\[ \Delta G_{Li_2O(1)} = \Delta G^0_{Li_2O(s)} + RT \ln a_{Li_2O(1)} = \Delta G^0_{Li_2O(s)} \]  \[3\]

where \( a_{Li_2O(1)} \) is the activity of Li\(_2\)O in the liquid electrolyte with respect to the pure liquid Li\(_2\)O standard state. Rearranging terms,

\[ RT \ln a_{Li_2O(1)} = \Delta G^0_{Li_2O(s)} - \Delta G^0_{Li_2O(1)} = -\Delta G^0_{m,Li_2O} \]  \[4\]

where \( \Delta G^0_{m,Li_2O} \) is the standard free energy of fusion for Li\(_2\)O at temperature \( T \) K. \( \Delta G^0_{m,Li_2O} \) was deduced from the suggested value of heat of fusion \( \Delta H^0_{m,Li_2O} = 58,576 \) J/mole, melting point of Li\(_2\)O = 1843 K and the heat capacity data(14). The following expression was obtained:

\[ \Delta G^0_{m,Li_2O} = 33127 - 25.907 T \ln T + 6.264 \times 10^3 T^2 - 9.411 \times 10^5/T + 165.556 T \] J/mole.  \[5\]

Combining equations 4 and 5, the activity and activity coefficient of Li\(_2\)O at several temperatures were calculated and presented in Table 2. As seen from the table, dissolution of Li\(_2\)O in 4LiF.CaF\(_2\) electrolyte melt exhibits a non-ideal behavior and follows a negative deviation from the Raoult's law.

**CONCLUSIONS**

The following conclusions can be made from the present experimental determination of solubility of Li\(_2\)O in 4LiF.CaF\(_2\) melt:

1) Liquidus temperature of 4LiF.CaF\(_2\) + Li\(_2\)O (saturated) melt is 1004.5 ± 2.5 K.

2) Solubility of Li\(_2\)O in Li\(_2\)O-LiF-CaF\(_2\) melts increases with increase in temperature, with a value of 10.6 wt% at 1058 K and 14.8 wt% at 1133 K.

3) Dissolution of Li\(_2\)O in 4LiF.CaF\(_2\) electrolyte melt exhibits a negative deviation from Raoult's law in the composition range studied.
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### Table 1. Liquidus Temperature of 4LiF.CaF₂ + Li₂O (saturated) Melt

| Melt Composition          | Liquidus Temperature (K) | Thermal Arrest Time (min.) |
|---------------------------|--------------------------|----------------------------|
| 4LiF.CaF₂ + Li₂O (saturated) | 1005 ± 1                  | 3.5                        |
| "                         | 1006 ± 1                  | 4.6                        |
| "                         | 1003 ± 1                  | 3.8                        |
Table 2. Solubility, Activity and Activity Coefficient of Li₂O in 4LiF.CaF₂ Melts at Different Temperatures

| Temp. (K) | 1/T x 10⁴ (K⁻¹) | Li₂O wt% | X_{Li₂O} | ln X_{Li₂O} | a_{Li₂O} | γ_{Li₂O} |
|-----------|------------------|----------|----------|-------------|---------|---------|
| 1058      | 9.450            | 10.63    | 0.147    | -1.917      | 0.069   | 0.469   |
| 1078      | 9.276            | 11.66    | 0.159    | -1.839      | 0.077   | 0.484   |
| 1093      | 9.149            | 13.20    | 0.176    | -1.737      | 0.083   | 0.473   |
| 1113      | 8.985            | 14.22    | 0.187    | -1.676      | 0.092   | 0.494   |
| 1133      | 8.826            | 14.82    | 0.193    | -1.645      | 0.102   | 0.529   |
1. Gases inlet
2. Thermocouple
3. Offgases
4. Oxide additions
5. O-ring seal
6. Thermal insulating wool
7. Kanthal heating element
8. Superalloy chamber
9. Graphite crucible
10. Bottom support brick
11. To vacuum pump

Figure 1. Sectional View of the Experimental Set-up.
Figure 2. Cooling Curve for 4LiF·CaF$_2$ + Li$_2$O (saturated) Melt Showing Thermal Arrest at 1006 K.
Figure 3. Variation of $\ln X_{\text{Li}_2\text{O}}$ in 4LiF.CaF$_2$ Melt with Temperature.