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Thermodynamic characterization of acid cryolite systems

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Abstract: Measuring of the electromotive force in molten system is used to characterize thermodynamic properties of the system at equilibrium. Values of the electromotive force are very important for the determination of activity and standard electrode potential. Investigation of the electromotive force of Al + TiB_2 and Al-Al cell was the main aim of this work leading to the characterization of acid cryolite systems. The measurements were realized using a molten aluminum electrode and the electromotive force of an electrochemical cell was investigated in electrolytes at various molar ratios (NaF/AlF_3) at equilibrium. Thermodynamic properties were measured in acid cryolite melts at three different temperatures: 800 °C, 900 °C, and 1000 °C, for all experiments.

Keywords: acid cryolite melts, aluminum electrode, electromotive force, molar ratio, standard electrode potential

Introduction

Measurement of electromotive force is used to determine thermodynamic properties in molten salt systems. The most important molten salt systems are based on trisodium hexafluoroaluminate, Na_3AlF_6. This compound, named cryolite, is industrially used as an electrolyte in aluminum production. Temperatures of primary crystallization of fluoride electrolytes with high addition of aluminum fluoride (acid cryolite melts) have relatively low melting temperatures (below 800 °C). Determination of the thermodynamic properties of given low-temperature systems is the key point in their use in industrial applications due to energy and economic reasons.

Several scientific groups studied the electromotive force in molten systems. Plambeck et al. (1967) studied the electromotive force in molten salts LiCl-KCl, NaCl-KCl, $MgCl_2$-NaCl-KCl, $AlCl_3$-NaCl-KCl, NaF-KF, Li_2SO_4-Na_2SO_4-K_2SO_4 and Li_2SO_4-K_2SO_4 characterizing the electromotive force by determining the equilibrium potential. This method is one of the most exact methods of potential determination. Jendrzejczyk-Handzlik and Fitzner (2011) studied the electromotive force in high temperature systems. They found that electrochemical measurements provide a versatile and flexible approach to measuring high temperature molten systems determining thermodynamic properties of solid or liquid phases. Moreover, it is possible to monitor concentration changes in the liquid or gas phase with suitable apparatus. Konečný et al. (1997) determined the activity of oxygen in graphitic cast iron by measuring the electromotive force with the aim to suggest and verify methods for oxygen activity measurement in melt under different conditions.

This work deals with the measurement of electromotive force of electrochemical cells Al + TiB_2, Al-Al. The results were used to characterize the thermodynamic properties of acid cryolite molten systems, which represent an alternative type of electrolytes in the aluminum industry. Changes of electromotive force in various acid cryolite melts were measured at different molar ratios (MR = $n(NaF)/n(AlF_3)$) and the measurements were performed in the temperature range from 800 °C to 1000 °C.

Material and Methods

Chemicals

The measurements were realized with high purity metal aluminum (purity 99.99 %, HiChem). Titanium diboride (TiB_2, RHP Technology GmbH) was prepared by the "hot-press" method and its density corresponded to at least 99 % of the theoretical density (Basu, 2006). Aluminum trifluoride (AlF_3, Sigma Aldrich) was purified by sublimation in a platinum crucible at 1250 °C for 20 hours. Sodium fluoride (NaF, p.a. 99.5 %, Merck), calcium fluoride (CaF_2, p.a. 99 %, Alfa Aesar) and alumina (Al_2O_3, p.a. 99.5 %, Sigma Aldrich) were annealed in a muffle furnace at (400–500) °C for (3–5) hours before use.

Experimental apparatus

The experimental electrochemical cell (Fig. 1) consisted of an alumina crucible (1) placed in the vertical furnace with a water-cooled jacket. A TiB_2 tablet (2) was placed at the bottom of the alumina crucible (1) and covered with molten aluminum (3). Above the molten aluminum cover was a layer

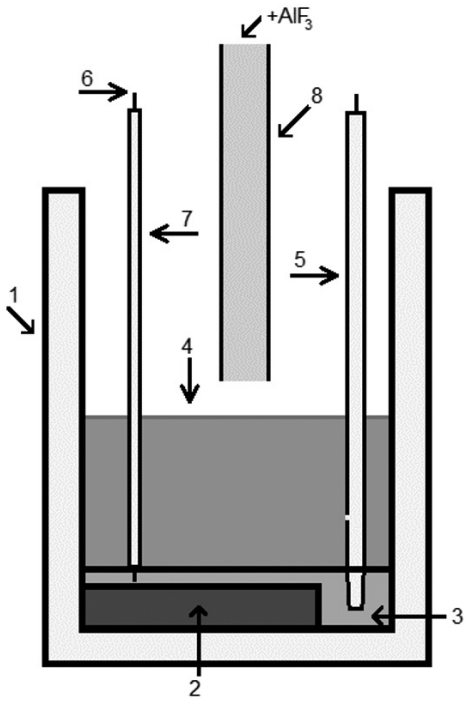


Fig. 1. Electrochemical cell: alumina crucible (1), TiB_2 tablet (2), molten aluminum (3), fluoride melt (4), aluminum reference electrode (5), tungsten contact wire (6), alumina insulating tube (7), alumina tube for AlF_3 feed (8).

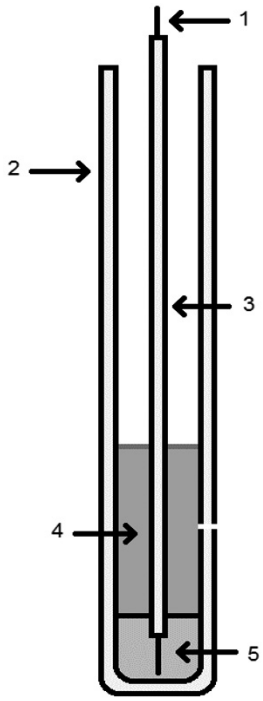


Fig. 2. Reference electrode: tungsten wire (1), outer alumina tube (2), insulating alumina tube (3), molten fluoride melt (4), molten aluminum (5).

of molten fluoride melt. A reference aluminum electrode (5) and a tungsten wire (6) were placed in the molten aluminum (3). A tungsten wire, insulated from the fluoride melt by an alumina tube (7), was used as an electrical contact. An alumina tube (8) was placed above the melt as a feeding tube for AlF_3. During the entire measurement, pure argon (99.96 %) flowed through the furnace providing inert atmosphere.

The reference aluminum electrode (Fig. 2) consists of a tungsten wire (1) placed in an alumina tube (2) with outer diameter of 0.8 cm. Molten aluminum (5) with the height of 1 cm at the bottom of the capillary was covered by an electrolyte (4) containing 2 wt. % of Al_2O_3, 5 wt. % of CaF_2, and NaF and AlF_3 in the appropriate molar ratio corresponding with the chosen temperature. The height of the molten electrolyte reached 3 cm. The end of the tungsten wire was immersed in the layer of molten aluminum, the remaining wire was insulated from the melt by an alumina tube (3) with outer diameter of 0.3 cm to prevent contact with the molten fluoride melt. A small hole in the outer alumina tube (at the height of 3 cm) ensured the contact with surrounding melt. EMF (electromotive force) between the reference electrode and the melt in the alumina crucible was measured according to changes in the molten cryolite system composition.

Experimental conditions

The experiments were based on the selection of operating temperatures and concentrations of aluminum trifluoride in the melt according to the phase diagram of system NaF-AlF_3 (Fig. 3) (Thonstad, 2001). The temperature of current aluminum production varies in the range (960—980) °C. Especially in industrial scale, it is necessary to focus on lower temperatures. Temperatures of 800 °C and 900 °C are more interesting for future innovation of aluminum production. The temperature of 1000 °C was chosen to compare temperature dependence of EMF within the currently used temperatures. Based on the phase diagram NaF-AlF_3 (Fig. 3), it is obvious that the ratio between NaF and AlF_3 varies for different temperatures representing different MR. The lowest possible MR for each studied temperature was chosen just above the temperature of the primary crystallization of molten mixture. Subsequently, AlF_3 (four times for each temperature) was added in a defined quantity to reduce MR by a value of 0.1 down to the required lower value of MR for each temperature. Three basic temperature areas were chosen. Lowest temperature of 800 °C was selected for MR in the range of 1.5—1.2 (Fig. 3, red numbers), temperature of 900 °C belongs to the MR range of (1.9—1.6) (Fig. 3, blue numbers), and temperature of 1000 °C was selected for MR values

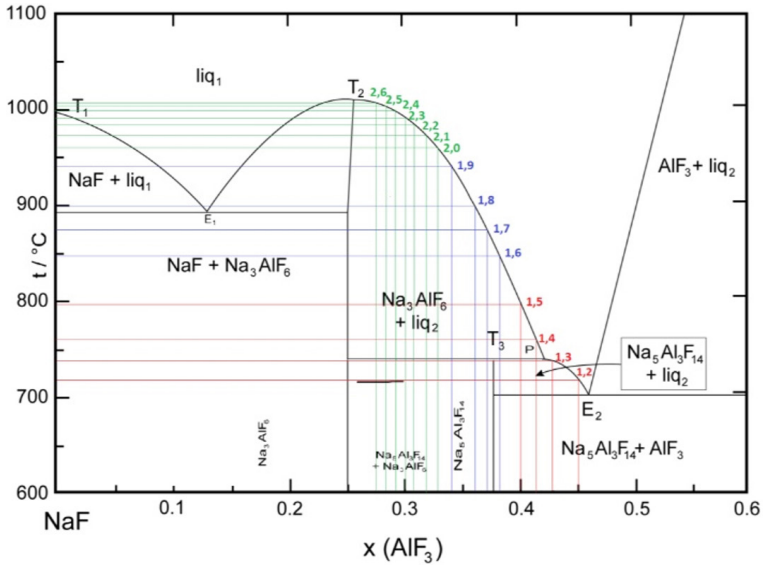


Fig 3. Phase diagram of the NaF-AlF_3 system; temperature of 800 °C was selected for MR = (1.5—1.2) (red numbers), 900 °C for MR = (1.9—1.6) (blue numbers), and 1000 °C for MR = (2.6—2.0) (green numbers) (Benköová, 2019).

from 2.6 to 2.0 (Fig. 3, green numbers). Molar ratio in the given interval was reduced from the highest chosen value of MR by adding a calculated amount of AlF_3 during the experiment. The change of MR was studied in steps of 0.1 at all three temperatures. The total weight of the electrolyte was 60 g with constant additions of 2 wt. % of Al_2O_3 and 5 wt. % of CaF_2 for all studied systems.

Results and Discussion

At all three temperatures, 800 °C, 900 °C, and 1000 °C, two parallel measurements with the same reference electrode were realized. A new alumina crucible and fresh electrolyte were used for each experiment. For comparison, EMF cell measurement without TiB_2 with a new reference electrode was also performed. The main aim was to express the standard electrode potential in the presence of TiB_2 based on the Nernst-Peters equation (Atkins, 2006; Obdržálek, 2003):

$$E_r = E_r^\circ - \frac{RT}{zF} ln \frac{a_{AlF_3}^{melt}}{a_{AlF_3}^{ref}} \quad (1)$$

Derivation of standard electrode potential was based on the measurements without TiB_2 assuming that at the beginning of each experiment, the activity of AlF_3 in the melt was the same as in the reference electrode as the electrolyte in the measuring pot and the electrode were also the same (Equation 2, derived from Equation 1):

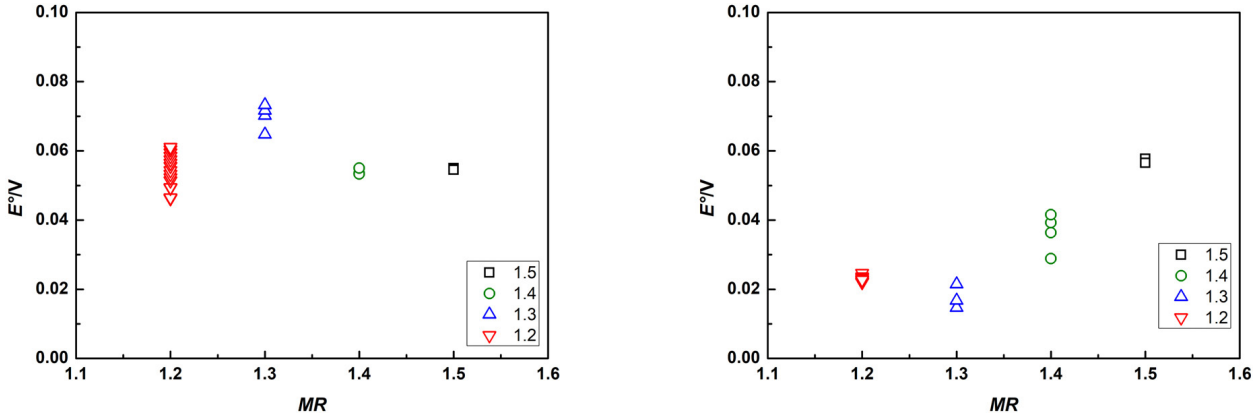
$$e^{\frac{(E_r - E_r^\circ) \times zF}{RT}} = \frac{a_{AlF_3}^{melt}}{a_{AlF_3}^{ref}} \quad (2)$$

The ratio of activity calculated from the data without TiB_2 was used to calculate the standard electrode potential in the presence of TiB_2 for a given composition (Equation 3).

$$E_r^\circ = \left(\frac{E_r}{1000}\right) + \frac{RT}{zF} ln \frac{a_{AlF_3}^{melt}}{a_{AlF_3}^{ref}} \quad (3)$$

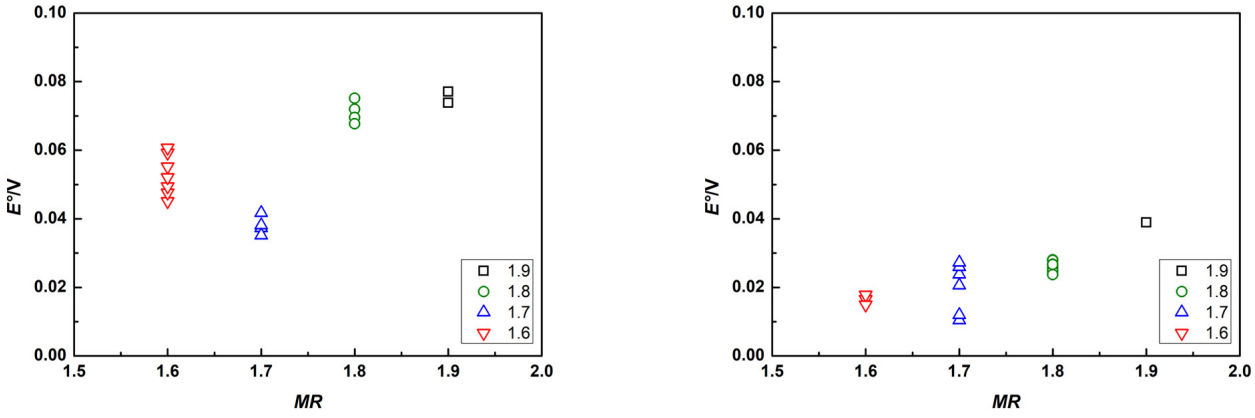
Dependences of the calculated standard electrode potentials on the molar ratio for the first and second measurements at 800 °C are shown in Figs. 3a and 3b.

In the first measurement (Fig. 4a), a new aluminum reference electrode was used. The second measurement (Fig. 4b) was performed to verify the stability of the reference electrode in a highly aggressive environment of fluoride melts. The dependence of the standard electrode potential vs. EMF in the first measurement is constant while it is exponential in the second measurement, which is probably due to the tungsten wire used as a conductor in the first measurement. In repeated measurements, the aluminum reference electrode also contained a certain proportion of dissolved tungsten. Activity of the contaminated aluminum cannot be expressed and therefore could not be considered. It can be said that the activity changes due to the slow dissolution of tungsten. Electrode potential of the reference



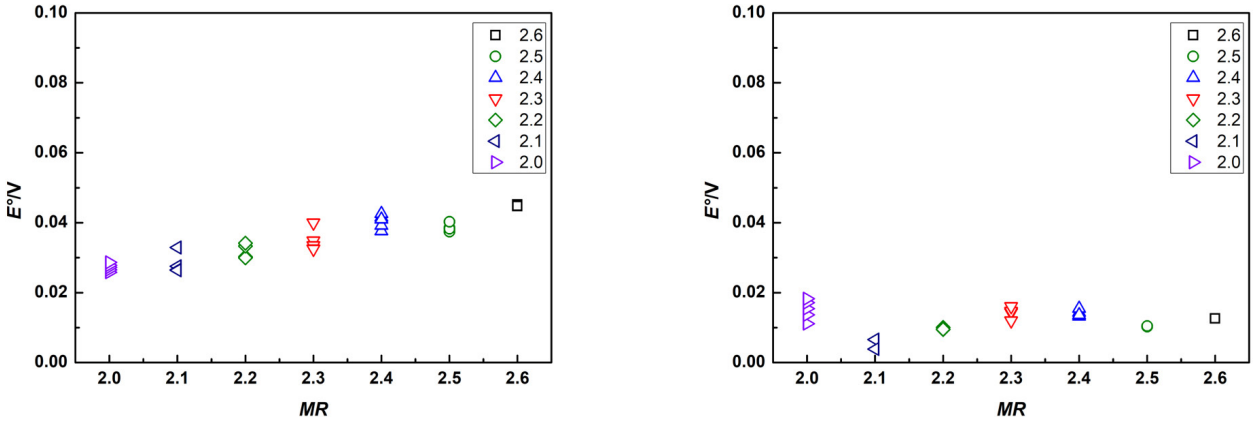
a) b)

Fig. 4. Dependence of the standard electrode potential on the molar ratio for the first **a)** and the second measurement **b)** at 800 °C.



a) b)

Fig. 5. Dependence of the standard electrode potential on the molar ratio for the first **a)** and the second measurement **b)** at 900 °C.



a) b)

Fig 6. Dependence of the standard electrode potential on the molar ratio for the first **a)** and the second measurement **b)** at 1000 °C.

electrode is not wholly stable, and the reference electrode can be used only one time as it changes with each subsequent measurement.

In Fig. 5, repeated measurements with the same reference electrode (Fig. 5b) show that the dependence is clearly linear. This can be caused by gradual dissolution of tungsten in the reference aluminum electrode.

A quasi-linear dependence of the standard electrode potential was observed in the first measurement at 1000 °C (Fig. 6a), while quasi-constant dependence was obtained in the second experiment (Fig. 6b). This behavior was explained by the EDS analysis (energy dispersive X-ray spectrophotometry) which showed that at higher temperatures (1000 °C), the dissolution of tungsten in aluminum was more intense than at 800 °C and 900 °C (Labuda, 2012). In the second measurement, the maximum rate of tungsten dissolution in aluminum was reached.

At the end of the experiments, melts from the alumina pot were characterized also by X-ray powder diffraction analysis to determine the extent of melt composition changes after the addition of AlF_3 in repeated experiments. The difference in melt composition after solidification at different temperatures was also studied (Dutrow, 2012). The rate of tungsten penetration into the reference aluminum electrode was determined by EDS analysis.

X-ray slides for repeated measurements within one temperature showed only negligible differences. Based on these results, it can be concluded that the composition of measured electrolytes was the same during the whole experiment. Analogous results were obtained at all three temperatures, even though the measured system was overheated to about (80—90) °C. Results from EDS are shown in Table 1.

Tab. 1. Quantities of tungsten in quasi-reference aluminum electrode at the measured edge / center of aluminum pool at temperatures of 800 °C, 900 °C, and 1000 °C.

Sample	Measured edge/center	Quantity W/wt. %
800 °C	edge	0,9 ±0,1
	center	1,3 ±0,2
900 °C	edge	5,4 ±0,2
	center	12,1 ±0,2
1000 °C	edge	15,6 ±0,2
	center	31,8 ±0,2

Table 1 shows that at 800 °C the tungsten content in aluminum in the middle of the sample is about 1.3 wt. %, while it is only 0.9 wt. % at the edge of the sample. At 900 °C, the dissolution rate of tungsten is higher and the tungsten content at the edge is 5.4 wt. %, while it increases to about 12.1 wt. % at the center of the sample. The analysis shows the dependence of tungsten dissolution in aluminum on temperature. At the lowest temperature of 800 °C, tungsten dissolved in aluminum much more slowly than at the highest temperature of 1000 °C.

Conclusion

This work is focused on measuring the electromotive force of the electrochemical cell Al + TiB_2, Al-Al to characterize thermodynamic properties of acidic cryolite systems. These types of fluoride electrolytes with high addition of AlF_3 have lower melting temperatures than those used currently in aluminum industry. They seem to be a perspective electrolyte in the innovation of aluminum production technology which includes TiB_2 as an inert cathode material.

Electromotive force of cell Al + TiB_2, Al-Al was measured in different types of sodium fluoride melts with gradual change of MR in a wide temperature range (from 800 °C to 1000 °C). Based on the electromotive force of the cell without TiB_2, the ratio of AlF_3 activity in the melt to that in the reference electrode was determined. Standard electrode potential of the system in the presence of TiB_2 for the acidic cryolite electrolytes composition was determined at 800 °C, 900 °C, and 1000 °C on the obtained ratio of activities.

At 800 °C, the standard electrode potential deviation was calculated as an average for the first measurement to be 57 mV with standard deviation of 7 mV and for the second measurement it was 26 mV with standard deviation of 16 mV. In the second system, at 900 °C, the standard electrode potential deviation was found to be 52 mV on average and the standard deviation was 17 mV. In repeated measurements, the value was 37 mV with standard deviation of 21 mV. At the temperature of 1000 °C, after the addition of all doses of aluminum fluoride, the deviation of the standard electrode potential for the first measurement was found to be 35 mV with the standard deviation of 6 mV. In the second measurement, the standard potential deviation value was 14 mV and the standard deviation was 5 mV. This temperature was the highest and therefore the tungsten dissolution into the aluminum electrode was much more intense.

Acknowledgement

This work was supported by the Ministry of Education, Science, Research and Sport of the SR: VEGA 1/0343/19; and the Slovak Research and Development Agency: APVV-17-0183.

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