Used method of isothermal saturation solubility of aluminium oxide in alkali and alkaline-salt melts has been investigated at temperature range 673 - 873 K. It was determined that solubility of Al₂O₃ in the order of melts LiOH - KOH - NaOH - (0.5KOH - 0.5NaOH) are increased. The effect of temperature on the Al₂O₃ solubility in alkali melts are described of the equation of straight line ln C = A - B/T, where C is concentration of the Al₂O₃ in the melts, mole fract., A and B are constants. It was indicated that when alumina is dissolved in alkali melts, the solutes are alkaline meta-aluminates. The salt additions of sodium chloride, potassium chloride, sodium carbonate and sodium nitrate to sodium hydroxide melt are decreased the solubility of alumina. It was calculated the thermodynamic parameters of process solubility of aluminium oxide in alkali hydroxide melts.

INTRODUCTION

In the past melts of alkali hydroxides and their mixture with salts were widely used in industry for removing alumina-based ceramics from metal surfaces (1). Besides the regularity of process solubility these systems are of interest for ionic melts chemistry. Only a few papers addressing the interaction of aluminium oxide with alkali metal hydroxides have been published (2 - 6). Goret and Tremillon (2) measured the solubility of alumina in a molten eutectic mixture of sodium and potassium hydroxides at 500 K. They proposed that alumina dissolved with chemical interaction and production of sodium meta-aluminates. In (3 - 6) the kinetics of interaction of aluminium oxide with alkali hydroxides by differential thermogravimetric method are reported. It was shown that in this process the only products are alkaline meta-aluminates. However, in the literature there are no data on the solubility of alumina in alkali and alkaline-salt melts. This investigation was undertaken to examine the process in this systems.
EXPERIMENTAL

Chemicals. The following chemicals were used sodium, potassium and lithium hydroxides, sodium and potassium chlorides, sodium nitrate, sodium carbonate and aluminium oxide analytical grade. The hydroxide of alkali metals was dried at 723 - 773 K. The melting points of these chemicals are 593, 672, 745 K respectively for NaOH, KOH, LiOH. The concentrations of water in these alkali hydroxides are 0.02, 0.08, 0.02 wt.% for NaOH, KOH, LiOH, respectively. The sodium and potassium chlorides, sodium carbonate and sodium nitrate were dried at 500 - 550 K for of 2 - 3 h. The aluminium oxide (99.8 % Al₂O₃, particle size ~ 100 μm) was dried at 850 K for 5 h.

Experimental procedure. The solubility of aluminium oxide has been determined by the method of isothermal saturation (7, 8). The experiments were performed as follows. A nickel crucible was used and filled with alkali hydroxides or alkaline–salt mixtures (80 - 100 g) and placed in vertical tube furnace. The temperature was measured chromel–alumel thermocouple located in the melt. The temperature of the melt was determined with an uncertainty of ±2 K. Into the solvent was added aluminium oxide in excess relative to saturation and mixed for 30 min. The equilibration time for Al₂O₃ dissolution was determined by measuring the oxide content of the molten mixtures as a function of time. Melt samples for analysis were withdrawn from the melts using quartz tube (φ = 12 - 13 mm). The samples were analyzed for aluminium content by atomic absorption spectrophotometry using a spectrophotometer S - 115 (made in USSR). It was found that to ensure alumina saturation 2.5 - 3.0 h were required (Fig. 1).

Fig. 1. Alumina dissolution as a function of time. 1, LiOH; 2, KOH; 3, NaOH at a temperature 773 K.
RESULTS AND DISCUSSION

Aluminium oxide solubility has been determined in alkali metal hydroxide melts (LiOH, KOH, NaOH, 0.5NaOH-0.5KOH), alkaline-salt melts (NaOH-NaCl, NaOH-KCl, NaOH-NaNO₃). The effect of temperature on the solubility of alumina in (LiOH, KOH, NaOH, 0.5NaOH-0.5KOH, NaOH-NaCl, NaOH-KCl, NaOH-NaNO₃) was investigated in the temperature range 673 - 873 K. Results are presented in Table 1 and Table 2. The influence of salt additions was studied in (NaOH-NaCl, NaOH-KCl, NaOH-NaNO₃, NaOH - Na₂CO₃) molten systems at 773 K. The range of concentration of salts are from 0.0 to 0.25 mole fract. Results are given in Fig. 2.

Table 1. Solubility of aluminium oxide in alkali hydroxide melts.

| Melts          | Solubility of Al₂O₃ (mole fract. x 10⁴) at a temperature of (K) |
|----------------|---------------------------------------------------------------|
|                | 673    | 723    | 748    | 773    | 798    | 823    | 848    | 873    |
| LiOH           | —      | —      | —      | 1.65   | 2.53   | 3.75   | 5.35   | 7.68   |
| KOH            | —      | 0.85   | 1.36   | 2.02   | 3.08   | 4.77   | 6.40   | 9.07   |
| NaOH           | 0.765  | 1.69   | 2.71   | 4.08   | 6.10   | 8.80   | 12.3   | 17.4   |
| 0.5NaOH-0.5KOH | 0.842  | 2.86   | —      | 7.10   | —      | 18.2   | —      | 39.0   |

Fig. 2. Solubility of aluminium oxide as a function of concentration of added salt. 1, NaNO₃; 2, NaCl; 3, KCl; 4, Na₂CO₃.

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Table 2. Solubility of aluminium oxide in alkaline–salt melts.
Concentration of salt additions is 0.10 mole fract.

| Melts          | Solubility of Al₂O₃ (mole fract. x 10⁴) at a temperature of (K) |
|----------------|---------------------------------------------------------------|
|                | 673   | 723   | 773   | 823   | 873   |
| NaOH           | 0.765 | 1.69  | 4.08  | 8.80  | 17.4  |
| NaOH–NaCl      | 0.439 | 0.983 | 2.34  | 5.06  | 10.1  |
| NaOH–KCl       | 0.574 | 1.17  | 2.61  | 5.73  | 11.2  |
| NaOH–NaNO₃     | 0.423 | 0.934 | 2.27  | 4.85  | 9.60  |

Our data indicate that the solubility of aluminium oxide was determined by the temperature and nature of the solvent. Considering the high enthalpy of fusion of Al₂O₃, the solubility shows the expected increase with temperature. Knowledge the Al₂O₃ liquidus line is obtained from following equation:

\[
\frac{d (\ln a_{\text{sat}}^{\text{Al}_2\text{O}_3})}{d (1/T)} = - \frac{\Delta H_f^o (\text{Al}_2\text{O}_3)}{R},
\]

where \( \Delta H_f^o (\text{Al}_2\text{O}_3) \) is the enthalpy of fusion for aluminium oxide, \( a_{\text{sat}}^{\text{Al}_2\text{O}_3} \) is the activity of Al₂O₃ in the melt using pure liquid alumina as standard state. In our case the good experimental data on the solubility were obtained and fitted well the equation of a straight line \( \ln C = A - B/T \), where \( C \) is the concentration of Al₂O₃ in molten solution, mole fract. (Fig. 3), \( A \) and \( B \) are constants. Using the method of least squares (\( P = 0.95 \)) the following equations were obtained:

\[
\begin{align*}
\text{NaOH} & \quad \ln C = 4.44 - 9550.9/T & r = 0.9971 & [2] \\
\text{KOH} & \quad \ln C = 4.35 - 9928.9/T & r = 0.9998 & [3] \\
\text{LiOH} & \quad \ln C = 5.31 - 10904.6/T & r = 0.9806 & [4] \\
(0.5\text{NaOH} - 0.5\text{KOH}) & \quad \ln C = 7.31 - 11219.1/T & r = 0.9994 & [5]
\end{align*}
\]

where \( r \) is the correlation coefficient.

It was found that the solubility of aluminium oxide increased in the order LiOH, KOH – NaOH - (0.5NaOH - 0.5KOH). It can be explain of different relation alkali hydroxide to alumina.

In (9, 10) it was proposed that use of the values of the average orbital electronegativity \( \chi \) was required to find the correlation between the solubility and properties of the system. Witing (9, 10) considered that in a system with chemical interaction there exists a correlation between the solubility of the substances in an ionic melt and the absolute difference in the average orbital electronegativities of the components of the system. We find that as the absolute difference in the average orbital electronegativities of alumina and molten solvent \( (\Delta \chi) \) increased the solubility of Al₂O₃ decreases.
| Property | LiOH | KOH | NaOH | (0.5NaOH–0.5KOH) |
|----------|------|-----|------|-----------------|
| 12 eV    | 0.12 | 0.09| 0.05 | 0.02            |
| Cx 10^4, mole fract. at 773 K | 1.65 | 2.02| 4.08 | 7.10            |

Fig. 3. Solubility of alumina as a function of 1/T. 1, LiOH; 2, KOH; 3, NaOH; 4, 0.5NaOH - 0.5KOH

As a rule, industry uses alkaline–salt melts (1) and therefore there is a need to research the influence of salt additions (such as sodium and potassium chlorides, sodium nitrate, sodium carbonate) on the solubility of aluminium oxide. The results of our experiments are presented in Table 2 and Fig. 2.

The salt additions, we used reduced the solubility of alumina when compared with the solubility of Al₂O₃ in molten sodium hydroxide. It was shown that in the order of the melts (NaOH - Na₂CO₃) - (NaOH-KCl) - (NaOH-NaCl) - (NaOH-NaNO₃) the content of aluminium oxide in the melts decreased. This is attributed to the salt additions reducing the effect of sodium hydroxide towards alumina, both through dilution and complex formation in the (NaOH-NaNO₃) system (1).

Previously a thermodynamics method has been widely used to describe the phase equilibrium in many-components systems (11). This method is based on the well-known
Gibbs rule concerning equality of chemical potential in solid ($\mu_S$) and saturated solution ($\mu_L$):

$$\mu_S = \mu_L = \Delta G^o_S = \Delta G^o_L,$$  \[6\]

When a solid substance deliquesces its partial molar Gibbs energy $\Delta G_i$ can be determined by the following equation:

$$\Delta G_i = \Delta G_{i}^{id} + \Delta G_{i}^{E} = -\Delta G_{ir}^o,$$ \[7\]

where $\Delta G_{i}^{id}$ is the partial molar Gibbs energy of component $i$ in the ideal solution, $\Delta G_{i}^{E}$ is the excess partial molar Gibbs energy of component $i$, which indicates the deviation from ideal solution, and $\Delta G_{ir}^o$ is the change of free energy of component $i$ upon its transfer into the solution \(11\). For the determination of the enthalpy and entropy part of $\Delta G_{ir}^o$ the following thermochemical cycle was employed \(12\):

$$\Delta H_{ir}^o = \int_{T}^{T_f} C^o_p dT + \Delta H_f^o \frac{C^o_p}{T_f} dT,$$

$$\Delta S_{ir}^o = \int_{T}^{T_f} C^o_v dT + \Delta S_f^o \frac{C^o_v}{T_f} dT,$$ \[8\]

where $\Delta H_{ir}^o$ and $\Delta S_{ir}^o$ are the enthalpy and entropy contribution in $\Delta G_{ir}^o$, $\int_{T}^{T_f} \Delta C^o_p dT$ and $\int_{T}^{T_f} \Delta C^o_v dT$ are the change in enthalpy and entropy upon raising the solid from temperature $T$ to fused temperature $T_f$, $\Delta H_f^o$ and $\Delta S_f^o$ are the enthalpy and entropy of fused, $\int_{T_f}^{T} \Delta C^o_p dT$ and $\int_{T_f}^{T} \Delta C^o_v dT$ are the change in enthalpy and entropy upon taken the solid from fused temperature $T_f$ to temperature $T$, $C^o_p$ is heat capacity of solid, $C^o_v = \text{const.}$ is the heat capacity of the liquid at the temperature of fusion.
If we combine the equations [7] and [8] we can calculate the excess partial molar Gibbs energy of aluminium oxide in the alkali melt solutions. From these equations we calculated the enthalpy \( \Delta H_f^E \) and entropy \( \Delta S_f^E \) parts of the excess partial molar Gibbs energy \( \Delta G_f^E \) of alumina in the alkali melts solutions. For this calculations we used the thermodynamics data from (13) and obtained:

| Melts       | \( \Delta H_f^E \), J/mole\(^{-1} \) | \( \Delta S_f^E \), JK\(^{-1}\)mole\(^{-1} \) |
|-------------|-----------------------------------|---------------------------------|
| NaOH        | 5742.6±5                          | 65.82±2                         |
| KOH         | 8885.3±5                          | 65.08±2                         |
| LiOH        | 16997.2±10                        | 73.06±5                         |
| 0.5NaOH-0.5KOH | 19612.0±10                      | 89.70±5                         |

These results indicate that alumina dissolution occurs with strong chemical interaction. Using X-ray analysis were found that the solute form of aluminium oxide were the correspondly alkali meta-aluminates. Using the method proposed in (14) we calculated the values of the enthalpy and entropy of fusion of meta-aluminates. The data obtained are comparable to the values of the enthalpy and entropy of fusion from (13) (see Table 3).

| Substances | Experimental data | Literature data (13) |
|------------|------------------|----------------------|
|            | \( \Delta H_f^o \), kJ/mole\(^{-1} \) | \( \Delta S_f^o \), JK\(^{-1}\)mole\(^{-1} \) | \( \Delta H_f^o \), kJ/mole\(^{-1} \) | \( \Delta S_f^o \), JK\(^{-1}\)mole\(^{-1} \) |
| NaAlO\(_2\) | 77.90            | 41.80                | 83.720                     | 48.590                     |
| KAlO\(_2\)  | 82.40            | 41.80                | 82.000                     | 41.289                     |
| LiAlO\(_2\) | 85.90            | 44.48                | 87.864                     | 46.662                     |

On the basis of our experimental data we propose a model for the aluminium oxide solubility in these melts. According this model alumina dissolution follows the equilibria:

\[
\text{Al}_2\text{O}_3\text{(s)} + 2\text{MeOH}_{(l)} \leftrightarrow 2\text{MeAlO}_2\text{(s)} + \text{H}_2\text{O}, \\
\text{MeAlO}_2\text{(s)} \leftrightarrow \text{Me}^+_{(l)} + \text{AlO}_2^-_{(l)}.
\]

Thus using the method of isothermal saturation the aluminium oxide in alkali and alkaline-salt melts has been investigated over the temperature range 673 - 873 K. It was shown that when aluminium oxide dissolved, the solute is alkali meta-aluminates. This sheds gives new data which is impotent for industry and molten salt chemistry. The model proposed in this article may used for the explanation of solubility process for a solid in melts having strong chemical interactions between solid and solvent.
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