ON THE SOLUBILITY OF LANTHANUM OXIDE IN MOLTEN ALKALI FLUORIDES

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The solubilities of lanthanum oxide in LiF, NaF, KF and eutectic melt LiF–NaF–KF (46.5 mole% LiF; 11.5 mole% NaF and 42.0 mole% KF) were measured in order to find the suitable electrolyte for electrodeposition of lanthanum. Solidus-liquidus lines were obtained by the method of thermal analysis. The solubility of lanthanum oxide in alkali fluorides is rather low and decreases in the order LiF>NaF>KF.

It was found that lanthanum oxide reacts with the components of the melt. LaOF and alkali metal oxide are formed during dissolution of La_2O_3 in the melt.

Introduction

Treatment of the spent nuclear fuel is one of the alternatives to the present storage of fuel in deep geological caves. The basic idea of the treatment is based on the transmutation of radionuclides that have a long radioactive period into the nuclides with short period. The possibility of chemical separation of long-living and short-living nuclides is also under study. Components forming spent fuel can be separated on the basis of their different physical and/or electrochemical properties (solubility, evaporation, formation of alloys, electrochemical deposition potentials, etc.). A promising way of separation of metals from spent oxide nuclear fuels can be based on their electrolysis in fluoride melts. It is known that molten alkali fluorides (for instance cryolite, lithium fluoride, sodium fluoride or potassium fluoride) are good solvents for oxides.

This work is a part of a project dealing with electroseparation of the components forming the spent nuclear fuel. Lanthanum compounds dissolved in fluoride melts were chosen as a model system. This paper deals with the solubility and phase diagrams of the systems lanthanum oxide – molten alkali fluoride. No data on the solubility or phase diagrams of the mentioned systems are available. Only a few data on solubility of other lanthanide oxides (CeO_2, Sm_2O_3, Nd_2O_3) are known [1].

The solubilities of CeO_2 and Sm_2O_3 in NaF–KF melt and CeO_2, Sm_2O_3 and Nd_2O_3 in cryolite (Na_3AlF_6) were investigated by Berul and Voskresenskaya [1]. It was found that oxides of these trivalent lanthanides form LnF_3 and $LnOF$ (Ln=Sm, Nd) during their dissolution. In the case of samarium the formation of Na_3SmF_6 in NaF–KF melt was proposed. In cryolitic melts the formation of lanthanide oxyfluorocomplexes was mentioned. Stefanidaki *et al.* [2] studied the electrodeposition of neodymium in $LiF–NdF_3$, $LiF–Nd_2O_3$ and $LiF–NdF_3–Nd_2O_3$ melts. They found that neodymium oxyfluorides might be formed when neodymium oxide is added to the molten LiF.

Experimental

The temperatures of phase transitions were determined by the means of thermal analysis, recording the cooling and heating curves of mixtures at 2–5°C min^{-1} in a resistance furnace with an adjustable cooling rate. A platinum crucible containing 30 g of sample was placed into the furnace which was pre-heated to the temperature of fusion of pure alkali fluoride. (At the compositions where crystallization of other substance than alkali fluoride was expected, the temperature was higher). The sample was kept for 3 h at the chosen temperature in the closed platinum crucible and melt was regularly stirred by a platinum ladle. The sample was slowly cooled after that time. The temperature was measured by a PtRh10-Pt thermocouple which was calibrated to the melting points of NaF, $BaCl_2$, NaCl, KCl, LiF and Na_2SO_4. The measured transition temperatures were reproducible within ±2°C and they are listed in Table 1.

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Table 1 Measured transition temperatures in the systems MF–La$_2$O$_3$ (M=Li, Na, K) and (LiF–NaF–KF)$_{eut}$–La$_2$O$_3$. (t_{pc} – temperature of primary crystallization; t_e – eutectic temperature)

x (La$_2$O$_3$)	t_{pc}/°C	t_e/°C
LiF–La$_2$O$_3$		
0	848	
0.01	840.1	827.4
0.01	841.3	828.7
0.01	840.9	828.2
0.015	836.3	
0.02		827.9
0.02	832.4	828.3
0.025	833.8	
0.03	850.3	828.2
0.03		830
0.05		829.2
0.06		828.6
0.06		829.4
0.07		828.4
0.07		828.8
0.08		829.1
NaF–La$_2$O$_3$		
0	996	
0.005	992	979.8
0.01	987.8	981.4
0.01	988	980.2
0.01	988.5	980.6
0.01		980
0.02	982.6	980.6
0.02	981.4	979.3
0.025	994.6	
0.04		982.3
0.05		979.4
0.06		982.4
0.07		980.6

The following chemicals were used: LiF (Merck, Suprapur), NaF (Lachema, analytical grade), AlF$_3$, KF, La$_2$O$_3$ (Mikrochem, pure) and P$_2$O$_5$ (Mikrochem, analytical grade). LiF and NaF were dried in a drying oven at 600°C for 2 h; La$_2$O$_3$ and KF were dried in a vacuum drying oven in the presence of P$_2$O$_5$ for 1 week; AlF$_3$ was purified by sublimation.

The samples of the melt were analysed by X-ray diffraction (STOE automated theta/theta diffractometer, Germany, CoK$_{\alpha_1}$ radiation, λ=0.17902 nm) from 5–80° 2θ. The positions of the basal reflections were determined by Bede ZDS program.

Table 1 Continued

KF–La$_2$O$_3$		
0	858	
0.002	856.2	849.4
0.005	853.8	849.6
0.005	854.3	849.8
0.01	850.8	
0.01	850.1	
0.01	850.3	
0.015	859.6	849.7
0.02	870.8	849.1
0.02	870.4	849.3
0.03		849.8
0.04		849.6
0.04		849.4
(LiF–NaF–KF)$_{eut}$–La$_2$O$_3$		
0	454	
0.005	452.3	446.6
0.01	449.4	446.5
0.015	447.2	
0.02	453.9	447.3
0.03	470	446.5
0.04	489.5	446.2
0.05	512.7	444.8
0.06	535.2	446

Results and discussion

Solubility of lanthanum oxide in molten alkali fluorides is lower than 3 mole%. Therefore only parts of the phase diagrams near pure alkali fluorides were measured. A thermodynamic model suitable for description of the phase diagrams near the pure components was adopted. The thermodynamic model is based on the modified LeChatelier–Schröder equation [3, 4]

$$\ln x(MF) = \frac{\Delta H_{fus}^0(MF)}{Rk_{St}}\left(\frac{1}{T_{fus}(MF)} - \frac{1}{T}\right) \quad (1)$$

where $x(MF)$ is the mole fraction of alkali fluoride in the molten mixture, $\Delta H_{fus}(MF)$ is the enthalpy of fusion of the alkali fluoride, $T_{fus}(MF)$ is the temperature of fusion of the pure alkali fluoride and T is the temperature of primary crystallization of the molten mixture. R is the gas constant and k_{St} is the Stortenbeker factor [5] which equals the number of new foreign particles that La$_2$O$_3$ brings into the solution.
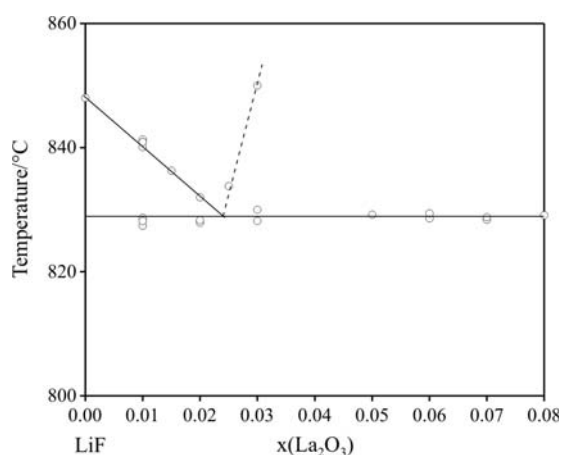
This 'cryoscopic' model is valid only in the composition range where the melt contains only a low concentration of the additive (La$_2$O$_3$). As can be seen

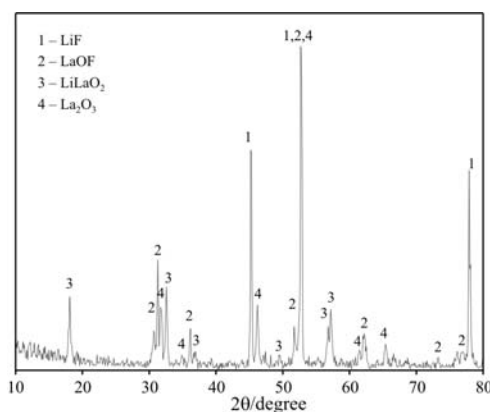from Figs 1, 3 and 5 this model describes the experimental data quite well.

System LiF–La$_2$O$_3$

The liquidus temperatures in the system LiF–La$_2$O$_3$ were measured up to 8 mole% La$_2$O$_3$. The measured part of the phase diagram is shown in Fig. 1. Temperatures of primary crystallization were recorded only at the composition up to 3 mole% La$_2$O$_3$. At higher concentrations, lanthanum oxide was not dissolved completely even after 3 h at the heating temperature of 1050°C. It means that the dissolution of lanthanum oxide is very slow. The eutectic temperature and composition are 829°C and 2.4 mole% La$_2$O$_3$, respectively. The calculation was made under assumption that lanthanum oxide brings two new particles into the melt (k_{St}=2). This assumption gives the best agreement between the measured and calculated data. From the obtained results it follows that the chemical reaction has to occur during dissolution of lanthanum oxide.

In order to identify the main substances in the melt, X-ray diffraction analysis of the sample containing 4 mole% of La$_2$O$_3$ was made. The melt was equilibrated for 3 h and then quenched. The XRD record is shown in Fig. 2. It follows that the melt consisted of LiF, LaOF, LiLaO$_2$ and some undissolved La$_2$O$_3$. It can be assumed that the following chemical reaction takes place in the system:

$$LiF+La_2O_3=LaOF+LiLaO_2 \qquad (2)$$
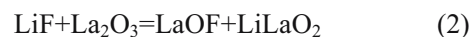
However, as in the case of aluminates [6], LiLaO$_2$ can be actually a mixed oxide of spinel type (Li$_2$O·La$_2$O$_3$) which is formed during solidification. Dissolution of La$_2$O$_3$ can be described by the reaction scheme

$$2LiF+La_2O_3=2LaOF+Li_2O \qquad (3)$$

According to the Berul and Voskresenskaya [1] also another reactions may occur:

$$6LiF+La_2O_3=3Li_2O+2LaF_3 \qquad (4)$$

$$12LiF+La_2O_3=2Li_3LaF_6+3Li_2O \qquad (5)$$
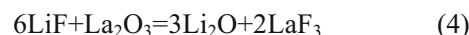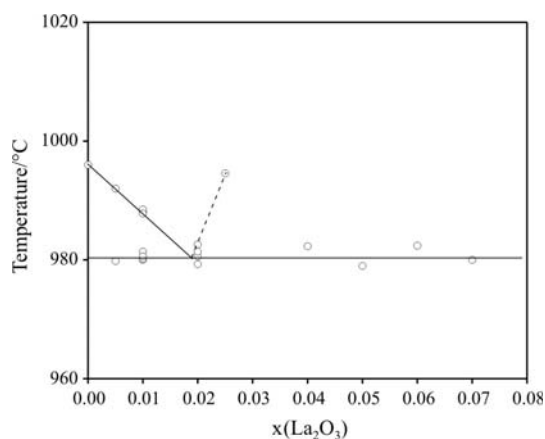
However, according to van der Meer *et al.* [7] lithium lanthanide cryolites (Li$_3$LnF$_6$) are not formed from elements with atomic numbers from 57 to 62 (La–Sm). It means that the reaction (5) is not probable. Standard reaction Gibbs energy of reaction (4) is positive $(\Delta_r G^{\varnothing}_{1173K}(3)=340.112$ kJ mol$^{-1})$ and LaF$_3$ was not recorded in the XRD pattern. This implicates that reaction (4) is not probable.

System NaF–La$_2$O$_3$

The liquidus temperatures in the system NaF–La$_2$O$_3$ were measured up to 7 mole% La$_2$O$_3$. The measured part of the phase diagram is shown in Fig. 3. Temperatures of primary crystallization were recorded only at the composition up to 2.5 mole% La$_2$O$_3$. As in the case of LiF–La$_2$O$_3$ system higher concentrations of the lanthanum oxide did not dissolve completely even after 3 h at 1050°C. The eutectic temperature and composition are 980°C and 1.9 mole% La$_2$O$_3$, respectively. The calculation was made under the assumption that lanthanum oxide brings two new particles into the melt. This assumption gives the best agreement between the measured and calculated data.

In order to identify the main species in the melt, X-ray diffraction analysis of the solidified samples containing 4 and 8 mole% of La$_2$O$_3$, respectively, was made. The melt was equilibrated for 3 h and then quenched. The XRD record of the sample containing 8 mole% La$_2$O$_3$ is shown in Fig. 4. The sample consisted of NaF, LaOF, Na$_2$O and some undissolved La$_2$O$_3$. This means that in the system NaF–La$_2$O$_3$ proceed similar chemical reaction as in the system LiF–La$_2$O$_3$:

$$2NaF+La_2O_3=2LaOF+Na_2O \qquad (6)$$

Fig. 1 LiF-rich part of the phase diagram of the system LiF–La$_2$O$_3$. ○ – experimental; full line – calculated

Fig. 2 XRD pattern of quenched melt of the system LiF–La$_2$O$_3$ (4 mole% of La$_2$O$_3$)
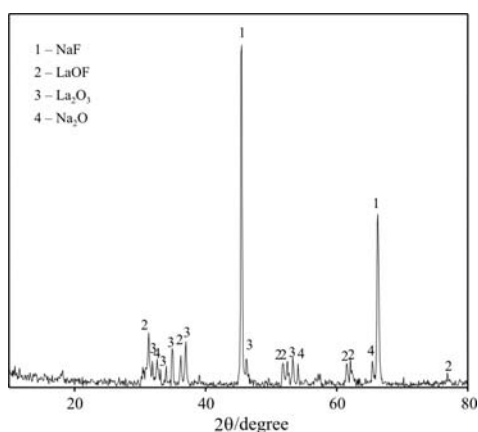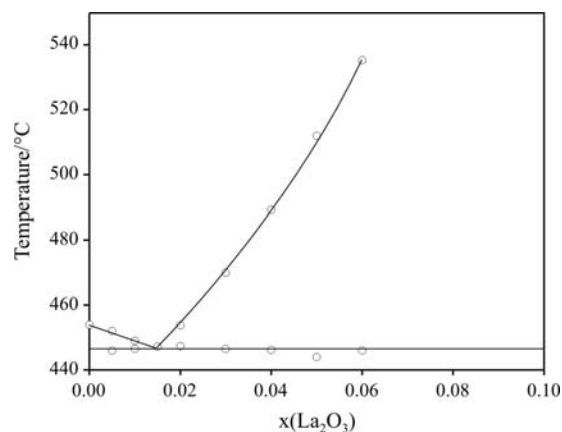
Fig. 3 NaF-rich part of the phase diagram of the system NaF–La$_2$O$_3$. ○ – experimental; full line – calculated
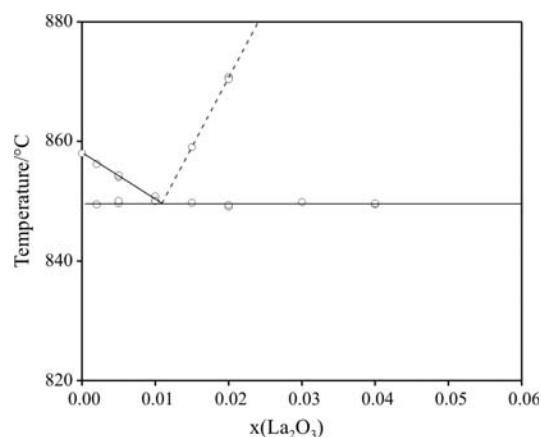
Fig. 5 KF-rich part of the phase diagram of the system KF–La$_2$O$_3$. ○ – experimental; full line – calculated

Fig. 4 XRD pattern of quenched melt of the system NaF–La$_2$O$_3$ (8 mole% of La$_2$O$_3$)

Fig. 6 Part of the phase diagram of the system (LiF–NaF–KF)$_{eut}$–La$_2$O$_3$

System KF–La$_2$O$_3$

The liquidus temperatures in the system KF–La$_2$O$_3$ were measured up to 4 mole% La$_2$O$_3$. The measured part of the phase diagram is shown in Fig. 5. It should be noted that temperatures of primary crystallization were recorded only at the composition up to 2.0 mole% La$_2$O$_3$. As it was mentioned above, higher amounts of La$_2$O$_3$ dissolve rather slowly. The solubility of lanthanum oxide in potassium fluoride is the lowest among the investigated pure alkali fluorides. The eutectic temperature and composition are 849.5°C and 1.1 mole% La$_2$O$_3$, respectively. The calculation was made under assumption that lanthanum oxide brings two new particles into the melt.

It seems that the same behaviour as in the other alkali fluoride melts occurs. Therefore the X-ray diffraction analysis was not realised in this system.

System (LiF–NaF–KF)$_{eut}$–La$_2$O$_3$

The liquidus temperatures in the system La$_2$O$_3$ – eutectic melt LiF–NaF–KF (46.5 mole% LiF;

11.5 mole% NaF; 42.0 mole% KF) were measured up to 6 mole% La$_2$O$_3$. The measured part of the phase diagram is shown in Fig. 6.

The measured system is a part of a quaternary system LiF–NaF–KF–La$_2$O$_3$. In this case the eutectic mixture is considered as an invariant point and one may expect up to 4 measured transition temperatures at each measured composition. However, the temperature during measurements was recorded below 200°C and only two transition temperatures were obtained. This phenomenon occurs in the case when the measured system copies the line of the monovariant equilibrium of the quaternary system [8, 9]. Then, one may conclude that all alkali fluorides crystallize together in the area 0–1.5 mole% La$_2$O$_3$.

The solubility of lanthanum oxide in the eutectic mixture of the system LiF–NaF–KF is lower than in pure LiF and NaF but higher than in KF. The coordinates of eutectic point are 1.5 mole% La$_2$O$_3$ and 446.5°C.

Conclusions

The solubility of lanthanum oxide in molten alkali fluorides was studied. It was found that it decreases in the order LiF>NaF>KF. Solubility of La_2O_3 in the eutectic mixture $(LiF–NaF–KF)_{eut}$ lies between the solubilities of La_2O_3 in the systems NaF and KF.

During dissolution lanthanum oxide reacts with the fluoride melt according to the scheme:

$$2MF+La_2O_3=2LaOF+M_2O \qquad (7)$$

where M=Li, Na, K.

This dissolution mechanism is supported by X-ray patterns of quenched melt.

Acknowledgements

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