Novel Molten Salts Media For Production of Functional Materials

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Abstract. Physical-chemical properties of molten salt media based on potassium cryolite with additions of boron or scandium oxides have been considered from the point of view of their feasibility in production of functional materials, such as aluminum alloys. Liquidus temperature in the quasi-binary systems: $[KF–AlF_3]-B_2O_3$, $[KF–AlF_3]-Sc_2O_3$, $[KF–NaF–AlF_3]-B_2O_3$, and $[KF–NaF–AlF_3]-Sc_2O_3$ has been measured by thermal analysis. Solubility of Al_2O_3, B_2O_3, and Sc_2O_3 in potassium and potassium-sodium cryolites has been determined. The potassium-cryolite-based melts were found to have an enhance protective function due to a low melting point, and an effective refining ability due to a good alumina solubility. It has been assumed that for aluminum alloys production the potassium-cryolite-based melts can be used as fluxes with improved properties as well as electrolytes for low-temperature electrolysis.
Keywords: potassium cryolite, potassium-sodium cryolite mixture, liquidus temperature, solubility of oxides, fluxes.

1 Introduction

A modern industry is closely connected with a development of functional materials, to which the aluminum alloys belong. They can be used as constructional materials in aviation, space, nuclear industry and machine-building. In practice, the aluminum master alloys (Al-B, Al-Sc) are produced by the direct introduction of alloying constituent to the molten aluminum or by the aluminothermic reduction of the compound (salt or oxide) of alloying component. Production of aluminum alloys by electrolysis in cryolite-alumina electrolytes is also considered to be promising.

Molten salts media can be used as fluxes in aluminothermy or as electrolytes-solvents in electrochemical co-reduction of metals.

Flux for aluminum alloys usually presents a mixture of alkali and alkali-earth halides because it is possible to obtain compositions with variable density and liquidus temperature on their basis [1]. A NaCl-KCl eutectic with melting point of 665°C is typically used as a

covering flux, which creates chemically passive layer protecting the aluminum alloy from oxidation. A density of molten flux has to be much less than the molten aluminum density to the effect that the layer of liquid flux could be settled on the aluminum surface. A refining effect of flux consists in adsorption and dissolution of impurities. For a better separation of molten aluminum from alumina, which always covers the aluminum surface or forms as a result of the aluminum interaction with a substance of alloying component, the flux has to be a good solvent for alumina. In general, a reaction of molten aluminum with oxides of alloying component can be written as:

$$2Al(l) + M_2O_3 = 2M(in\ Al) + Al_2O_3 \qquad\qquad (1)$$

where M is alloying component.

It is known that the alkali fluorides are capable to dissolve alumina. They act as surface-active additives, enhance wetability and conduce to separation of oxides, flux and molten aluminum. Chlorides, as well as AlF_3 and MgF_2, exhibit this property in much less degree. In general, fluxes can contain such fluorides as sodium cryolite (Na_3AlF_6), CaF_2, Na_2SiF_6. However, fluorides have a high melting point that limits its application. A conventional covering flux usually contains NaCl, KCl and Na_3AlF_6 up to 20% [1].

Potassium cryolite ($KF-AlF_3$) and potassium-sodium cryolite mixture ($KF-NaF-AlF_3$) with low cryolite ratio (CR), which is determined as $CR = N_{KF}/N_{AlF3}$ (mol/mol) for the $KF-AlF_3$ or as $CR = (N_{KF} + N_{NaF})/N_{AlF3}$ (mol/mol) for the $KF-NaF-AlF_3$ mixture, are worth to be tested as basic components of flux. For instance, the $KF-AlF_3$ with CR=1.3 has the liquidus temperature of 627 °C [2]. An undeniable advantage of the molten potassium cryolite with CR<1.7 is a good alumina solubility within a temperature range of 700-800 °C [3]. The NaF addition to the $KF-AlF_3$ melt results in decreasing the alumina solubility. However, the alumina solubility in the $KF-NaF-AlF_3$ mixture with NaF 10 wt% and CR=1.5 still has an acceptable value of 6.7 wt% at 800 °C. Density of molten potassium cryolite is rather low in comparison to sodium cryolite that is favorably for flux. For example, density of the $NaF-AlF_3$, $KF-NaF-AlF_3$ and $KF-AlF_3$ melts with CR=1.5 is 2.0, 1.8 and 1.7 g/cm^3, respectively [4]. It should be mentioned that for the last decade the fundamental and applied research in the field of low-temperature aluminum electrolysis proved an efficiency of electrolytes based on potassium cryolite, which allows carrying out electrolysis at 700-800 °C [5].

The purpose of the present study is to determine an effect of the boron-containing (B_2O_3) and scandium-containing (Sc_2O_3) additions to the molten $KF-AlF_3$ and KF-NaF(10 wt%)-AlF_3 mixtures with CR=1.3-1.5 on the key electrolyte properties: liquidus temperature and solubility of alumina and alloying additions, in order to identify a feasibility of the potassium-cryolite-based melts as fluxes or as electrolytes-solvents in production of aluminum alloys.

2 Experimental

2.1 Salt mixture preparation.

The individual salts (chemically pure grade) AlF_3, NaF, and KF (as KF·HF) were used for electrolyte composition. The $KF-AlF_3$ electrolyte was obtained by mixing the KF·HF and AlF_3 salts (in a glassy carbon container) and following heating to 700 °C. The mixture was exposed of this temperature over four hours in order to remove HF from the melt due to the thermal decomposition of the KF·HF (T=238.7 °C). The $KF-NaF-AlF_3$ cryolite system was prepared by mixing the $NaF-AlF_3$ and $KF-AlF_3$ binaries. Before testing the alumina (Al_2O_3) was dried at 400 °C over 4-6 hours.

2.2 Liquidus temperature measurement.

A thermal analysis (TA) was used for measuring liquidus temperature of the cryolite-based systems. This method consists in registration of thermal effects during cooling. A scheme of the installation for measuring liquidus temperature is shown in Fig.1.

2.3 Alumina solubility determination.

The Al_2O_3 solubility was determined according to the phase diagrams "molten cryolite mixture - Al_2O_3". As a rule, the phase diagrams of such quasi-binary systems have a type of a simple diagram with one eutectic. The left descending line of liquidus corresponds to the temperature of primary crystallization of the molten cryolite. It was measured using the TA. The right ascending curve of the liquids is determined by the Al_2O_3 crystallization temperature and corresponds to its solubility in molten salt at a definite temperature. In some tests the Al_2O_3 crystallization temperature was found using an isothermic saturation technique, which lies in the fact that the Al_2O_3 weight portions are to be added to the molten salt, suspended at constant temperature, until Al_2O_3 dissolves in it and the melt remains homogeneous. The saturation point for Al_2O_3 is determined using as chemical analysis as visual observation.

3 System "potassium-cryolite-based melt – B2O3"

In aluminothermy the KBF_4 is used usually as an alloying component [6]. The main losses of this expensive substance can be a thermal decomposition with formation of a volatile BF_3. In worldwide scientific practice nowadays a trial of B_2O_3, cheaper and more saturated with boron compound, have been carried out [7]. The boron oxide during interaction with molten aluminum forms alumina, which should be eliminated from the molten aluminum due to dissolution in molten salt.

The B_2O_3 influence on the liquidus temperature of the $KF–AlF_3$ and $KF–NaF(10wt\%)–AlF_3$ systems is shown in Fig.2. In potassium cryolite melts the liquidus temperature increases up to 40-50 degrees Centigrade with introduction of B_2O_3 up to 3 mol.%; further B_2O_3 addition up to 10 mol.% does not impact the liquidus temperature. In the molten mixture of potassium and sodium cryolites [$KF–NaF(10$ wt%)$–AlF_3$]-B_2O_3 the liqudus temperature dependence on the B_2O_3 concentration has slightly sloping character.
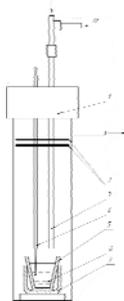

Fig.1 Set up for measuring liquidus temperature: 1 – cap, tightly closed;
2 – shields; 3 - tube for adding oxides in a flow of inert gas; 4 – thermocouple (Pt/Pt-Rh);
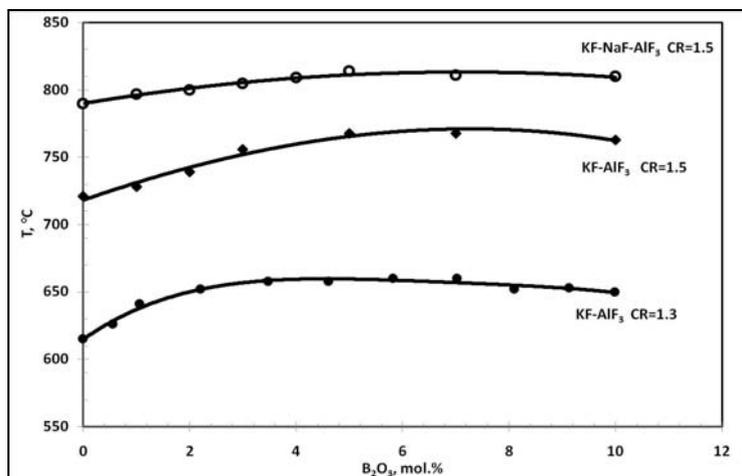5 – glassy-carbon crucible; 6 – molten cryolite;
7 – alumina container

Fig.2 - Liquidus temperature of the KF-NaF(10 wt%)-AlF3 (CR=1.5) and KF-AlF3 (CR=1.3 and 1.5) with B2O3 additions

The effect of aluminum oxide additions on the liquidus temperature of the [KF-AlF$_3$-B$_2$O$_3$(5 mol.%)]-Al$_2$O$_3$ and [KF–NaF(10wt%)–AlF$_3$-B$_2$O$_3$(4 mol.%)]-Al$_2$O$_3$ systems is presented in Fig.3. The liquidus lines for the [KF-AlF$_3$]-Al$_2$O$_3$ [2] and [KF-AlF$_3$-KBF$_4$(5mol.%)]-Al$_2$O$_3$ [8] with CR=1.3 are also shown in this figure for comparison. The liquidus temperature of the boron-containing potassium cryolite decreases when the Al$_2$O$_3$ up to 3.2 mol.% is added. However, at further additions of the alumina the temperature sharply increases. It is seen that the B$_2$O$_3$ additions (up to 5 mol.%) in KF-AlF$_3$ almost does not impact the Al$_2$O$_3$ solubility in the temperature range from the liquidus point to 750 ^{0}C. At temperatures as high as 750 ^{0}C the Al$_2$O$_3$ solubility in the boron-containing salts is higher than that in the KF-AlF$_3$ and, for example, at 800 ^{o}C it is about 4 mol.%. The other behavior can be observed in the potassium cryolite with the KBF$_4$ (Fig.3). The additions of this compound give an increase in the aluminum oxide solubility. In sodium-potassium cryolites the aluminum oxide mixtures immediately and sharply increase the liquidus temperature. The low solubility of Al$_2$O$_3$ in molten salts containing B$_2$O$_3$ is explained by the fact that oxides form the nAl$_2$O$_3$·mB$_2$O$_3$ compounds with limited solubility in the cryolite melts.

Thus, mixed sodium-potassium cryolite melts cannot be recommended as fluxes in aluminothermy for obtaining the aluminum alloys at temperature as high as 800 ^{0}C, when B$_2$O$_3$ is used as the boron-containing raw material. Nevertheless, the KF-AlF$_3$ melts, in which the B$_2$O$_3$ solubility is about 4 mol.% at 800 ^{0}C, can be likely applied in electrolytic method. The B$_2$O$_3$ solubility reaction in the potassium cryolite can be written as

$$KAlF_4 + B_2O_3 => 2KBF_4 + Al_2O_3 \tag{2}$$

Formed aluminum oxide will be subjected to electrolytic decomposition, and its slugs will not be accumulated in electrolytic bath.
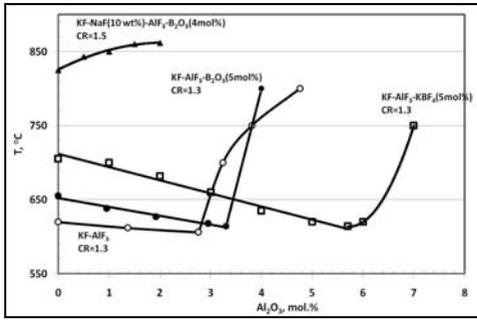
Fig.3 - Liquidus temperature of the
KF-NaF(10 wt%)-AlF$_3$-B$_2$O$_3$(4 mol%);
KF-AlF$_3$-B$_2$O$_3$(5 mol%);
KF-AlF$_3$-KBF$_4$(5 mol%) [8];
KF-AlF$_3$ [2] with Al$_2$O$_3$ additions
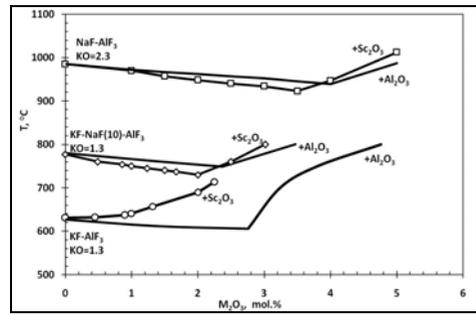
Fig.4 – Liquidus temperature in the systems:
[KF–AlF$_3$]-Sc$_2$O$_3$ and [KF–AlF$_3$]-Al$_2$O$_3$
(CR=1.3); [KF–NaF(10 wt%)–AlF$_3$]-Sc$_2$O$_3$ and
[KF–NaF(10 wt%)–AlF$_3$]-Al$_2$O$_3$ (CR=1.5);
[NaF–AlF$_3$]-Sc$_2$O$_3$ and [NaF–AlF$_3$]-Al$_2$O$_3$
(CR=2.3) [9]

4 System "potassium-cryolite-based melt – Sc2O3"

The results of the liquidus temperature measurements in the systems "potassium-cryolite-based melt – Sc$_2$O$_3$", promising media for performing the process of the Al-Sc alloys production are demonstrated in Fig.4. It is possible to determine the operating temperature for the process with the use of molten salts based on potassium and sodium cryolites, containing dissolved Sc$_2$O$_3$. However, choosing a molten media composition for the Al-Sc alloys production it should be considered not only the operating temperature but a solubility of the Sc$_2$O$_3$ and Al$_2$O$_3$ in these melts.

As it is seen in Fig.4, the Sc$_2$O$_3$ solubility in molten salts containing sodium cryolite is almost the same as the Al$_2$O$_3$ solubility. An exception is the potassium cryolite KF-AlF$_3$, in which the Sc$_2$O$_3$ solubility is almost 1.5 times low than the Al$_2$O$_3$ solubility. It can be explained by formation of the slightly-soluble K$_3$ScF$_6$ compound, the melting point of which is beyond 1000 ^{0}C, as a result of scandia dissolution in potassium cryolite according to the following reaction:

$$2KAlF_4 + Sc_2O_3 + 2KF = 2K_3ScF_6 + Al_2O_3 \qquad\qquad (3)$$

Nevertheless, the KF-AlF$_3$ can be successfully used as flux in aluminothermy because it possesses a low liquidus temperature that positively affects its covering function, and at the same time it has a good alumina solubility that conduces removing the alumina from the reaction zone.

5 Conclusions

According to the experimental data obtained in the systems "potassium-cryolite-based melt – B$_2$O$_3$/Sc$_2$O$_3$" it was assumed that the KF-AlF$_3$ and KF-NaF (10wt. %-AlF$_3$) molten mixtures with CR=1.3-1.5 can be applied as fluxes in aluminothermy. Apart from protective function these molten salts have more effective refining ability in comparison with well-known chloride-fluoride fluxes due to good solubility of the alumina; low melting temperature, which helps to increase the flux's fluidity and strengthen its protective function. At that, it is possible to decrease a thickness of the molten flux layer over the melt, which obstructs a heat transfer because of accumulated slug (alumina) in the molten salt.

On the other hand, the some molten compositions KF-AlF$_3$ and KF-NaF-AlF$_3$ having a good solubility of the scandium or boron oxides can be recommended for electrolytic production of alloys at temperature as low as 800 ^{0}C.

Acknowledgements

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