PHYSICO-CHEMICAL PROPERTIES OF $NaF-AlF_3-BaCl_2-NaCl$ ELECTROLYTE SYSTEM①

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ABSTRACT

To reduce energy consumption, the physico-chemical properties of $NaF-AlF_3-BaCl_2-NaCl$ system were systematically studied. The mathematical models of the liquidus temperature and electrical conductivity were obtained and the density was also studied about this system. Based on these experiments, three groups of energy-saving electrolyte composition were proposed. This achievement has been applied in the aluminium refining industry, and it was demonstrated that the energy consumption was reduced by 1 200 kWh per ton of refined aluminium.

Key words: Aluminium refining electrolyte energy-saving

1 INTRODUCTION

In our country, the DC energy consumption of three layers aluminium refining is up to 21 000 kWh per ton of aluminium. Higher energy consumption is the obstacle to developing our country's refining aluminiun industry. Addition of NaCl to the electrolyte system $NaF-AlF_3-BaCl_2$ to improve the performance of the molten electrolyte has been studied, but the studies were not perfect. To find an energy-saving electrolyte of high electrical conductivity, we broadened the research range and used different methods to study the $NaF-AlF_3-BaCl_2-NaCl$ system. This paper might provide theoretic and technical foundation for further developing the aluminium refining industry.

2 EXPERIMENTAL AND RESULTS

2.1 *Liquidus Temperature of* $NaF-AlF_3-BaCl_2-NaCl$ *System*

Gradual cooling curve method was adopted to measure the liquidus temperature. The experiments were designed using orthogonal regressive method. Mathematical models of the three-factor quadratic regressive equation were used to describe the liquidus temperature of this system.

In this paper, k repersents NaF/AlF_3 mole ratio; C_{BaCl_2} represents $BaCl_2$ content (wt.-%); Q_{NaCl} represents adding amount of NaCl (wt.-%).

(1) While $k = 1.5 \sim 2.3$, $C_{BaCl_2} = 40 \sim 60$, $Q_{NaCl} = 0 \sim 15$

$$t = 624.643 + 172.860k - 4.492C_{BaCl_2} + 4.944Q_{NaCl} + 1.933kC_{BaCl_2} - 5.145kQ_{NaCl} + 0.026C_{BaCl_2}Q_{NaCl} - 41.932k^2 - 0.01394C^2_{BaCl_2} - 0.102Q^2_{NaCl} \quad (1)$$

(2) While $k = 2.3 \sim 3.0$, $C_{BaCl_2} = 40 \sim 60$, $Q_{NaCl} = 0 \sim 15$

$$t = 2533.232 - 1195.874k$$

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$$-5.630C_{BaCl_2} - 44.558Q_{NaCl} - 1.194kC_{BaCl_2} + 6.860kQ_{NaCl} + 0.397C_{BaCl_2}Q_{NaCl} + 232.889k^2 + 0.064C_{BaCl_2}^2 + 0.249Q_{NaCl}^2 \quad (2)$$

(3) While $k = 3.0 \sim 6.7$, $C_{BaCl_2} = 40 \sim 60$, $Q_{NaCl} = 0 \sim 15$

$$t = 1\,690.958 + 108.186k + 45.974C_{BaCl_2} - 24.626Q_{NaCl} + 0.233kC_{BaCl_2} + 0.060kQ_{NaCl} + 0.383C_{BaCl_2}Q_{NaCl} - 11.517k^2 + 0.432C_{BaCl_2}^2 + 0.305Q_{NaCl}^2 \quad (3)$$

The relationships between liquidus temperature and NaF/AlF_3 mole ratio k, $BaCl_2$ content C_{BaCl_2} and NaCl adding amount Q_{NaCl} were shown in Figs. 1, 2 and 3.

2.2 *Temperture-Varied Electrical Conductivity of* $NaF-AlF_3-BaCl_2-NaCl$ *System*

Temperature-varied properties were adopted to describe the electrical conductivity of this system. Different bath composition was studied at different temperature which is 20 ℃ higher than the liquidus temperature of this given bath. Parallel four-electrode method was used to measure the electrical conductivity.

(1) While $k = 1.5 \sim 2.3$, $C_{BaCl_2} = 40 \sim 60$, $Q_{NaCl} = 0 \sim 15$

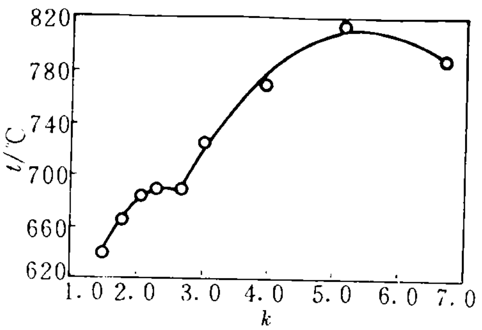

Fig. 1 Influence of NaF/AlF_3 mole ratio(k) on liquidus temperature(t) of molten bath
($C_{BaCl_2} = 60$, $Q_{NaCl} = 8$)

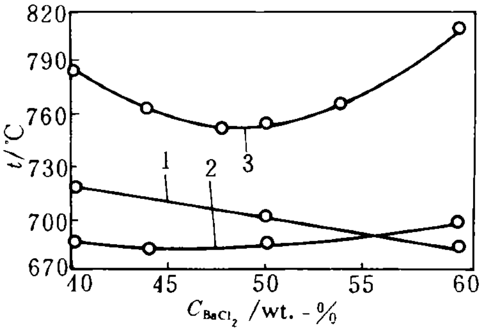

Fig. 2 Influence of $BaCl_2$ content (C_{BaCl_2}) on liquidus temperture(t) of molten bath
1— $k = 2.1$, $Q_{NaCl} = 8$;
2— $k = 2.7$, $Q_{NaCl} = 8$;
3— $k = 4.2$, $Q_{NaCl} = 8$

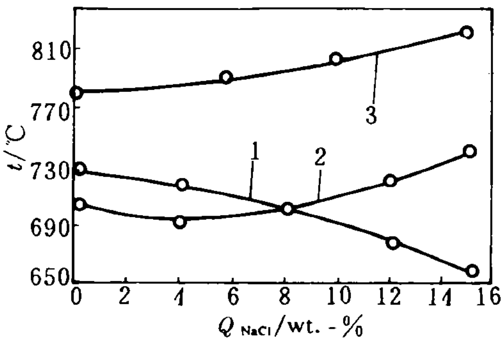

Fig. 3 Influence of NaCl adding amount Q_{NaCl} on liquidus temperature (t) of molten bath
1— $k = 2.1$, $C_{BaCl_2} = 60$;
2— $k = 2.7$, $C_{BaCl_2} = 60$;
3— $k = 4.2$, $C_{BaCl_2} = 60$

$$\lambda = 5.389 + 1.032k - 0.212C_{BaCl_2} + 0.020Q_{NaCl} + 0.028kC_{BaCl_2} - 0.014kQ_{NaCl} + 0.001C_{BaCl_2}Q_{NaCl} - 0.516k^2 + 0.001C_{BaCl_2}^2 - 0.002Q_{NaCl}^2 \quad (4)$$

(2) While $k = 2.3 \sim 3.0$, $C_{BaCl_2} = 40 \sim 60$, $Q_{NaCl} = 0 \sim 15$

$$\lambda = 1.004 - 1.138k + 0.086C_{BaCl_2} - 0.129Q_{NaCl} - 0.008kC_{BaCl_2} + 0.020kQ_{NaCl} + 0.001C_{BaCl_2}Q_{NaCl} + 0.287k^2 - 0.001C_{BaCl_2}^2 - 0.003Q_{NaCl}^2 \quad (5)$$

(3) While $k = 3.0 \sim 6.7$, $C_{BaCl_2} = 40 \sim 60$, $Q_{NaCl} = 0 \sim 15$

$$\lambda = 4.391 + 1.026k - 0.201C_{BaCl_2} - 0.089Q_{NaCl} - 0.003kC_{BaCl_2} - 0.005kQ_{NaCl} + 0.002C_{BaCl_2}Q_{NaCl} - 0.052k^2 + 0.002C_{BaCl_2}^2 + 0.003Q_{NaCl}^2 \quad (6)$$

The effects of bath ratio k, $BaCl_2$ content and adding amount of NaCl on electrical conductivity are shown in Figs. 4, 5 and 6.

2.3 *Temperature-Varied Density of* NaF-AlF3-BaCl2-NaCl *System*

Hydrostatic weighing method was adopted to measure the density of the molten electrolyte.

The effects of bath ratio k, $BaCl_2$ content C_{BaCl_2} and NaCl adding amount Q_{NaCl} on density of the molten electrolyte were shown in Figs. 7 and 8.

3 DISCUSSION

3.1 *General Description of Physico-Chemical Properties of* NaF-AlF3- BaCl2- NaCl *System*

Based on the research above, some important conclusions can be made as follows:

(1) NaF/AlF3 mole ratio has remarkable effect on electrical conductivity of the molten electrolyte. In the condition of our experiments, molten salt's conductivity increases with increasing bath ratio except that electrical conductivity varies slowly in the bath range from 2.3~2.8. But increase in bath ratio can make liquidus temperature higher. Raising bath ratio to some degree can drops the density of the molten electrolyte.

(2) As a kind of additive studied, NaCl plays an important role in raising electrical conductivity of the molten electrolyte. From

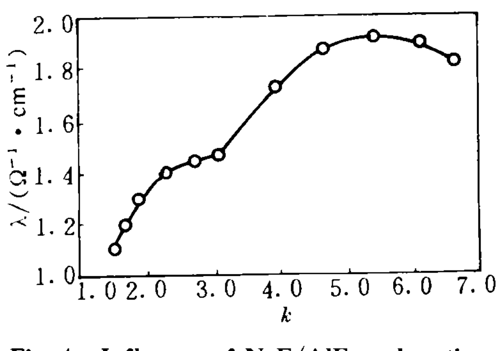

Fig. 4 Influence of NaF/AlF3 mole ratio k on electrical conductivity of molten bath
($C_{BaCl_2} = 60$, $Q_{NaCl} = 8$)

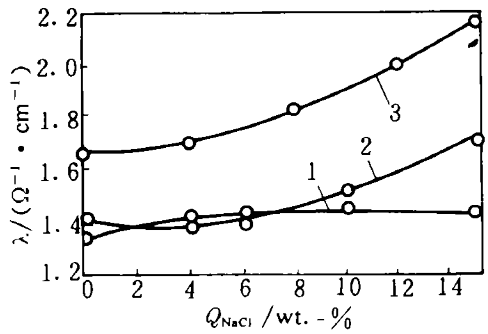

Fig. 5 Influence of NaCl adding amount (Q_{NaCl}) on electrical conductivity λ of molten bath
(1)— $k = 2.1$, $C_{BaCl_2} = 60$;
(2)— $k = 2.7$, $C_{BaCl_2} = 60$;
(3)— $k = 4.2$, $C_{BaCl_2} = 60$

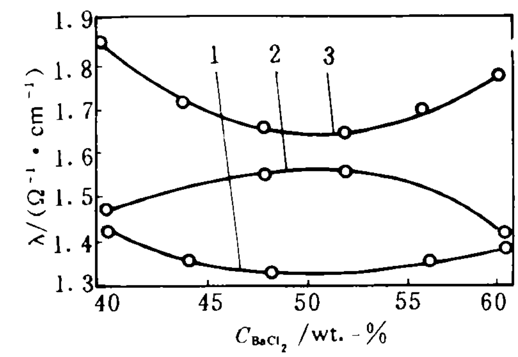

Fig. 6 Influence of BaCl2 content (C_{BaCl_2}) on electrical conductivity λ of molten bath
(1)— $k = 2.1$, $Q_{NaCl} = 8$;
(2)— $k = 2.7$, $Q_{NaCl} = 8$;
(3)— $k = 4.2$, $Q_{NaCl} = 8$

general trends, the electrical conductivity of the molten electrolyte rises with increasing NaCl adding amount, but the rising is gradual. In the low bath ratio range, adding NaCl to the electrolyte can drop the liquidus temperature. There is a disadvantage that adding NaCl to the elecrolyte can drop the density of the molten salts.

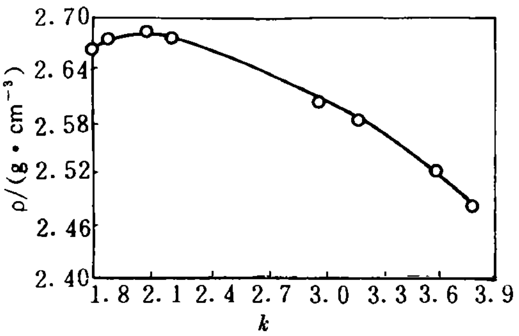

Fig. 7 Influence of NaF/AlF$_3$ mole ratio k on density(ρ) of molten bath

($C_{BaCl_2}=60$, $Q_{NaCl}=8$)

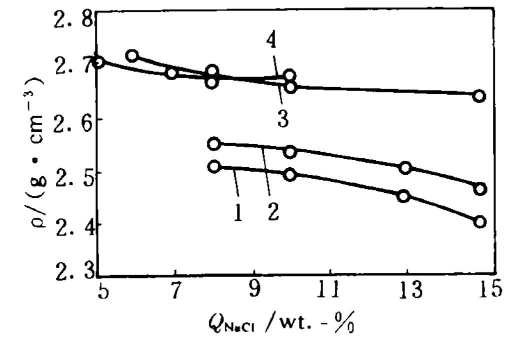

Fig. 8 Influence of BaCl$_2$ content and NaCl adding amount on density of molten bath

(1)— $k=3.4$, $C_{BaCl_2}=50$;

(2)— $k=3.4$, $C_{BaCl_2}=60$;

(3)— $k=2.7$, $C_{BaCl_2}=60$;

(4)— $k=2.1$, $C_{BaCl_2}=60$

(3) BaCl$_2$ in the molten electrolyte plays an important role in adjusting the density to meet with the request of ordinary industry production for electrolyte's density and to counteract the adverse effects on electrolyte because of adding NaCl and raising bath ratio.

(4) Except for effects of the bath ratio BaCl$_2$ content and NaCl adding amount respectively on physico-chemical properties of electrolyte, these factors also interact on physico-chemical properties. While selecting the appropriate electrolyte composition, the effective interaction between these factors should be considered sufficiently to overcome the bad effects of signal factor on some properties.

3.2 *Selection of Energy-Saving Electrolyte*

While selecting the electrolyte composition, these rules should be followed: presupposing the density of the bath meeting with request, the molten electrolyte having higher electrical conductivity and lower liquidus temperature as soon as possible. Considering the request of practical industry production for the electrolytes, three groups of energy-saving electrolyte composition range were proposed on the basis of studies above.

(1) When bath ratio is 2.1 ± 0.2, NaCl adding amount is (6～12) wt.-%, BaCl$_2$ content is (60 ± 5) wt.-%, the liquidus temperature is 665～705 ℃, the density is 2.65～2.70 g/cm^3, the electrical conductivty is 1.3～1.5 $\Omega^{-1}\cdot cm^{-1}$. The electrical conductivity increases by 30～50 percent than that of the traditional electrolyte.

(2) When bath ratio is 2.5 ± 0.2, NaCl adding amount is (12 ± 3) wt.-%, BaCl$_2$ content is (60 ± 5) wt.-%, the liquidus temperature is 700～740 ℃, the density is 2.60～2.70 g/cm^3, the electrical conductivity is 1.45～1.70 $\Omega^{-1}\cdot cm^{-1}$. The electrical conductivity increases by 45～70 percent than that of thetraditional electrolyte.

(3) When Bath ratio is 3.4 ± 0.2, NaCl adding amount is (11 ± 2) wt.-%, BaCl$_2$content is (58～65) wt.-%, the liquidus

temperature of the molten electrolyte is 760 ～ 795 ℃, the density is 2.50 ～ 2.60 g/cm^3, the electrical conductivity is 1.6～1.9 $\Omega^{-1} \cdot cm^{-1}$. The electrical conductivity increases by 60～90 percent than that of the traditional electrolyte.

4 SUMMARY

(1) In this paper, the research range of the NaF-AlF_3- $BaCl_2$- $NaCl$ system was widened. In past studies, bath ratio was up to 2.5, adding amount of NaCl was up to 8%. In this paper, the bath ratio was raised to 6.7, NaCl adding amount was raised to 15%.

(2) Liquidus temperature, temperature-varied electrical conductivity and density of this electrolytic system were studied. Conclusions reached in varing temperature conditions were very different from that under constant temperature condition, which can closely represent practical condition.

(3) The relaionships between each physico-chemical property and each factor of the electrolyte system NaF- AlF_3- $BaCl_2$-$NaCl$ were summarized and described. Considering the requests of industry production for electrolyte, three groups of energy-saving electrolyte compsition whose electrical conductivity was increased by 30～90 percent than that of the electrolyte adopted traditionally in industry and other properties which also meet with request were proposed in the basis of researches.

(4) One of the three groups of electrolyte composition proposed above has come into use in Guizhou Aluminium Plant. The energy consumption was reduced by 1200 kWh/t·Al, the output of refined aluminium was increased by 8 percent.

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MPA acts both as reacting medium and reacting extractant, then leads to the change of the reaction mechanisms. The accelerating characteristics of the MPA micelle are different from those of the micelle catalysis which only acts as reacting medium and accelerates the reactions, but does not changes its mechanism.

4 CONCLUSIONS

(1) It was proved that the controlling reaction of the micelle mixed extractant system D_2EHPA-MPA for the Al^{3+} extraction occurs inside the micelle phase.

(2) The reaction rate equations were established for Al^{3+} extraction of the studied extractant system.

(3) The two components, in the micelle region of the studied system, and their reaction mechanisms, in the micelle and liquid-liquid interfacial reaction regions, were proposed.

(4) The accelerating mechanisms and their characteristics of the studied micelle mixed system were proposed and analysed.

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