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FUSIBILITY AND DENSITY STUDIES OF SOME FLUORIDE MIXTURES RELATED TO ELECTROREFINING OF ALUMINIUM

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Fusibility and density of some salt mixtures formed among NaF, AlF_3 (the two constituents of cryloite ore) and an equimolecular NaCl-KCl mixture have been experimentally determined. It has been found that the primary crystallization point of the mixture comes down rapidly with the addition of equimolecular NaCl-KCl to cryolite and goes even below 700° when the proportion of NaCl-KCl in the mixture is kept 50 mole percent and above. It has also been found that the primary crystallization temperature of the salt mixture does not change significantly when the molar ratio of NaF to AlF_3 in the four component salt mixture was changed from 3:1 (as in natural cryolite ore) to 3:2. The density of the system decreases with increasing among of NaCl -KCl in the mixture.

Key words: Electrorefining, aluminium, physicochemical properties

INTRODUCTION

The conventional three layer method of electrorefining of aluminium employs a mixture of AlF_3, NaF and $BaCl_2$ as the electrolyte. In this process the impure metal in the form of an alloy is kept as the bottom layer while the pure refined metal is obtained at the top. The presence of $BaCl_2$ helps to keep the density of the electrolyte higher than that of the liquid metal at the operating temperature so that the pure metal is able to rise to the top of the electrolyte. In an altogether different approach which is supposed to avoid some of the operating difficulties of the above process, the density of the electrolyte is kept to a lower value than that of the liquid metal so that the refined metal could be collected at the bottom. Obviously, the amount of $BaCl_2$ used in the conventional electrolyte mixture has to be reduced or replaced by other suitable halides so that the density of the electrolyte becomes lower than that of the liquid metal maintaining the other properties of the bath.

In this regard the knowledge about the properties of such salt mixtures under different conditions are important and such relevant data are not readily available. In this connection a programme has been undertaken for the determination of various properties of different salt mixtures under different conditions. In the present paper, the work related to the determination of fusibilities and densities of different salt mixtures formed among NaF, AlF_3, NaCl, KCl has been described.

Fusibility

One of the ways to increase the energy and current efficiencies in the electrowinning and electrorefining of aluminium is to decrease the working temperature of the electrolysis. This can be achieved by the addition of various salts to the electrolytes.

In the electrorefining of aluminium where Al_2O_3 is absent in the electrolytic bath, the working temperature can be made near about 800°C or so. The addition of NaCl to cryolite does bring down the liquidus temperature but only down to around 800 [1]. In the present work the effect of addition of NaCl-KCl (in the proportion of 1:1 eutectic mixture) has been studied. Moreover in many of the electrolytic baths for electrowinning and electrorefining of Al, higher proportion of AlF_3 is being used for generating some specific advantages. So two series of salt systems viz. (1) cryolite (with AlF_3:NaF = 1:3) and NaCl-KCl (1:1) and (ii) cryolite (with AlF_3:NaF = 2:3) and NaCl-KCl (1:1) have been taken up for fusibility studies.

EXPERIMENTAL

All the chemicals are of extra pure quality and were used without further purification.

The primary crystallization points have been determined by thermal analysis using cooling curve method. A variable speed strip chart recorder was used along with a constant current generator which could apply different constant millivolts into the circuit according to the specific need. Other experimental details may be found elsewhere [2]. The well known hydrostatic weighing method has been used for density measurements [3]. Due to the corrosive nature of the melts, the bob used is made of platinum and it was shaped in the form of a biconical cylinder and the suspension wire was also of the same material (0.2 mm diameter).

RESULTS

Figure 1 shows the liquidus curves for the mixtures of cryolite AlF_3:NaF (1:3) + NaCl+KCl (1:1) and also of AlF_3:NaF (2:3) + NaCl + KCl (1:1)

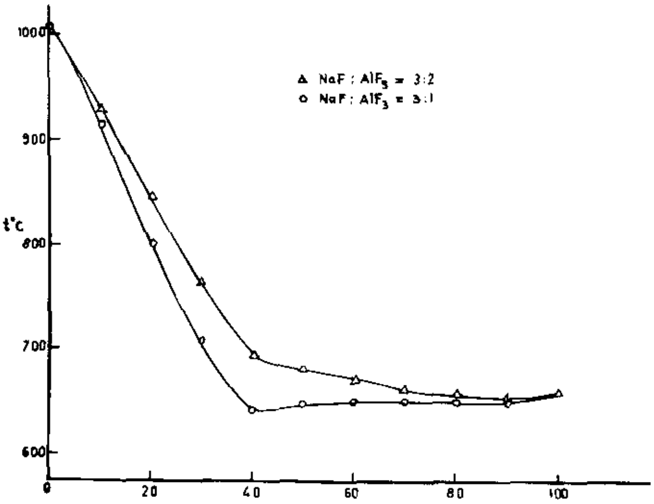

Fig. 1: Liquidus behaviours of the systems
Δ NaF: AlF_3 (3:2) and NaCl + KCl (1:1)
O NaF: AlF_3 and NaCl + KCl (1:1)

It seems that increase in the proportion of AlF_3 in the cryolite does not have much effect on the liquidus temperature of the mixture. Fig. 2 is a comparison of the liquidus curves of the two systems viz. (i) cryolite + NaCl and (ii) cryolite + (NaCl+KCl). It is evident from the graph that addition of equimolecular mixture of NaCl-KCl, instead of NaCl alone brings down the liquidus temperatures substantially and when the proportion NaCl-KCl is about 50 percent or more in the mixture the primary crystallization points come down to around 660°C.

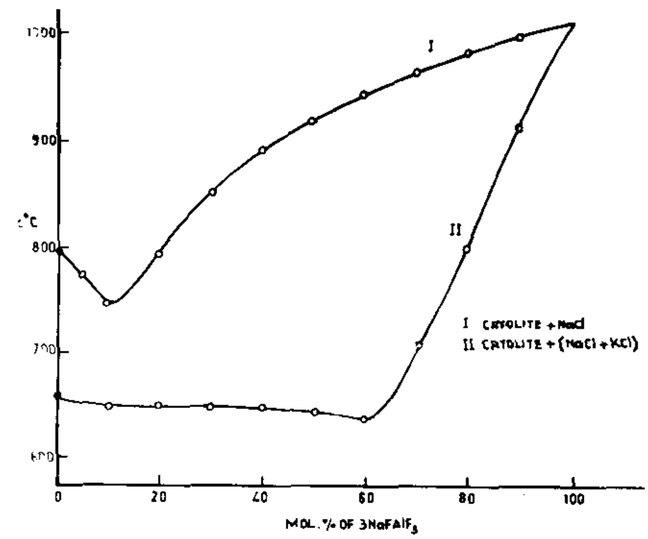

Fig. 2. Comparison of liquidus behaviours of the systems
I Cryolite and NaCl
II Cryolite and NaCl + KCl (1:1)

Density

In the electrorefining of aluminium the density of the electrolyte affects the separation of the metal deposited from the electrolyte. The densities of cryolite containing salt mixtures are available mostly at higher temperature ranges around 1000°C and above. It has been found from our present fusibility studies that the mixture of cryolite and NaCl-KCl (1:1) can stay as liquid without any solid separation down to the temperature of 700°C. Therefore the same mixtures have been taken for density study and the temperature range was from the liquidus temperature to about 900°C.

The estimated error due to surface tension is much smaller than the estimated uncertainty of our readings. The correction due to surface tension has therefore been neglected [1]. The overall uncertainty of the density readings were around two percent.

The density apparatus was tested by measuring the density of a 50 mol percent mixture of NaCl-KCl at different temperatures. The differences between our experimental readings and those available in literature [4] are within one percent.

Table I: Densities of 3:2 $NaF:AlF_3$ and NaCl + KCl (1:1) mixtures at different temperatures

Temperature °C	Composition M%	Density g cm^{-3}	Temperature °C	Composition M%	Density g cm^{-3}
678	20% $3NaF:2AlF_3$	1.7070	675	40% $3NaF:2AlF_3$	1.7347
712	+	1.6932	695	+	1.7250
738	80% NaCl +	1.6831	737	60% NaCl + KCl (1:1)	1.7064
787	KCl (1:1)	1.6634	790		1.6823
825		1.6482	837		1.6594
887		1.6230	895		1.6315

Table - II: Densities of $NaF:AlF_3$ (3:2) and NaCl + KCl (1:1) mixtures at rounded temperatures*

Temperature °C	Composition M%	Density g cm^{-3}	Temperature °C	Composition M%	Density g cm^{-3}
675	20% $3NaF:2AlF_3$	1.7080	675	40% $3NaF:2AlF_3$ +	1.7351
700	+	1.6982	700	60% NaCl + KCl	1.7232
725	80% NaCl + KCl	1.6884	725	(1:1)	1.7122
750	(1:1)	1.6781	750		1.7021
775		1.6672	775		1.6884
800		1.6585	800		1.6762
825		1.6487	825		1.6647
850		1.6384	850		1.6523
875		1.6282	875		1.6414
900		1.6182	900		1.6293

* Interpolated values.

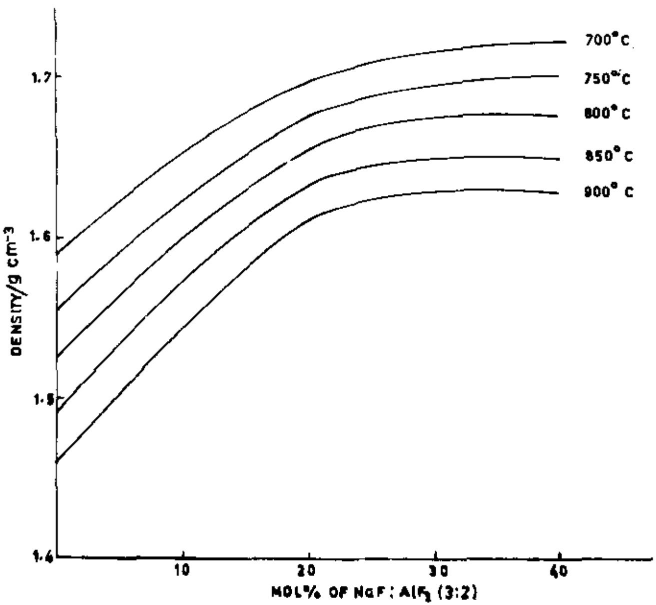

Fig. 3. Densities of the salt mixtures containing NaF:AlF$_3$ (3:2) and NaCl + KCl (1:1) at different temperatures

Table I shows the experimental density readings at different temperatures while Table II contains the densities of the same salt mixtures at rounded temperatures obtained from a graphical plot.

Figure 3 will give an idea how the addition of AlF$_3$ and NaF (2:3) will change the density of the mixture at different temperatures.

Evidently, a significant increase in the density value of the salt system due to the addition of NaF-AlF$_3$ (3:2) till its proportion reaches at least 40 mol percent upto which the range of the present study goes, can be observed from the graph (Fig.3).

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