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Fusibility study of the magnesium cell electrolyte containing $MgCl_2$, $CaCl_2$, NaCl and KCl

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The four-component magnesium cell electrolyte containing $MgCl_2$, $CaCl_2$, NaCl and KCl has been converted to a quasi-ternary system by keeping the proportion of NaCl and KCl in the mixture equimolecular. The triangular phase diagram has been drawn depicting the fusibility isotherms of the system. It has been possible to obtain complete liquid mixtures at temperatures as low as 400° C by suitably adjusting the proportions of the four components of the molten salt mixture.

1. Introduction

A molten salt mixture of $MgCl_2$–$CaCl_2$–$NaCl_2$–KCl often forms the basis for the electrolytic production of metallic magnesium. These chloride mixtures are, therefore, of considerable technical interest, and knowledge of the effects of variation of the salt compositions on the properties of the cell electrolyte is of paramount importance for choosing the optimum parameters for electrolysis.

Although recently there have been some reports of measurements on the physico-chemical properties of binary or, in some cases, ternary salt mixtures [1–4], containing the four chloride salts, very few have attempted to work with the complicated quarternary system as such. These studies have been oriented towards some very limited objectives [4]. In the present paper, the results of a complete fusibility study of the above four-component system is reported.

2. Experimental procedure

2.1. *Materials*

NaCl (m.p. 803° C), KCl (m.p. 772° C) and $CaCl_2$ (fused) (m.p. 774° C) salts were of extra pure quality. $MgCl_2$ (anhydrous) (m.p. 714° C) was supplied by the Nuclear Fuel Complex, Hyderabad. Precautions were taken to keep the exposure of the salts, particularly the highly hygroscopic $CaCl_2$ and $MgCl_2$, to the atmosphere to a minimum. Contamination by traces of moisture during storage and handling could not be completely ruled out, however.

2.2. *Method*

Visual and polythermal techniques were used simultaneously to determine the primary crystallization points of the salt mixtures. Details of the procedure and experimental set-up have been described elsewhere [3]. The method has, however, been modified slightly for improved accuracy. The variable speed strip chart recorder used in the present case can provide millivolt readings up to 5×10^{-4} mV. This corresponds to approximately 0.013° C in the chromel–alumel thermocouple, which was repeatedly calibrated during the course of the experiments. The overall observed reproducibility of the primary crystallization point with particular salt mixtures was within ± 2–3° C.

3. Results and discussion

In order to overcome the obvious difficulty of having an essentially three-dimensional space model with a two-dimensional drawing, for a general representation of the phase diagram of a quarternary system [5, 6] such as the present four-component magnesium cell electrolyte mixture, we have kept the proportion of NaCl and KCl in the present work equimolecular (which forms a

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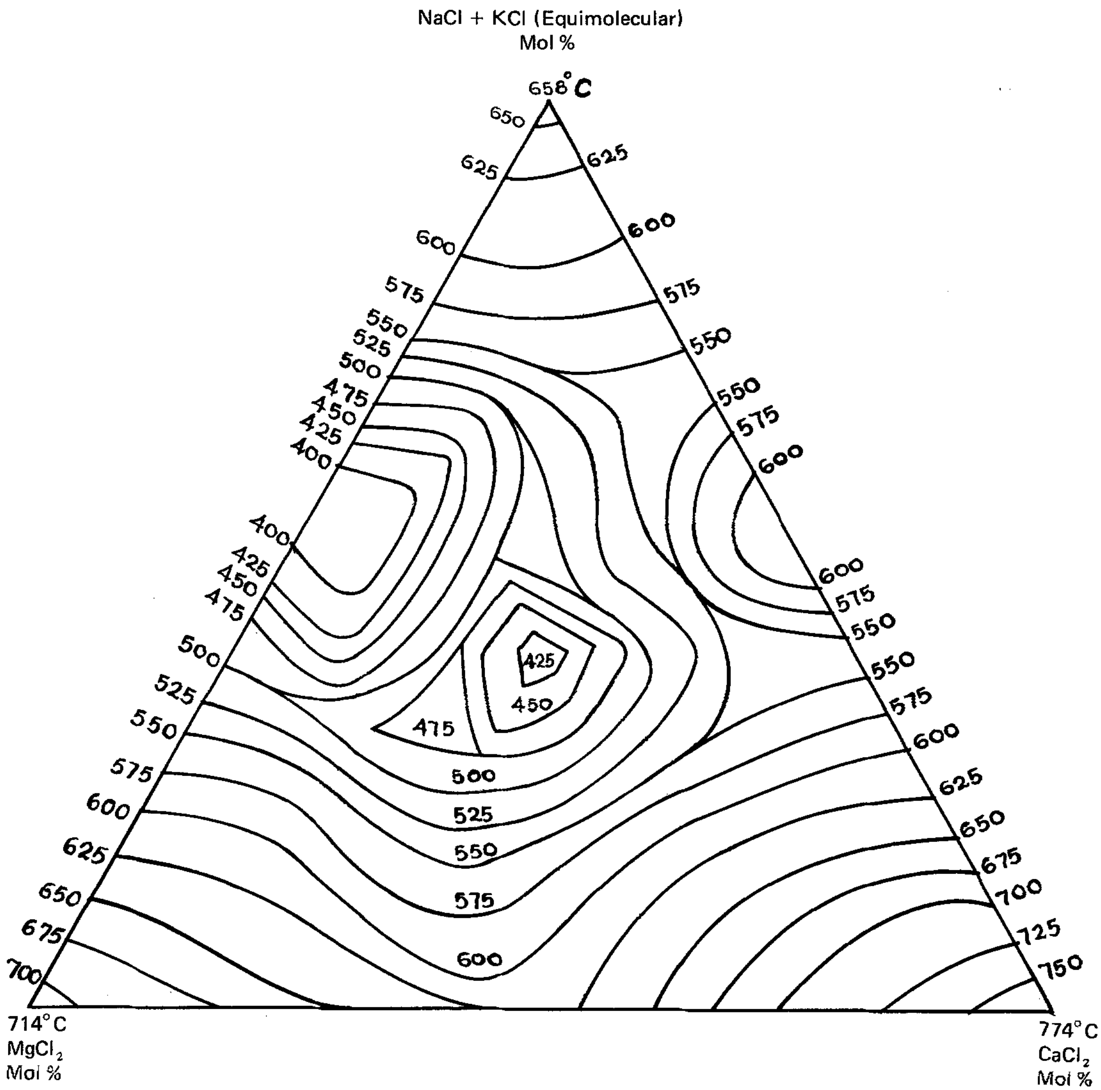

Fig. 1. Fusibility isotherms of the quasi-ternary system $MgCl_2$–$CaCl_2$–(NaCl + KCl equimolecular).

eutectic of melting point 658° C). In this way, the four-component system was converted to a quasi-ternary system and we were able to obtain a fusibility diagram in a single triangular-coordinate graph where the individual percentages of all the four components in the mixture vary from 0 to 100%. In earlier attempts [4] at a fusibility study of the four-component magnesium cell electrolyte mixtures, the amounts of magnesium chloride in the mixture were kept constant at 10 and 20 wt%, while the quantities of the other components were allowed to vary within the available range.

The primary crystallization points were determined by keeping the percentage of a particular component in the quasi-ternary system constant at different values from 0 to 100 mol%, while varying the percentages of the other two components throughout the available range. The liquidus curves were then drawn [3]. From such curves all the particular compositions corresponding to a particular temperature were obtained. These data were then used for drawing the corresponding triangular-coordinate fusibility diagram. For the sake of clarity in the phase diagram, fusibility isotherms at intervals of 25° C are depicted. Isotherms corresponding to any other temperatures could be drawn similarly.

Figure 1 shows a complete fusibility diagram for the system. A table containing the experimentally determined primary crystallization points with respective compositions in both mol and weight per cents of the corresponding salt mixtures, not included in the paper for economy of space, may be obtained from the authors on request.

It can be seen from Fig. 1 that a temperature as low as 400° C can be reached in the present four-component molten salt system without any solid separation. It is also evident from the figure that higher percentages of $MgCl_2$ (up to 50 mol%) in the salt mixture bring down the primary crystallization temperature. It may also be noted that the minimum primary crystallization points which can be obtained in the above system containing 10, 20, 30, 40 and 50 mol% $MgCl_2$ are around 550, 500, 425, 400 and 400° C, respectively. For higher percentages of $MgCl_2$ (above 50 mol%) in the mixture the trend would be generally reversed. The minimum crystallization temperatures in such cases seem to be around 500, 525, 600 and 650° C for 60, 70, 80 and 90 mol% $MgCl_2$ in the molten salt mixture, respectively.

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