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Description of the melt stoichiometry in the electrodeposition of boron from KCl–KF–KBF$_4$ melts

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ABSTRACT

This paper attempts to describe a plausible scheme of reaction(s) that governs the electrodeposition of boron from melts containing KCl, KF and KBF$_4$ (at 1073 K). Four different stoichiometric equations were formulated based on the existence of various chloride–fluoride complexes derived from the fluoroborate anion. During the electrolysis all these chloride–fluoride complex anions of boron would undergo decomposition. The net variation in the ratio $n_{\mathrm{Cl}^-}/n_{\mathrm{F}^-}$ thus computed based on these four equations by assuming uniform depletion of boron from the melt due to electrodeposition was compared with the experimental values obtained during many electrowinning runs. These analyses describe the progress of the electrodeposition of boron from KCl, KF and KBF$_4$ melt.

1. Introduction

High-density compacts of boron carbide containing enriched boron (65 at% ^{10}B) is the control rod material for Prototype Fast Breeder Reactor (PFBR) [1] in India. Boron carbide is synthesized by reacting elemental boron with carbon [2]. Highly pure elemental boron, in turn, is produced by a high-temperature molten salt electrowinning process. A pilot-plant facility was set-up at the Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, India, in order to develop a process suitable for the large-scale production of elemental boron, optimize the process parameters and carry out further investigations leading to process refinement and the development of alternate methodologies [3]. The process currently in use employs a high temperature (1073 K) electrolysis [3] of KBF$_4$ (18 wt%) dissolved in a mixed chloride–fluoride melt (70 wt% KCl–12 wt% KF) contained in a graphite crucible. Upon impressing an appropriate DC (direct current) potential, boron is electrodeposited on a mild steel cathode. It has been suggested [4] that a chloride–fluoride mixture is the most suitable medium for carrying out this electrolysis, for it minimizes the loss of boron due to the decomposition of KBF$_4$ with attendant release of BF$_3$ gas. Kuznetsov [5] reported that the progressive replacement of fluoride ions in the composite BF$_4{}^-$ anion by chloride leads to the release of BF$_3$ in a melt comprising pure chloride alone. Thus the latter is not suitable for the above application. Miller [6] electrodeposited boron from a melt containing KCl (70 wt%), KF (12 wt%) and KBF$_4$ (17.8 wt%) in the temperature range 1023–1073 K. This author described the overall reaction based on the composition of the electrolyte and analysis of the effluent gas (Eq. (1)) and proposed that Cl$_2$ and F$_2$ evolve simultaneously during the electrodeposition. However the actual composition of the effluent gas and its time dependent variation with the progress of the electrodeposition were not described by this author. Further, this author had stated vividly that the electrode processes pertaining to his experiments have not been resolved [6].

$$0.5\mathrm{KCl} + \mathrm{KBF_4} \rightarrow \mathrm{B} + 1.5\mathrm{KF} + 0.25\mathrm{Cl_2} + 1.25\mathrm{F_2} \qquad (1)$$

Nair et al. [7] carried out electrodeposition of boron from a melt containing KCl (70 wt%), KF (12 wt%) and KBF$_4$ (18 wt%) at 1073 K and proposed a reaction mechanism similar to the one reported by Miller [6].

IR emission spectroscopy of melts has been utilized for establishing the ionic species in the melt by Bezarashvili et al. [8] and Solovev et al. [9]. These investigators employed custom made attachments and cells for high temperature IR investigations of a molten mixture of NaCl, KCl and KBF$_4$. They reported that this system comprised the species BF$_4{}^-$, BCl$_4{}^-$ and $[\mathrm{BF}_{4-n}\mathrm{Cl}_n]^-$ (n = 1–3). These authors arrived at the conclusion that the concentration of BF$_4{}^-$ in the melt increased with an increase in KBF$_4$ concentration. The concentration of the “chloride–fluoride” complexes $[\mathrm{BF}_{4-n}\mathrm{Cl}_n]^-$ was found to increase with temperature [8].

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Shapoval et al. [10,11] have discussed the composition of the melts KCl–KF–KBF$_4$ and KCl–NaCl–KBF$_4$. These authors have also suggested a scheme for the formation of the electrochemically active species ($[BF_{4-x}Cl_x]^-$ and $[BF_{4-x}]^{x-1}$). Danek et al. [12] established (through IR spectroscopy) the substitution of a fluoride ion by a chloride ion in the co-ordination sphere of the BF_4^- anion in KCl–KF–KBF$_4$ melts. However, these authors [12] did not obtain any other evidence for the existence of these mixed anions through other methods. From these experiments it is evident that the actual processes involved in the electrodeposition of B from KCl–KF–KBF$_4$ are yet to be understood.

In the present work, four stoichiometric equations were formulated based on the earlier reports [10,12] that substantiate the existence of different boron containing chloride–fluoride complexes in the melt. The variation in the n_{Cl^-}/n_{F^-} ratio (where n_{Cl^-} is amount of Cl^- in g and n_{F^-} is amount of F^- in g) was computed based on these four equations and by assuming uniform boron depletion from the boron containing chloride–fluoride complexes. These values were compared with the experimentally measured n_{Cl^-}/n_{F^-} ratio in the melt samples collected during the electrowinning runs. The objective of this work is to find out a plausible scheme of reaction(s) that is consistent with the experimental observations. Neither a detailed thermodynamic analysis nor the aspects of kinetics, such as relative rates of reactions are addressed, for these require more elaborate experiments which are out of the scope of this study.

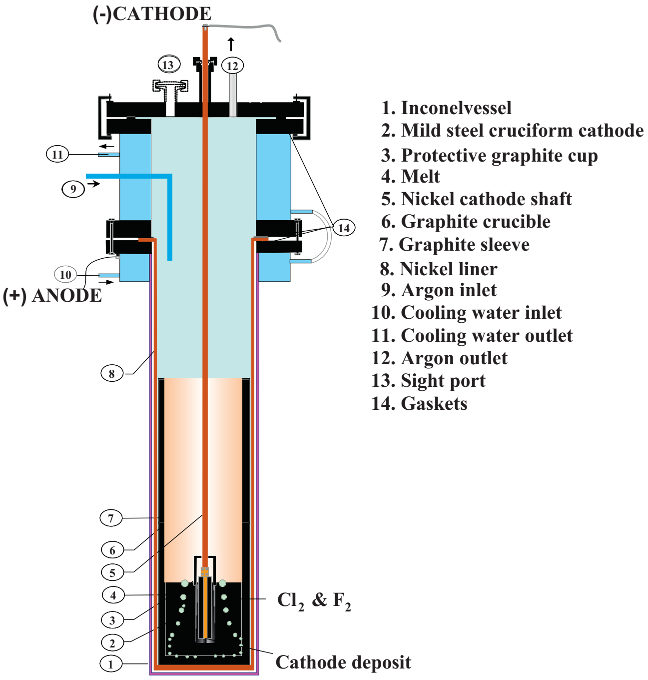

Fig. 1. Schematic of the electrowinning cell.

2. Experimental

2.1. Materials

KCl (99% purity), KBF$_4$ (99% purity, natural B) and KF (99% purity) were supplied by M/s. Loba Chemie Pvt. Ltd., Mumbai, India. KBF$_4$ derived from $BF_3{:}O(C_2H_5)$ and aqueous KF was obtained from Heavy Water Board, Talcher, India. High density (1.84 g cm^{-3}) graphite was procured from M/s. Nickunj Eximp Entp P Ltd., Chennai, India. Mild steel and nickel (purity 99%) were obtained from M/s. Mishra Dhatu Nigam Ltd., Hyderabad, India.

2.2. Cell design

The electrowinning cell (Fig. 1) essentially consisted of a cylindrical inconel retort (OD: 273 mm, height: 710 mm) made out of inconel 600. A liner made out of nickel was placed inside this vessel. A high density graphite crucible (OD: 240 mm, height 300 mm) was used as a container for ~12 kg of molten salt and also as an anode. This crucible in turn was placed inside the nickel liner. In order to protect the upper portion of the nickel liner from corrosion, a graphite liner was placed on top of the crucible such that it completely covered the internals of this liner.

A cooling collar was placed over the inconel retort. A water cooled top flange having provisions for an inlet for the mild steel cathode, a sight port, connecting the positive terminal of the DC power supply, argon inlet and an outlet for gaseous products was placed on the cooling collar. The circulation of chilled water through the collar and flange is essential in order to maintain the skin temperature below 313 K.

Boron was electrodeposited on a mild steel, “cruci form” cathode. In order to facilitate its immersion into the melt and subsequent withdrawal, the cathode was connected to a long shaft made of nickel. This shaft was introduced into the retort through a hermetically sealed feed through provided on the top flange. The electrolysis was initiated by lowering and dipping it into the molten salt. In order to avoid high temperature gas phase corrosion of the mild steel cathode, its upper portion was covered with a protective sleeve made out of high density graphite. This retort assembly was lowered into a “pit type” (pit type nichrome resistance furnace manufactured by M/s. Hightemp Industries, Kochi, India) furnace such that most of it, excepting the cooling collar was located inside the pit.

2.3. Process

KCl and KBF$_4$ salts were pre-dried under flowing argon for 48 h at 393 K and then vacuum dried for 48 h at 393 K, while KF was vacuum dried for 48 h at 503 K. A charge of about 6 kg (vacuum dried KCl (4.2 kg), KF (0.72 kg) and KBF$_4$ (1.08 kg)) was poured into the cell at 548 K under flowing argon. In situ vacuum (0.3 Pa) degassing of this salt mixture was then carried out for 12 h at 548 K by using a cryogenic moisture trap maintained at the boiling point of liquefied N$_2$. This mixture was then heated under flowing argon at a rate of 3 K min^{-1} to 1148 K. In order to ensure that the charge got melted completely, the latter was held at this temperature for about 2 h and then cooled to 548 K. Subsequently yet another (6 kg) charge was loaded into the crucible and the same sequence of operations described above was repeated. After the consolidation of the charge, the latter was maintained at 1073 K. A mild steel cathode was dipped into it and pre-electrolysis was carried out at 1.5 V (by using a DC power supply manufactured by M/s. Digitronics, Pune, India) until the cell current reached a value below 1 A. A fresh mild steel cathode was then lowered into the melt. The cell voltage was increased from an initial value of 1.5 to 3.5 V with an increment of 6.6×10^{-4} V s^{-1}. After it attained a value of 3.5 V the cell voltage was increased to 4.5 V with an increment of 3.3×10^{-4} V s^{-1}. The cell voltage was maintained at 4.5 V for 6 h in order to facilitate the electrolysis. After carrying out three such electrodepositions a “make-up” charge containing KCl (2 kg) and KBF$_4$ (1.12 kg) was added to the solidified salt mixture at 548 K. After vacuum degassing and melting this replenished charge, two more electrodepositions were carried out. Another “make-up” charge containing KCl (2 kg) and KBF$_4$ (1.12 kg) was then added to the solidified salt mixture at 548 K. Two more electrodepositions were carried out subsequently after vacuum degassing and melting. Each