Electrodeposition of Iron from Molten Mixed Chloride/Fluoride Electrolytes

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The electrochemical behavior of dissolved Fe_2O_3 and the electrodeposition of iron in molten $CaCl_2$-CaF_2 (80-20 mol %) and other mixed chloride/fluoride electrolytes was studied at 827 °C and 890 °C by cyclic voltammetry, chronoamperometry and galvanostatic electrolysis, and deposits were characterized by XRD and SEM. Pure iron was obtained in these melts at current efficiencies greater than 90 %. High cathodic current densities (~0.5 A cm^{-2}) were achieved by using a rotating cathode. The work is related to studies of the possible development of new processes for the production of iron and steel with large reductions of CO_2 emissions.

Introduction

The production of iron and steel causes large emissions of CO_2. Iron electrowinning in molten salts with dissolved Fe_2O_3 using an inert oxygen evolving anode is an alternative process to reduce or eliminate the formation of CO_2.

The earliest work on iron deposition was reported in 1944 by Andrieux and Weiss (1). Electrolysis experiments were carried out in sodium peroxide, sodium carbonate and sodium metaborate using iron electrode at 450-500 °C and 10-25 A. Instead of iron deposits, sodium and magnetite were deposited on the cathode. In the 1960s Zulkiewitz et al. (2, 3) used eutectic KCl-LiCl-$FeCl_2$·$4H_2O$ at 150-225 °C, and obtained iron deposits. However, due to the dehydration of the melt, $FeCl_2$ sublimation and decomposition occurred. In their further study, LiCl was replaced by NaCl, which made the iron crystal size drop from 2-3 mm to 1-10 μm (4). Great efforts on the electrodeposition of iron from molten salts were made in the former Soviet Union for powder metallurgy applications, but the process was never commercialized. A. B. Suchkov et al. (5) tested the electrorefining of scrap iron and pig iron. Dendritic iron was produced in NaCl-$FeCl_2$ (10 wt %) melt at 850-900 °C and the current efficiency decreased rapidly due to the dendritic growth of the deposit. By increasing the iron concentration of electrolytes and decreasing starting current, iron grains in the cathode grew coarsely (6). Electrorefining of iron from molten NaCl-KCl-$FeCl_2$-$MgCl_2$ and electrowinning of iron from molten NaF-KF, NaF-KF-NaCl, NaCl-KCl-$FeCl_2$, NaCl-KCl-$FeCl_2$-$MgCl_2$ and NaCl-KCl-$Na_4P_2O_7$-$K_4P_2O_7$ was also tried at 900-950 °C (7, 8). In NaF-KF electrolyte iron deposit grains were about 0.5 − 0.1 mm and decreased with the addition of NaCl. The iron

deposits in the phosphate containing electrolyte were contaminated by phosphorus and the phosphorus content in the iron deposit was about 1.5% P, and no iron was deposited in NaCl-KCl-FeCl$_2$ electrolyte. In 1987, Demidov et al (9) studied the reduction of Fe$_2$O$_3$ and Fe$_3$O$_4$ in LiCl-KCl eutectic electrolyte by the cyclic voltammetry method, and assumed the reduction Fe$_3$O$_4$ occurred in three steps. Haarberg et al. (10, 11) studied the electrochemistry of Fe$_2$O$_3$ dissolved in several chloride and fluoride containing electrolytes, and found that the solubility of Fe$_2$O$_3$ in CaCl$_2$-NaCl melts was greatly enhanced upon additions of AlCl$_3$, AlF$_3$ or MgCl$_2$, but a divalent iron species was produced by an exchange reaction between hematite and aluminium chloride, and chlorine gas was evolved. In molten fluorides and mixed fluoride/chloride electrolytes CaCl$_2$-KF (15-85 mol %), CaCl$_2$-KF-NaF (7-39-54 mol %), KF-NaF (50-50 mol %) and LiF-KF-NaF (46.4-42.1-11.5 mol %), the exchange reaction was avoided. However, the solubility of hematite was more limited in the absence of an acidic substance such as AlCl$_3$ (10). In a novel process of producing titanium, Chen et al (12) used CaCl$_2$ as the main electrolyte due to the high solubility of CaO in the melt. In the present work, the electrochemistry of iron in CaCl$_2$-CaF$_2$ (80-20 mol %) was studied.

Experimental

CaCl$_2$ and CaF$_2$ of analytical quality were dried in air for 48 h and kept and weighed in a glove box to avoid contact with moisture. An air tight cell with radiation shields of aluminum oxide, and carbon crucibles (75 mm × 60 mm in diameter, 117 mm in height) were used in the experiments. Argon gas was circulated through the cell to maintain an air-free atmosphere. The temperature inside the furnace was measured with a thermocouple of S type (Pt-Pt/10%Rh) placed in a closed aluminium tube. The salt (150 g) was heated to 200 °C and kept at this temperature overnight, and then heated to 800 °C. The electrochemical techniques of cyclic voltammetry and chronoamperometry were used to study the behavior of dissolved iron species. A molybdenum wire (2mm in diameter) and a platinum wire (1 mm in diameter) were used as the reference and the working electrodes, respectively. A magnetite rod (anode no: 1-2005, made at SINTEF Material and Chemistry, 100 % magnetite, axially pressed, sintered under argon atmosphere at 950 °C for two hours, with electrical conductivity at room temperature of 366 $\Omega^{-1}m^{-1}$ and size 25 mm in diameter, 60 mm in length) was used as the counter electrode in the electrolysis experiments and a carbon rod (10 mm in diameter, 200 mm in length) was used as the counter electrode in the electrochemical measurements. The electrodepositon of iron was performed by the galvanostatic electrolysis method and the iron deposits were washed in distilled water bubbled with argon, dried in air and characterized by XRD and SEM.

Results and Discussion

Several different electrolytes were tested. It was found that mixtures of chloride and fluoride salts were beneficial. In this paper only results obtained in molten CaCl$_2$-CaF$_2$ are presented.

CaCl$_2$-CaF$_2$ Melt

The electrochemical behavior of dissolved iron species Fe(III) in molten CaCl$_2$-CaF$_2$ (80-20 mol %) was studied by linear cyclic voltammetry and chronoamperometry in

greater detail as a function of Fe_2O_3 concentration. The cyclic voltammograms on a molybdenum working electrode with 0.5 mol % Fe_2O_3 concentration at different sweep rates have the quite typical shape for a metal deposition reaction (as shown in Figure 1) with steep anodic stripping peaks. No apparent cathodic background current was observed in the cyclic voltammograms. The deposition of iron takes place directly from Fe(III) species.
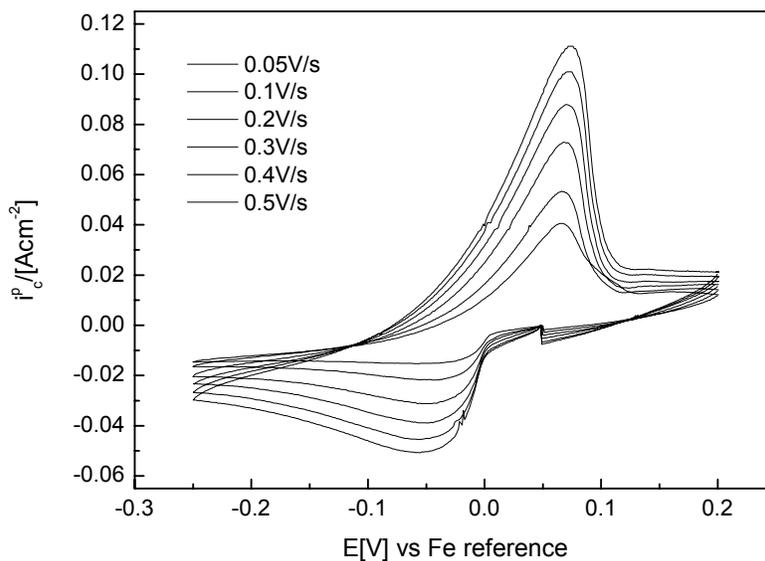

Figure 1. Cyclic voltammograms at a molybdenum working electrode in $CaCl_2$-CaF_2 (80-20 mol%) with addition of 0.5 mol % Fe_2O_3, 827 °C.
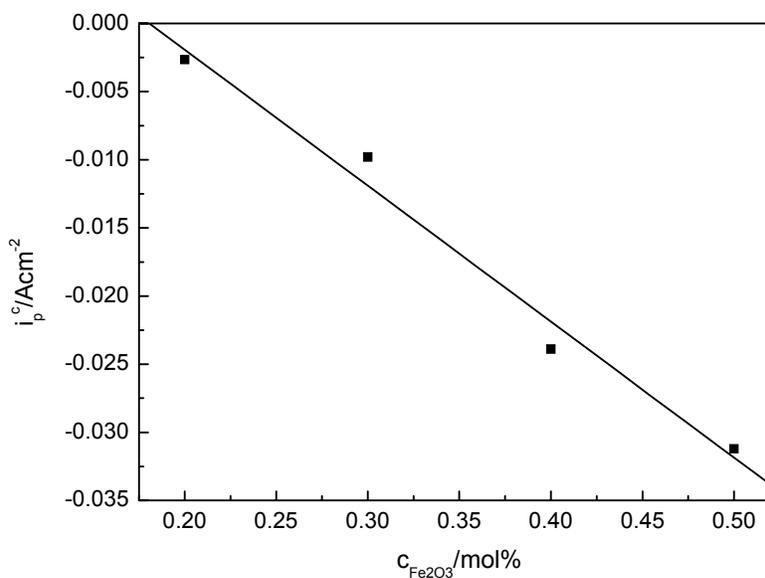

Figure 2. Voltammetric peak current density versus Fe_2O_3 concentration in $CaCl_2$-CaF_2 (80-20 mol %) with 0.2 V/s scan rate, 827 °C.

Figure 2 shows the cathodic peak current densities measured at different Fe_2O_3 concentrations in the electrolyte $CaCl_2$-CaF_2 (80-20 mol %). The current density for a diffusion controlled reaction is proportional to concentration, hence the current density plotted as a function of concentration should show a linear relationship if the iron deposition reaction is diffusion controlled. From Figure 2, it can be seen that the current densities measured in the electrolyte $CaCl_2$-CaF_2 (80-20 mol %) follow the linear relationship quite well. The cathodic peak current density increased with increasing Fe_2O_3 concentration, and the results obtained suggest that the solubility of Fe_2O_3 in molten $CaCl_2$-CaF_2 (80-20 mol %) is at least 0.5 mol % at 827 °C.

The cathodic peak current density was plotted as a function of the square root of the sweep rate for $CaCl_2$-CaF_2 (80-20 mol %), and very good linear fits were obtained. From the slope of the straight line the diffusion coefficient of the Fe(III) iron species in $CaCl_2$-CaF_2 (80-20 mol %) at 827 °C was calculated to be 3.0×10^{-5} $cm^2 s^{-1}$. Chronoamperometry did not reveal any signs of nucleation or phase formation.

Iron electrolysis was performed in $CaCl_2$-CaF_2 (80-20 mol %), with addition of 1 mol % Fe_2O_3 using a rotating iron cathode (210 rpm/min) at 890 °C by the galvanostatic electrolysis method. Pure iron was obtained, as can be seen from the XRD pattern in Figure 3. The current efficiency with respect to iron was found to be 92 % in this experiment. Small amounts of Fe_3O_4 were found in the iron product, and this could be due to partial reduction of Fe_2O_3 by the carbon crucible. CaF_2 is difficult to dissolve in water and therefore some CaF_2 remained in the iron product and lowered the purity of iron.
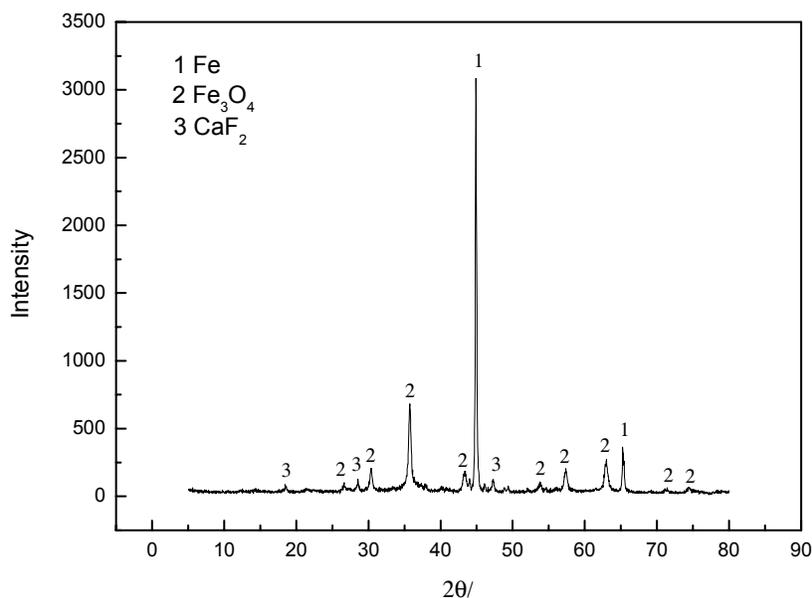

Figure 3. XRD pattern of iron deposit from $CaCl_2$-CaF_2 (80-20 mol %), 890 °C.

Conclusions

The electrochemical behavior of dissolved Fe_2O_3 in molten $CaCl_2$-CaF_2 (80-20 mol %) was studied at 827 °C and 890 °C by electrochemical techniques. Iron was found to be deposited from Fe(III) complexes; the diffusion coefficient of the Fe(III) species at 827 °C was determined by voltammetry to be 3.0×10^{-5} cm^2/s in $CaCl_2$-CaF_2 (80-20 mol %). Pure iron was electrodeposited at current efficiencies greater than 90 %. The solubility of Fe_2O_3 in the melt was estimated to be about 0.5 mol %. The results are promising for the possibility of developing a new process for the production of iron.

Acknowledgments

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