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Electrochemical Behavior of Dissolved Fe_2O_3 in Molten $CaCl_2$-KF

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Abstract: The electrochemical behavior of dissolved Fe_2O_3 in 82.5$CaCl_2$-17.5KF (mole percent, %) was studied using cyclic voltammetry, chronoamperometry, and galvanostatic electrolysis at 827 ℃, and the deposits were characterized by XRD and SEM. Pure iron was deposited on a rotating cylinder (210 r/min) with a cell voltage less than −1.0 V. Deposition rate was controlled by diffusion on a molybdenum electrode. The diffusion coefficient of iron species Fe(Ⅲ) in the melt at 827 ℃ was found to be 9.7×10^{-5} cm^2/s.

Key words: iron; electrolysis; electrochemistry; molten salt

Because iron and steel production causes large emission of CO_2, electrowinning of iron 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 initial 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 with 10—25 A current at 450—500 ℃. Instead of iron deposits, sodium and magnetite were deposited on the cathode. In the 1960s, Zulkiewitz et al[2,3] used eutectic KCl-LiCl-$FeCl_2 \cdot 4H_2O$ at 150—225 ℃ and obtained the iron deposits. However, due to the dehydration of the melt, $FeCl_2$ sublimation and decomposition occurred. Furthermore, in their study, LiCl was replaced by NaCl, which made the iron crystal size drop from 2—3 mm to 1—10 μm[4]. Considerable efforts on the electrodeposition of iron from molten salts were made in former Soviet Union for powder metallurgy applications, but the process was never commercialized. Suchkov A B et al[5] tested the electrorefining of scrap iron and pig iron. Dendritic iron was produced in NaCl-10$FeCl_2$ (mass percent, %) melt at 850—900 ℃, and the current efficiency decreased rapidly due to the dendritic growth of the deposit. By increasing the iron concentration of electrolytes and decreasing the initial 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-$Na_4P_2O_7$-$K_4P_2O_7$ were also run at 900—950 ℃[7]. In NaF-KF, the 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%, and no iron was deposited in NaCl-KCl-$FeCl_2$ electrolyte. In 1987, Demidov et al[8] studied the reduction of Fe_2O_3 and Fe_3O_4 in LiCl-KCl eutectic electrolyte by the cyclic voltammetry method and assumed that the reduction Fe_3O_4 occurred in three steps. Haarberg et al[9,10] studied the electrochemistry of Fe_2O_3 dissolved in several chloride and fluoride containing electrolytes, and found that the solubility of Fe_2O_3 in $CaCl_2$-NaCl melts was considerably enhanced upon additions of $AlCl_3$, AlF_3, or $MgCl_2$, but divalent iron species was produced by an exchange reaction between hematite and aluminum chloride, and chlorine gas is evolved. In molten fluorides and mixed fluoride/chloride electrolytes 15$CaCl_2$-85KF, 7$CaCl_2$-39KF-54NaF, 50KF-50NaF, and 46.4LiF-42.1KF-11.5NaF (mole percent, %),

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the exchange reaction was avoided. However, the solubility of hematite was more limited in the absence of an acidic substance, such as $AlCl_3$[9]. In a novel process of producing titanium, Chen et al[11] used $CaCl_2$ as main electrolyte.

1 Experimental

$CaCl_2$ and KF of high quality were dried in air for 48 h and weighed in a glove box to avoid contact with moisture. An airtight cell with radiation shields of aluminum oxide and carbon crucibles [75 mm (outer) and 60 mm (inner) 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) in a closed aluminum tube. The salt (150 g) was heated to 200 ℃ and kept at the same temperature for an overnight, then heated to 800 ℃. The electrochemical techniques of cyclic voltammetry and chronoamperometry were used to study the behavior of dissolved iron species. Molybdenum wire (2 mm in diameter) and platinum wire (1 mm in diameter) were used as the reference and the working electrodes (WE). A magnetite rod [100% magnetite, axially pressed, sintered under argon atmosphere at 950 ℃ for 2 h, the electrical conductivity at room temperature is 366 $(\Omega \cdot m)^{-1}$ with size 25 mm in diameter, 60 mm in length] was used as the counter electrode in the electrolysis experiment, and a carbon rod (10 mm in diameter, 200 mm in length) was used as the counter electrode in the electrochemical measurement. 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 X-ray diffraction (XRD) and scanning electron microscope (SEM).

2 Results and Discussion

The electrochemical behavior of dissolved iron species Fe (Ⅲ) in molten 82.5$CaCl_2$-17.5KF (mole percent, %) was studied using linear cyclic voltammetry and chronoamperometry in considerable detail. The cyclic voltammograms on a molybdenum electrode with 0.3% Fe_2O_3 (mole percent) addition at different sweep rates have the shape quite typical for a metal deposition reaction [as shown in Fig. 1 (a)] with steep anodic peaks, and no apparent background current was observed in the cyclic voltammograms. The couple peaks on the cyclic voltammograms

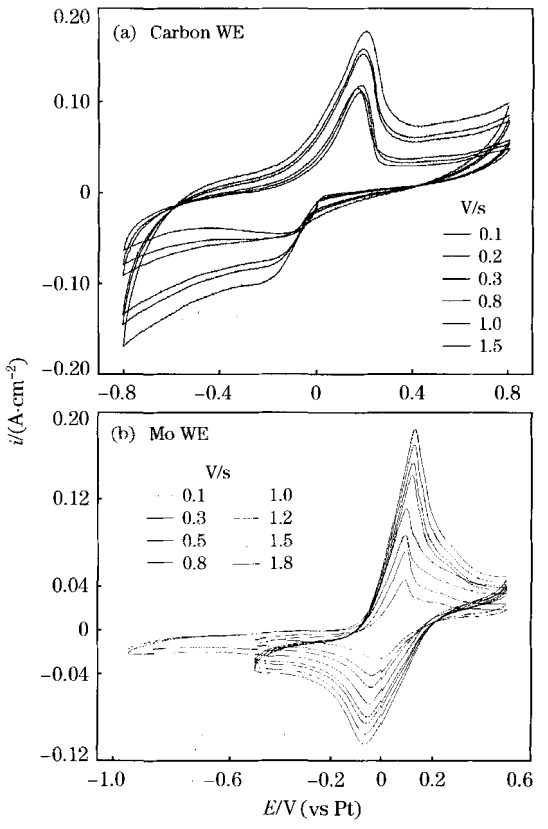

Fig. 1 Cyclic voltammograms in 82.5$CaCl_2$-17.5KF (mole percent, %) with Fe_2O_3 addition at 827 ℃

represent the deposition of Fe(Ⅲ) and the dissolution of iron in 82.5$CaCl_2$-17.5KF (mole percent, %). The cyclic voltammograms on a carbon electrode with addition of 0.5% Fe_2O_3 (mole percent) show a couple of peaks, corresponding to the deposition of Fe(Ⅲ) and the dissolution of iron [see Fig. 1 (b)], and an obvious background current was observed. Harrberg et al also found cathodic background current on a carbon electrode in 85KF-15$CaCl_2$ (mole percent, %)[9].

Iron deposition from the melt is a coupled reaction consisting of two steps: diffusion and charge transfer. Diffusion is the first step droved by potential and concentration difference. For a diffusion controlled deposition reaction, when plotting the cathodic peak current as a function of the square root of the sweep rate, following linear relationship is obtained[12]:

$$i_c^p = 0.61(nF)^{3/2}[D/RT]^{1/2}c^0v^{1/2} \quad (1)$$

where i_c^p, n, F, D, R, T, c^0, and v are the cathodic peak current density, the number of electron transfer, Faraday constant, the diffusion coefficient of iron species Fe(Ⅲ), gas constant, the thermodynamic temperature, the concentration of iron species Fe(Ⅲ) in