

Direct electrochemical reduction of hematite pellets in alkaline solutions

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Our previous studies on the electrowinning of iron from hematite particles suspended in sodium hydroxide solutions demonstrated that iron was produced through a direct solid phase electrochemical reduction of the oxide particles. This suggests that the electro-deoxidation of a hematite powder pellet by the FFC type process should be possible in aqueous solutions at a low temperature. We investigated the electrochemical reduction of a solid hematite pellet cathode manufactured by conventional mechanical pressing followed by sintering process in concentrated sodium hydroxide solutions using a nickel inert anode at 110 °C. The experimental results indicated that hematite was reduced to iron metal. Propagation of the reduction reaction front through the oxide phase occurred at a high speed, and the rate-determining step was the diffusion of the oxygen ion through the shrinking cores of the oxide particle.

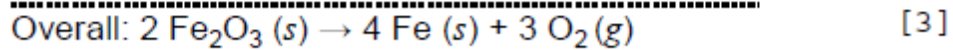
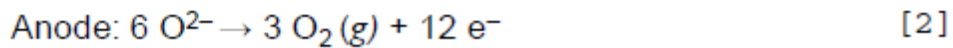
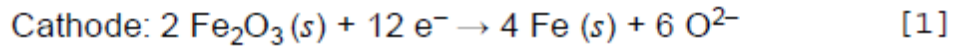
Introduction

The European 6th framework ULCOS project aims at the development of new technologies that significantly reduce the CO₂ emission from the steel smelters. The electrowinning of iron from iron ore in aqueous solutions utilizing renewable energy resources was investigated as an alternative to the conventional carbothermic reduction for iron and steelmaking (1-4). In the electrowinning process, hematite particles suspended in concentrated sodium hydroxide solutions were transferred to and reduced at a carbon rotating cathode, and oxygen was evolved at a nickel inert anode. In contrary to conventional electrowinning processes, the iron electrowinning reaction system contains scarcely dissolved species. Further studies on the mechanism of the conversion of the iron ore to iron concluded that that the reduction reaction occurred in a solid-state with magnetite as the intermediate phase (1-4). This initial electron transfer to the insulating oxide phase and the diffusion of the oxygen ions through the oxide phase at the very low temperature appears fairly doubtful. On the other hand, this unusual mechanism suggested that a very interesting process, the FFC Cambridge type process should be possible for the production of iron metal at a low temperature in alkaline solutions.

The FFC Cambridge process is based on electro-deoxidation of titanium oxide and other metal oxides cathode in molten salts at a high temperature invented by Professor Fray's group at University of Cambridge (5). The process represents a new generation of extractive metallurgy where electrons were provided onto an insulating porous oxide electrode with the electrolyte (molten salts) penetrating throughout its body. The oxide is

deoxidized to the metal through a series of charge and mass transfer processes in the solid state. Owing to its inherent advantages such as simple, sustainable, easily scale-up, cheap, continuous, this process has raised up world-wide interest in applying the process to other metals [6] and in the commercialization of the process. Nevertheless, an FFC Cambridge type process to be carried out not in molten salts at high temperatures but in aqueous solutions at low-temperatures has never been tried.

The purpose of the present work is thus to investigate the feasibility of the electrochemical reduction for iron metal production in concentrated sodium hydroxide solutions at a low temperature for iron production. As shown in Figure 1, in this process, a porous hematite powder pellet was manufactured by mechanical pressing followed by sintering. The sintered pellet was then immersed in a concentrated sodium hydroxide solution. A direct current was applied between the hematite pellet cathode and a nickel metal mesh anode at 110 °C. The oxygen in the hematite was ionized and was diffused through the solid and the electrolyte to the anode and was discharged as oxygen gas. The mechanism of the initial electron transfer to the apparently insulating hematite, the diffusion of the oxygen ion in the solid phase, and the propagation of the reduction reaction front were discussed in accordance with the obtained experimental results.



$$T = 110 \text{ }^\circ\text{C}$$

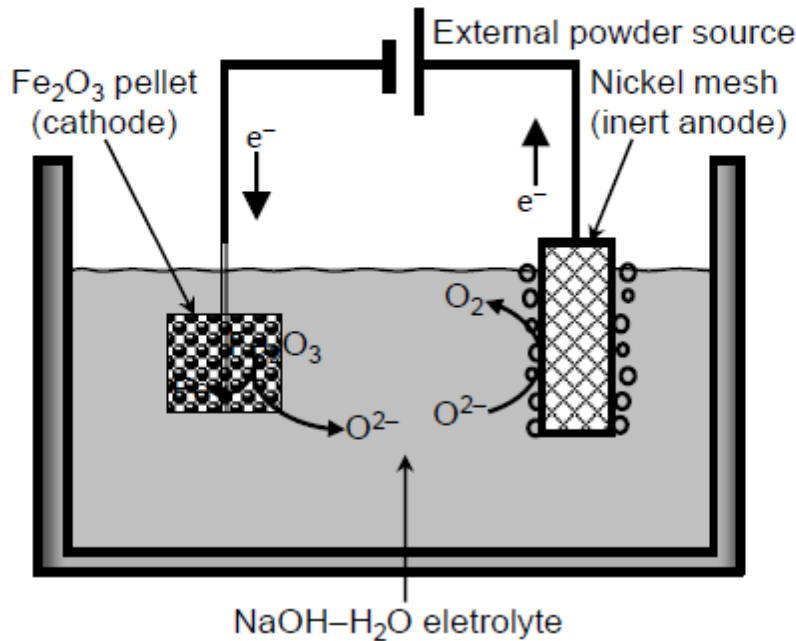


Figure 1. Schematic illustration of the electrochemical reduction of hematite powder pellet in alkaline solutions at low temperatures.

Experimental

The hematite powder pellet was manufactured by mechanical pressing followed by sintering. About 1 g hematite powder (Alfa Aesar GmbH & Co KG, 99,5%) was loaded in a cylinder mold of diameter 10 mm with a platinum wire spring embedded. An uniaxial pressure of about 170 MPa was applied for about 1 minute. The pressed pellet was put in an alumina crucible and was sintered in air in an electric furnace at 800 °C for 3 hours. The sintered pellet possessed enough mechanical strength for the purpose of the subsequent electrochemical reduction.

Figure 2 (a) shows the experimental setup for the electrochemical reduction of the pellet. The electrolyte was a 50 wt. % NaOH-50 wt. % H₂O sodium hydroxide solution contained in a cylindrical Teflon container. The highly concentrated solution provided the advantages such as a high conductivity, suppressed H₂ evolution reaction, and possibility to apply higher temperature without considerable loss of water. A rectangular nickel mesh was attached to the wall of the container and was used as the inert anode for oxygen evolution. The powder pellet was suspended in the electrolyte corresponding to the geometric center of the anode for the sake of uniform current distribution. The electrolyte was heated up and the temperature was held constant by utilizing a thermostat filled with thermo oil (Julabo). A direct current of 300 mA was applied to the hematite powder pellet cathode and the nickel mesh anode by using the potentiostat (IM6, Zahner). The potential of the cathode was measured with reference to a Hg/HgO reference electrode.

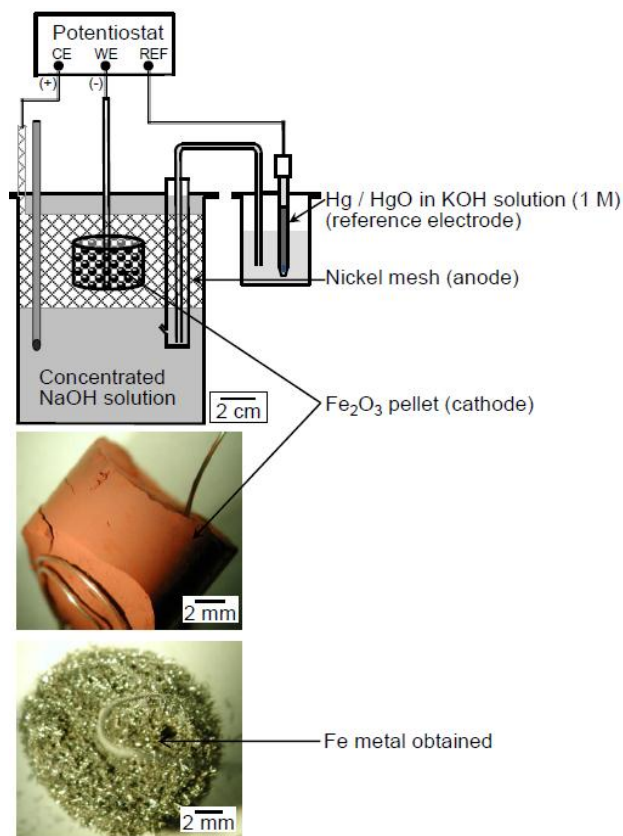


Figure 2. (a) Schematic drawing of the experimental step-up. Optical images of (b) the sintered pellet and (c) the reduced pellet.

The particle size of the as-received hematite powder and the powder after sintering was measured by Mastersizer 2000 particle analyzer. The phases in the reduced pellet were analyzed by X-ray diffraction (D8 Focus). The morphology of the partially and fully reduced pellets was observed under optical microscopy and SEM (Hitachi S-3400N).

Results and discussion

Figure 2 shows an optical image of (b) the pellet after sintering at 800 °C for 3 hours and (c) the pellet after the electrochemical reduction at 300 mA current for 29,5 hours. The geometry of the pellet was a thin cylindrical tablet of 10 mm in diameter and about 4 mm in thickness. The platinum wire embedded in the pellet was used to initiate multiple reaction sites throughout the body of the oxide. A rather shiny metallic pellet was produced after prolonged electrochemical reduction. Apparently the hematite was completely converted into the iron metal.

The cathode potential with reference to the Hg/HgO reference electrode is about -1.55 - -1.60 V (Figure 3). The potential at the onset of the reduction reaction is a larger value for about 15 minutes which is consistent with the reduction in the resistance of the pellet after the reduction reaction was initiated. This initial potential value is however not extremely large in consideration of the insulating properties of the hematite. The resistance of the pellet was low enough at about 1 hour when the potential of the cathode reached a steady-state value of -1.57 V. The relatively convenient initial electron transfer to the hematite phase may be explained in the following. The near-surface layer of the Fe₂O₃ exhibits much higher deviation from stoichiometry than the bulk phase owing to the segregation of intrinsic lattice defects to the surfaces and grain boundaries. The electron transfer reactions in the hematite lattice studied by the kinetic Monte Carlo model indicated that the electron transfer reactions in hematite involve the II/III valence interchange between nearest-neighbor iron atoms via a small polaron hopping mechanism (7).

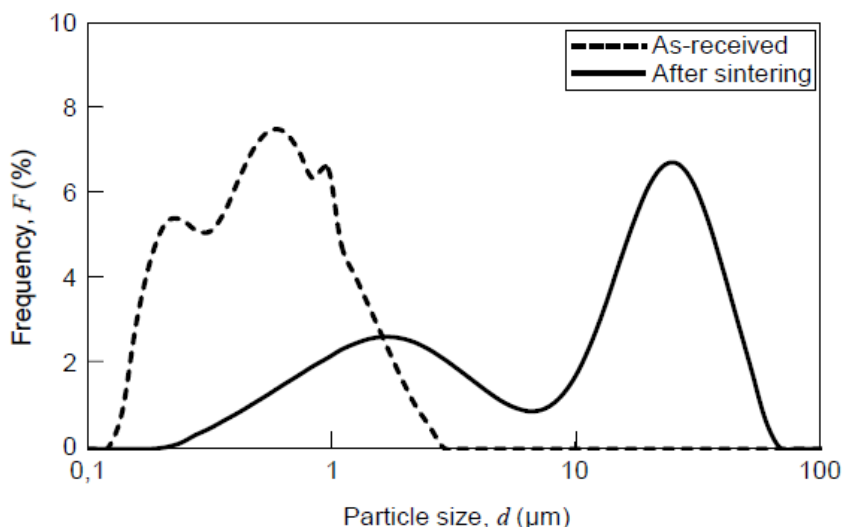


Figure 3. Particle size distribution of the hematite powders before and after sintering.

Figure 4 shows the particle size distribution profile of the hematite powder before and after sintering. The median particle size was increased from about 1 μm to 20 μm . The larger diameter of the particles after sintering may indicate that two or more particles are

fused together to form continuous particles during the sintering process by atomic diffusion through the grain boundaries. It was however not clear whether the neck growth was initiated at this temperature. The formation of a porous and interlinked network of the fused particles is very interesting for the propagation of the electrochemical reduction reaction from the site of the initiation of the reduction reaction. The isolated particles will remain difficult to be reduced which will attribute to the high oxygen concentration of the reduced metal.

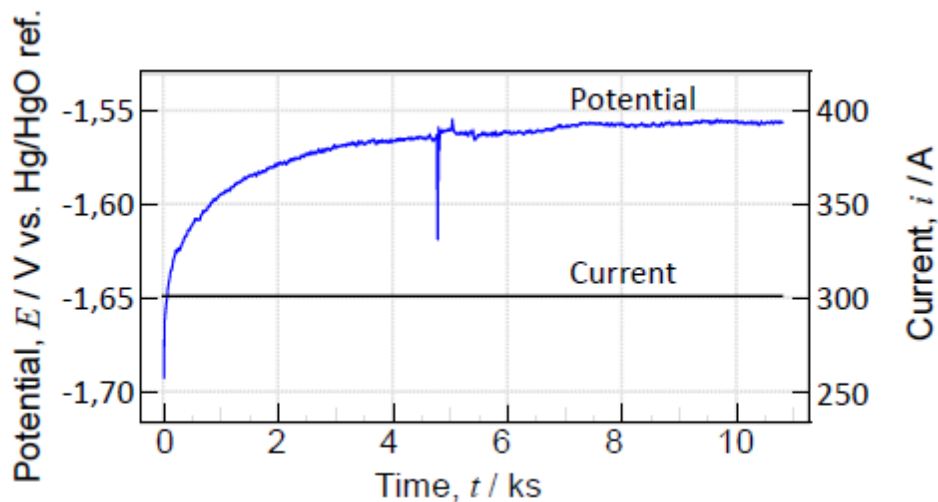


Figure 4. Potential-current curve under constant-current electrolysis.

The X-ray diffraction pattern of the powder after electrochemical reduction was shown in Figure 5. The powder was crystallized iron powder. The dissolved phase of the hematite, FeOOH was detected in the powder.

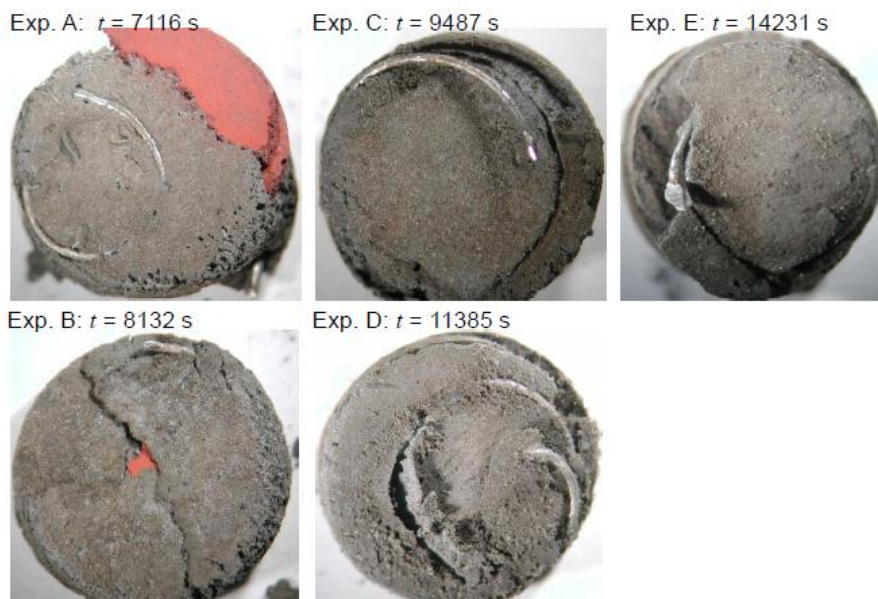


Figure 5. Optical images of the pellet reduced at 300 mA current and different electrolysis time.

Figure 6 shows optical images of the pellets (about 1 g hematite powder) when reduced at 300 mA but with different electrolysis time. For an electrolysis time of 7116 s (Fig.6 (a)), the propagation of the electrochemical reduction front went through 80% of the oxide tablet. With a further increase of the electrolysis time to 8132 s (Fig.6 (b)), the reduction front propagated 98% of the oxide tablet. At the electrolysis time above 9487 s (Fig. 6 (c, d, e)), the apparent appearance of the bulk oxide phase was not observed. It should be reasonable to state that the deoxidation reaction within the cores of the individual particles and the propagation of the reduction reaction front through the oxide phase occurs simultaneously.

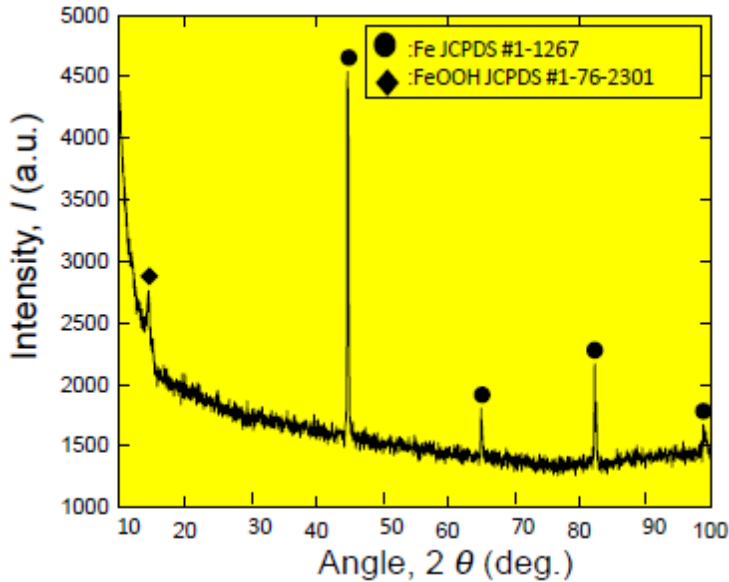


Figure 6. X-ray diffraction pattern of the obtained iron powder.

The scanning electron micrographs of the iron powder reduced at 300 mA with different reduction time were shown in Figure 7. The differences in the degree of the reduction were visualized in both the degree of deoxidation and degree of electro-crystallization. Given prolonged reduction time where the oxygen concentration was lower, the crystals were sharper and bigger and the pyramid structure was profoundly formed. In Figure 7 (a) at the reduction time of 8132 s, it could be observed that crystals with length of about 50-100 μm started to form. Some particles with diameter about 5 μm were observed. In considering the initial particle size of the oxide powder, they could be unreduced or partially reduced oxide particles. The diffusion of the iron atoms to the new lattice sites to form iron crystals occurred simultaneously with the diffusion of the oxygen ions in the oxide. When the electrochemical reduction time was increased to 11385 s, the iron crystals took the six-twin crystals pyramid shape. The metal appeared rather pure with no foreign phases observed. At some places on Figure 7 (c) there were many small crystals loosely packed together. However, big crystals with well-defined shape were formed.

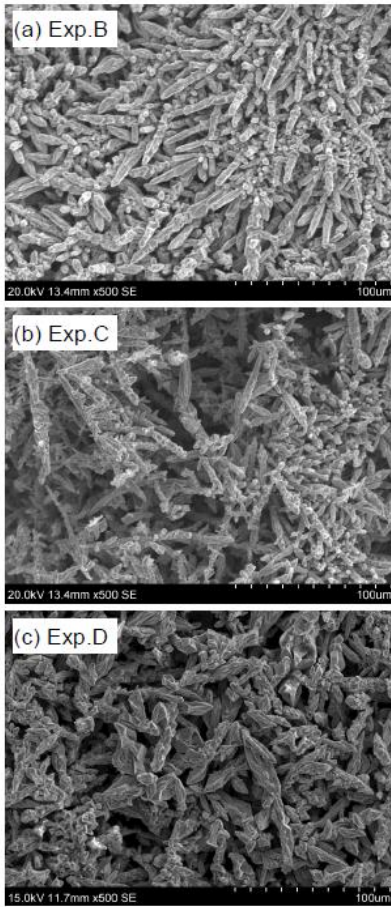


Figure 7. SEM images of the pellet reduced at 300 mA current and different electrolysis time.

Figure 8 (a) and (b) show propagation of the reduction reaction front in the oxide phase. The electrons were carried forward through the hematite body by the dendritic structure of the partially reduced lower oxide phase. This sharp pyramid penetrated the porous oxide layer from underneath and from the side, which contributed to the high rate of the propagation of the reduction reaction front. It could be again confirmed that the dendritic shape was taken into place before the complete de-oxidation. During the electro-winning of hematite particles suspended in sodium hydroxide solution on the rotating cathode experiments, the deposited iron crystals was oriented clusters of stacked six-fold twins grew layer-by-layer in the direction perpendicular to the cathode surface (refer to Figure 8 (d)). The process was mass-transferred controlled, namely, the transfer of the hematite particle by convection onto the disk electrode was the rate-determining step and the electrochemical reduction of the individual particles in its volume involving the diffusion of the oxygen ions and iron electro-crystallization was considered to be rapid.

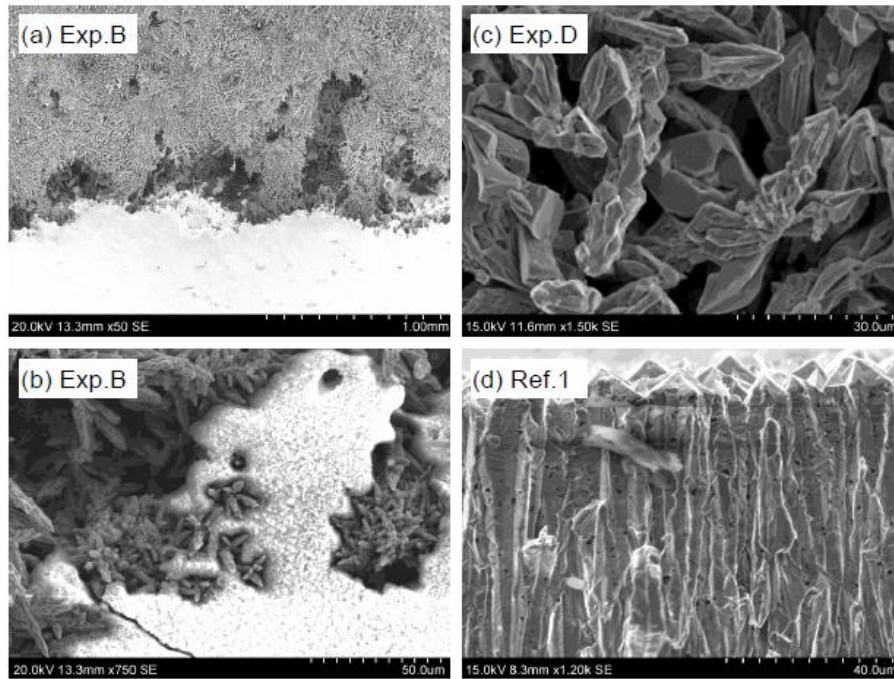


Figure 8. SEM images of (a, b) partially reduced pellet, (c) fully reduced pellet in comparison with the iron produced by electrowinning on a rotating cathode (d).

By combining the above obtained experimental results and the shrinking model (8,9) shown in Figure 9 where the intermediate magnetite phase formation was ignored, new understandings to the electrochemical reduction of the hematite powder at the low temperature in alkaline solutions are provided here. In the electrochemical reduction process, a series of physical processes occurred: the initial electron transfer on the oxide particles outer shell by the small polaron hopping mechanism, the propagation of the reduction reaction front by the partially reduced oxide, and the simultaneous shrinking of the oxide core until a complete conversion to the metal. The diffusion of the oxygen ions in the oxide phase and through the electrolyte to the anode driven by diffusion and migration, and the electro-crystallization of the iron crystal through the diffusion of the iron atoms occurred under the shrinking core deoxidation mechanism. By combining the experimental results, it was reasonable that the diffusion of the oxygen ions and simultaneous diffusion of the iron atoms were the rate-determining steps in the electrochemical reduction process. The parameter that determines the reduction reaction is thus the diffusion pathway length of the oxygen ions in the oxide phase where the particle size and morphology of the oxide powder is the determining factor. These results suggested that thin pellets having a flake-like geometry with a high surface area should facilitate the speed of the reduction reaction.

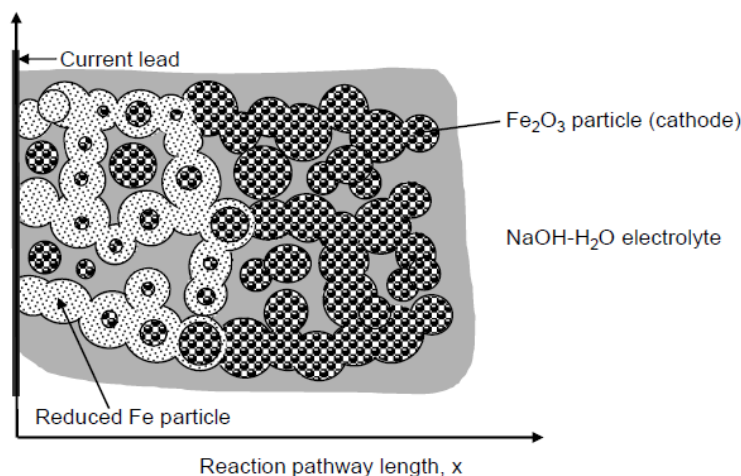


Figure 9. A shrinking core model for the electrochemical reduction of the hematite pellet in alkaline solutions.

Conclusions

The feasibility of the electrochemical reduction of a hematite powder pellet in concentrated sodium hydroxide solution at 110 °C was demonstrated. New understanding of the mechanism of the electro-deoxidation of the hematite pellet at the low temperature was provided. The reduction reaction front was carried forward in the oxide phase by the partially reduced oxide. Simultaneously with the propagation reaction, a complete conversion of the oxide core to the metal iron occurred through the shrinking of the oxide core. The electro-crystallization of the iron took place and an incomplete twin-crystals pyramid was formed. The diffusion of the oxygen ions in the solid oxide phase was the rate-determining step in the electrochemical reduction process. This fairly simple FFC Cambridge type process shows a high potential for the industrial production of pure electrochemical iron and iron alloys.

Acknowledgment

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References

1. B. Yuan, O.E. Kongstein, and G.M. Haarberg, "Electrowinning of iron in aqueous alkaline solution using a rotating cathode", *J. Electrochem. Soc.*, **156**, D64 (2009).
2. B. Yuan and G.M. Haarberg, "Electrodeposition of iron in aqueous alkaline solution: an alternative to carbothermic reduction", *ECS Trans.*, **16**, 31 (2009).
3. A. Allanore, H. Lavelaine, G. Valentin, J.P. Birat, and F. Lapique, "Iron metal production by bulk electrolysis of iron ore particles in aqueous media", *J. Electrochem. Soc.*, **155**, E125 (2008).
4. A. Allanore, H. Lavelaine, G. Valentin, J.P. Birat, F. Lapique, and P. Delcroix, "Observation of the reduction of iron oxide particles to metal in alkaline solution by electrolysis", *Electrochimica Acta*, **55**, 4007 (2010).

5. G.Z. Chen, D.J. Fray, and T.W. Farthing, "Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride", *Nature*, **407**, 361 (2000).
6. A. Cox and D.J. Fray, "Electrolytic formation of iron from haematite in molten sodium hydroxide", *Ironmaking and Steelmaking*, **35**, (2008).
7. S. Kerisit and K.M. Rosso, "Kinetic Monte Carlo model of charge transport in hematite", *J. Chem. Phys.*, **127**, 1 (2007).
8. K. Pritish and J.W. Evans, "A model for the electrochemical reduction of metal oxides in molten salt electrolytes", *Electrochimica Acta*, **54**, 835 (2008).
9. K. Pritish and J.W. Evans, "A shrinking core model of the electro-deoxidation of metal oxides in molten halide salts", *Electrochimica Acta*, **53**, 5260 (2008).