J. Min. Metall. Sect. B-Metall. 47 (2) B (2011) 193 - 198

Journal of
Mining and
Metallurgy

DEOXIDIZATION MECHANISM OF PREPARATION FeTi ALLOY USING ILMENITE CONCENTRATE

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(Received 28 December 2010; accepted 09 June 2011)

Abstract

An investigation into the deoxidization mechanism of the electrochemical reduction of ilmenite concentrate to FeTi alloy in molten calcium chloride has been performed. The results show that deoxidization proceeds through a number of individual stages some of which involve reduction of iron, formation and desposition of calcium titanates($CaTiO_3$), reduction of the various low value titanium oxides and formation of Fe_2Ti and FeTi. $CaTiO_3$ is formed because Ca^{2+} contained in electrolyte take part in the deoxidization process.

Keywords: Mechanism; Ilmenite concentrate; FeTi alloy.

1. Introduction

Since the novel molten salt electrochemical process, namely FFC process, was advanced, a number of metals and alloys were prepared by this process [1-5]. Recently, preparation of FeTi alloy using FFC process has received much more attention [6, 7]. The raw material of the traditional processes to produce FeTi alloy are Fe_2O_3 and TiO_2 powders, which Fe/Ti ratio was 1:1. The powder mixtures are compacted into a cylinder at definite pressure and sintered at elevated temperatures in a tube furnace. FeTi alloy was prepared directly using the sintered sample as cathode by FFC process.

The results of the former study show that

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DOI:10.2298/JMMB101228004H

FeTi alloy can be prepared from ilmenite concentrate by FFC process. In this work, to gain an insight into the deoxidization mechanism that occurred during the electrochemical reduction from ilmenite concentrate to FeTi alloy, partially time dependent experiments and weight change experiment are completed.

2. Experimental

2.1. Materials

Ilmenite concentrate, supplied by Panzhihua steel, was used in the present study. The average particle size of the powder was less than 74µm. Table 1. show the main elements of the ilmenite concentrate and Figure 1. is XRD pattern of of the ilmenite concentrate.

Anhydrous calcium chloride was used as the electrolyte. Graphite rod and graphite crucible were used as anode and reactor, respectively.

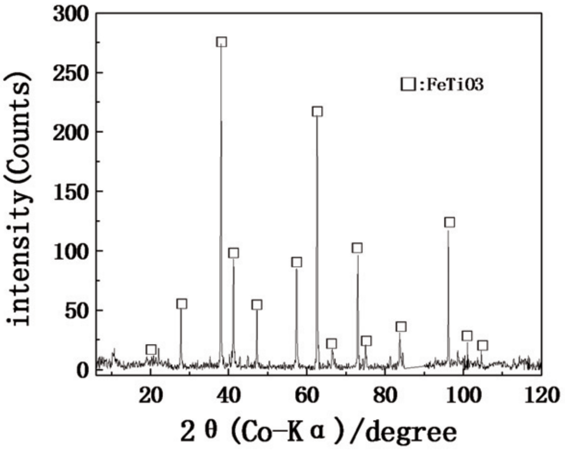

Fig.1 XRD pattern of the ilmenite concentrate

2.2. Measurement

XRD profiles were measured using a X-ray diffractometer system (XRD, Rigaku D/max-2000, and Tokyo, Japan) and recorded using Cu-Ka radiation (l = 1.5418 Å) at room temperature. Morphology analysis was examined by scanning electron microscopy (TESCAN VEGA II). The weight loss was measured by thermo-gravimetric analysis (TG/DSC-LF-1100) Switzerland.

2.3. Electrochemical process

A vertical tubular reactor vessel 300mm inner diameter (400 mm height and with a 6mm thick flange welded at its open end) was used in the experiments. Three holes were drilled on the top lid of the reactor vessel through which the electrodes were introduced to the reactor. Stainless steel tubes (5mm) were welded to the top lid to serve as gas inlets to the reactor. The experiments were conducted in argon atmosphere by continuously purging the reactor with argon gas. The argon gas was made moisture free by passing through drying system before entering reactor.

The electrolyte needed to be dehydrated by slowly heat before pre-electrolysis. The heating program involved heating from room temperature to 300°C, dwelling for 1 hour.

Table 1. Main elements of the ilmenite concentrate

Elements	O	Fe	Ti	Mg	Si	Ca	Al	Mn	S	P
Mass%	34.01	28.9	26.93	3.44	3.31	1.35	1.2	0.56	0.27	0.03

Heating to 750°C from 300°C, dwelling for 1hour, and heating to the desired temperature of 900°C from 750°C. The calcium chloride, dried as described earlier, still contained little CaO [8].The roasted sample, wrapped around with fine molybdenum wire, was introduced to the reactor. Electrolysis was carried out in the constant voltage of 3.1v at 900°C. After electrolysis, the cathode were lifted out of the molten salt and positioned in the upper part of the reactor and cooled to room temperature under a continuous flow of argon gas. Finally, taken out the reduced samples and immersed in water for approximately 12h to remove the frozen calcium chloride. After that, dried samples in air at 80°C and polished to provide an even section for X-ray diffraction (XRD) analysis. The fresh surface of the plates, obtained by fracturing the plate, was used in the microstructural and chemical composition analysis by a scanning electron microscope (SEM).

3. Results and discussion

The electrochemical process was interrupted at different reaction times to analysis phases produced during electrochemical reduction. They were 0.5h (sample a), 2h (sample b), 6h (sample c) and 10h (sample d), respectively. Figure 2. showed XRD patterns of the products at different times. The precursor and Fe,

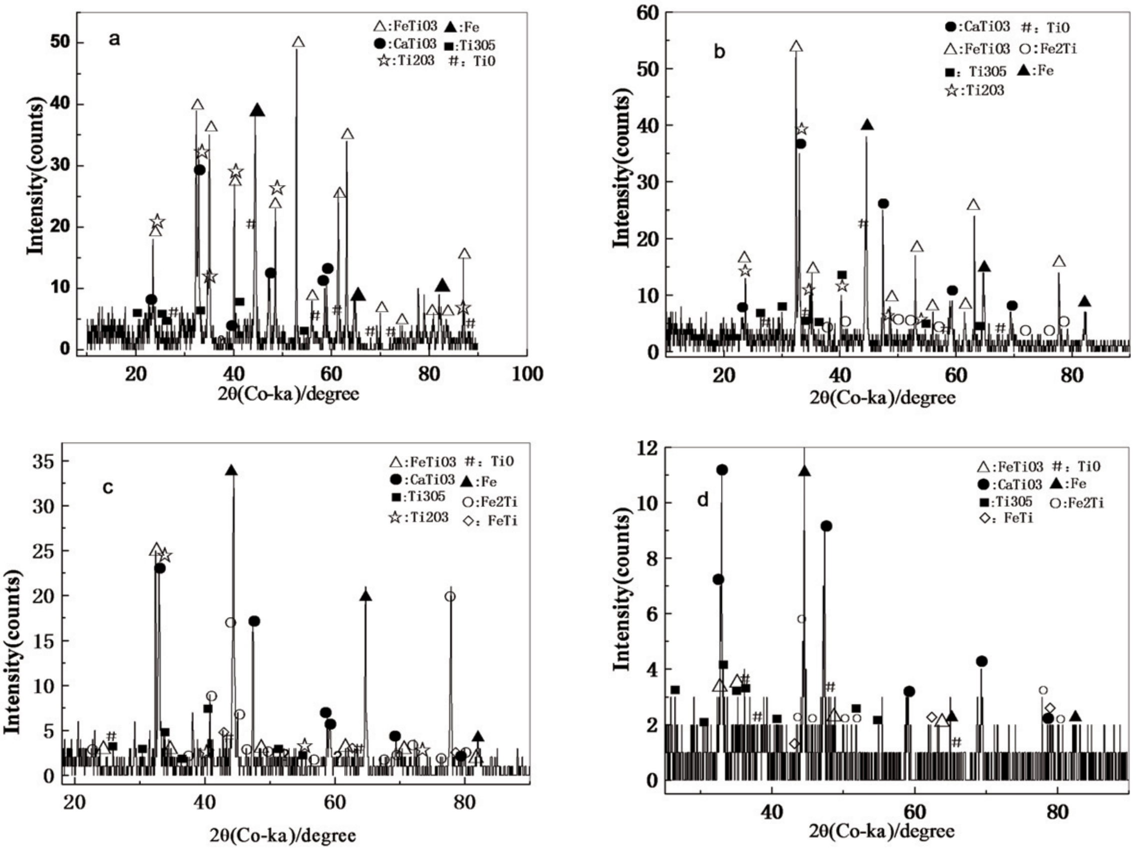

Fig.2 XRD patterns of the products at different times (a.0.5h, b.2h, c.6h, d.10h)

$CaTiO_3$ were the main phases in the sample a. Sample recovered after about 2h was composed various low value titanium oxides, such as Ti_2O_3,Ti_3O_5, TiO, and appeared Fe_2Ti alloy. Sample c predominately comprised $CaTiO_3$, Fe and low value titanium oxides, and Fe_2Ti, FeTi alloys were appeared obviously and ilmenite concentrate almost disappeared. Sample d showed the amount of ilmenite concentrate declined while more Fe_2Ti and FeTi alloys were increased. From above results we can obtain the deoxidization way of the ilmenite concentrate to FeTi alloy. Fe and $CaTiO_3$ were first produced. Various low value titanium oxides were received by electrolysis of the $CaTiO_3$ at the second stage. Then Ti, reduced from low value titanium oxides, and Fe which produced at the first stage formed Fe_2Ti alloy. Lastly, FeTi alloy was obtained. Table 2. was the main phases produced at different electrolysis time.

Ca^{2+} in electrolyte also took part in deoxidation process of the ilmenite concentrate. These deoxidization experience can be proved by Fray's research [9]. They thought $CaTiO_3$ and TiO can form $CaTi_2O_4$ during electrolysis. However, $CaTi_2O_4$ was not founded in our present research. So the overall reactions in cathode may be written as follows:

$$FeTiO_3+Ca^{2+}+2e^-=Fe+CaTiO_3 \quad ...(1)$$

$$xCaTiO_3+2(2x-y)\ e^-=xCa^{2+}+Ti_xO_y+(3x-y)\ O^{2-} \quad ...(2)$$

$$Ti_xO_y+2ye^-=xTi+yO^{2-} \quad ...(3)$$

$$2Fe+Ti=Fe_2Ti \text{ (or FeTi)} \quad ...(4)$$

Which Ti_xO_y: Ti_2O_3 or Ti_3O_5 or TiO. ...(5)

From above study, The deoxidization mechanism from ilmenite concentrate to FeTi alloy by FFC process can be depict as follows: $FeTiO_3$-Fe+$CaTiO_3$-Ti_xO_y-Fe_2Ti-FeTi. Figure 3. and Figure 4. are line scan and surface scan of the reduced sample d. It can be found Ca on the electrolytic layer was obviously more than the centre. Because the surface reoxidation causes oxygen content both electrolytic layer and inner no obvious difference. Ti and Fe contained both electrolysis layer and inner layer homogeneously distributed. The results of the line scan and surface scan proved the deoxidization mechanism further.

To further know deoxidization process, on-line monitoring of the cathode weight change was proceeded. Figure 5. is Weight change curve of the cathode.

From weight change curve it can be found that cathode weight changes were dramatically. Firstly, cathode weight decreased and then slightly increased. This

Table 2. the compositions of the samples at different electrolysis times

Time/h	Phase compositions
0.5	$FeTiO_3$, $CaTiO_3$, Ti_2O_3, Ti_3O_5,TiO, Fe, Fe_2Ti
2	$FeTiO_3$, $CaTiO_3$, Ti_2O_3, Ti_3O_5,TiO, Fe, Fe_2Ti
6	$FeTiO_3$, $CaTiO_3$, Ti_2O_3, Ti_3O_5,TiO, Fe, Fe_2Ti, FeTi
10	$FeTiO_3$, $CaTiO_3$, Ti_3O_5, TiO, Fe, Fe_2Ti, FeTi

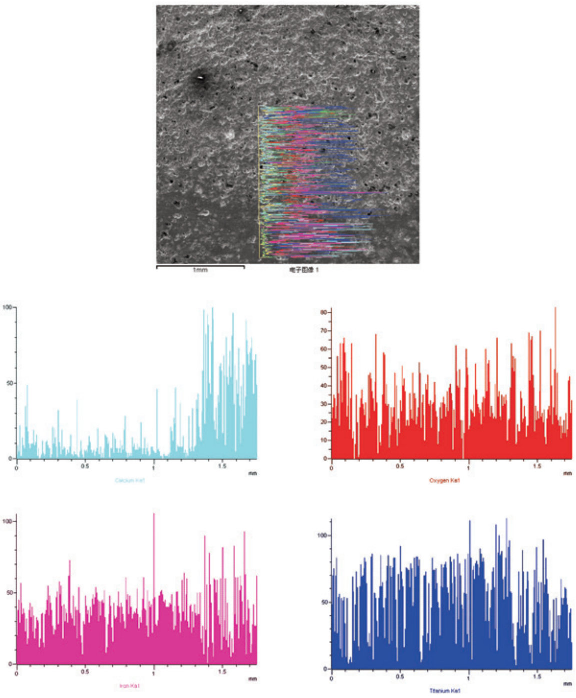

Fig. 3. Line scanning of the electrochemical samples at 10h

stage was mainly deoxidization of ilmenite concentrate and Ca^{2+} distributed near cathode area gradually deposition in cathode. The second stage was a relatively slow weight change process, in which Fe was obtained and $CaTiO_3$ gradually formed. Then there was a short and obvious weight decrease. In this stage, the reaction of electrolysis and formation of $CaTiO_3$ were occured at the same time. Then a mass of $CaTiO_3$ formed and ilmenite concentrate disappeared completely. The fifth stage, as a noticeable weight change stage, was mainly electrolyzed of low value titanium oxides and Fe_2Ti and FeTi alloys formed at the same time. Finally, electrolyte volatilization caused the curve presenting clear ascendant trend.

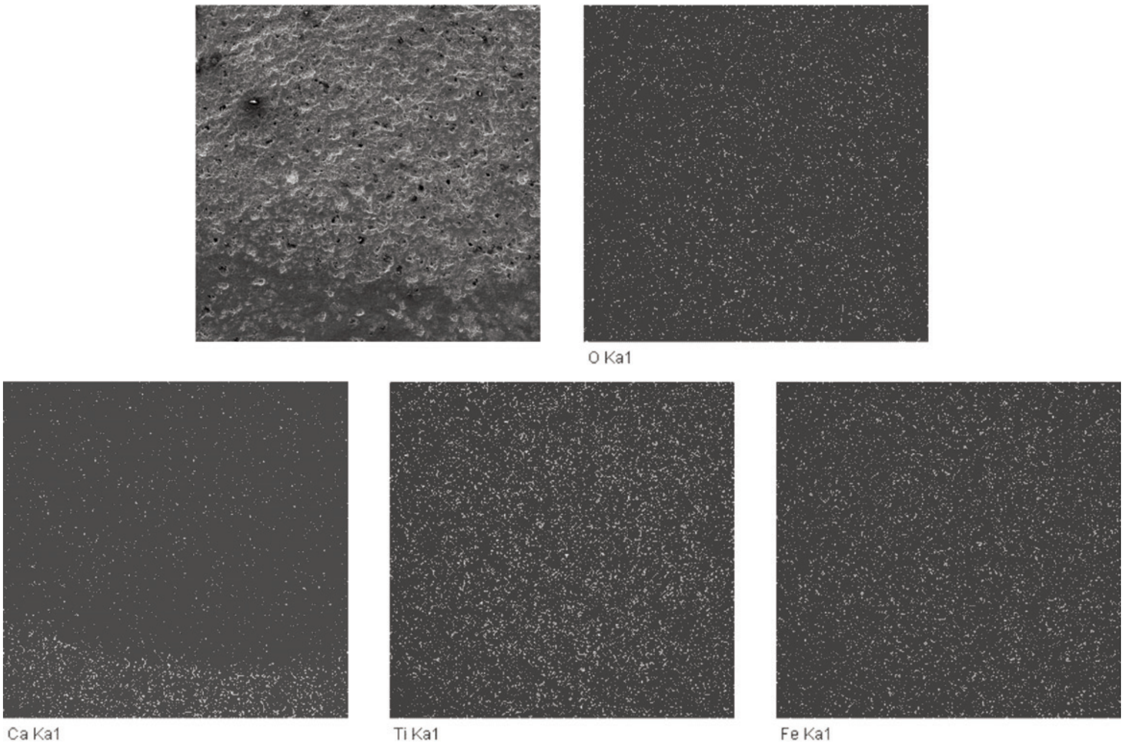

Fig. 4. Surface scanning of the electrochemical samples at 10h

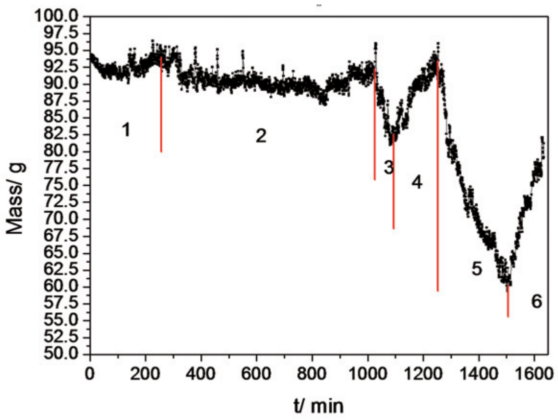

Fig. 5. Weight change curve of the cathode

4. Conclusions

From the above results, the deoxidization mechanism of the preparation FeTi alloy using ilmenite concentrate as precursor by FFC process can be obtained. Analysis of the partially reduced samples proved that the reduction process completed through a series of defined reaction steps. In the first stage, Ca^{2+} from the electrolyte was inserted into the cathode and a small quality of oxygen departs from cathode. Then Fe was reduced from ilmenite concentrate and perovskite was formed. In the third stage, perovskite, which was thought to originate mainly from the reaction between the Ca^{2+} and low value titanium oxides, was reduced and Fe_2Ti and FeTi alloys formed. The results had demonstrated that the process was fast as long as the reduction may be accomplished through the uptake of calcium but became sluggish as soon as the reduction may be achieved through the removal of oxygen. So the objective of further work is to detect the control step of oxygen removal and to improve electrolytic efficiency.

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