

Preparation of Ferrotitanium Alloy from Ilmenite by Electrochemical Reduction in Chloride Molten Salts

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Ferrotitanium alloy is prepared by electrochemical reduction from ilmenite in LiCl–KCl and LiCl–KCl–CaCl₂ molten salts, respectively. The products prepared are observed by x-ray diffraction (XRD). It is shown that Fe₂Ti can be prepared from ilmenite in LiCl–KCl molten salt at 1073 K with a cell voltage of 3.2 V. Ilmenite can be electrochemically reduced to FeTi in LiCl–KCl–CaCl₂ molten salt under the same condition. It is indicated that CaCl₂ can promote the reaction and is favors the deoxidization of the FeTiO₃.

INTRODUCTION

Ferrotitanium alloy is not only a significant material in steel smelting which can improve the quality of steel but also an important magnetic material and one of the most promising hydrogen storage materials. It is used widely in various industries. Nowadays, the ferrotitanium alloy is mainly produced by the aluminothermic reduction method and the remelting process. But with the former method, the ferrotitanium alloy has a high content of oxygen and impurities. Although the content of oxygen in the alloy can be controlled effectively by the remelting process, its raw materials are limited and energy consumption is high. Therefore, it is urgently required to develop a new process to produce ferrotitanium alloy with energy saving and low cost.

A new method, the cathodic electrochemical reduction of TiO₂ to Ti, which is also called the FFC (Fray–Farthing–Chen) Cambridge process,^{1,2} is a simple process with low energy consumption. Based on the FFC Cambridge process, various reactive metals (e.g., Ti, Si, Cr, Nb, Dy)^{2–6} and many functional alloys (e.g., Fe–Ti, La–Ni, Ce–Ni–Cu, Zr–Cr–Ni)^{7–11} have been extracted from their oxides. The reduction of metal oxides in situ has been studied in various molten salts, e.g., CaCl₂, CaCl₂–NaCl, LiCl–KCl and LiCl–KCl–CaCl₂^{5,9,12–17} molten salts. The ferrotitanium alloy has been successfully obtained by the electro-reduction of ilmenite in CaCl₂ and

CaCl₂–NaCl molten salt. However, the electro-reduction of ilmenite in LiCl–KCl has not been reported. In the present study, we used LiCl–KCl as the supporting electrolyte, the eutectic point (625 K) of which is lower than those of CaCl₂ (1045 K) and CaCl₂–NaCl (777 K), to prepare ferrotitanium alloy from ilmenite.

The electrolysis experiments were performed with a two-electrode system consisting of an ilmenite cathode and a graphite anode. A constant voltage applied between the cathode and anode was lower than the theoretical decomposition potential of LiCl–KCl but higher than the theoretical decomposition potential of ilmenite. This work demonstrates that the electro-reduction of ilmenite in LiCl–KCl is available. The electro-reduction process of ilmenite was studied by constant voltage electrolysis. For comparison, some CaCl₂ was added to LiCl–KCl molten salt. It is shown that the electro-reduction of ilmenite can be accelerated by the addition of CaCl₂ into LiCl–KCl molten salt.

EXPERIMENTAL

Chemical Reagents

According to the procedures reported in the literature,¹⁸ the ilmenite (FeTiO₃) powder used in this work was synthesized by the co-precipitation method using Ti(O–Bu)₄ (99.9%; Aldrich), FeCl₂·4H₂O (99.9%; Aldrich) and Na₂CO₃ (99.9%; Aldrich) as raw materials.

Anhydrous LiCl (AR) and KCl (AR) were supplied by Sinopharm Chemical Reagent, China. The LiCl and KCl were dehydrated under 573 K for 24 h and then kept in an argon glove box prior to use. The electrolyte (the molar ratio of LiCl to KCl was 0.6:0.4) was prepared by mixing appropriate amounts of LiCl and KCl.

Preparation of FeTiO₃ Electrodes

The FeTiO₃ powder was manually pressed (20 MPa) into small cylindrical pellets (13 mm in diameter with thickness ranging from 2.0 mm to 3.0 mm) mixed with 10 wt.% polyvinyl alcohol (PVA) and 15 wt.% NH₄HCO₃. The FeTiO₃ pellets were sintered at 1073 K for 3 h in an argon flow to gain sufficient strength and high porosity. A typical program used in this work was as follows: (1) heating from room temperature to 573 K at 5 K/min and holding at 573 K for 1 h, (2) heating from 573 K to 1123 K at 6 K/min and holding at 1123 K for 3 h. The programmed heating is aimed at promoting dehydration and pore-forming. The porosity of the sintered pellets ranged from 30% to 40% by volume. The sintered ilmenite pellets were used as cathodes, which were wrapped tightly with molybdenum wire and connected to a DC power source.

Electrochemical Experiments

Electrolysis experiments were performed in a crucible furnace with a standard two-electrode system. The experimental apparatus is shown in Fig. 1.

A molybdenum bar loaded with a sintered FeTiO₃ pellet acted as the cathode and a graphite rod (Φ5 × 80 mm, 99.9%) served as the anode. The electrolysis was conducted in an alumina crucible (Φ60 × 60 mm, 99.9%) at a constant cell voltage of 3.2 V in the temperature range of 673 K to 1073 K under Ar atmosphere. The distance of the inter-electrode was 2 cm. The constant cell voltage was controlled by a DC power source (Zhejiang Yueqing Yizhan Electronics, China). When the temperature reached the melting point of the electrolyte used, the

electrodes (cathode and anode) were lowered into the molten salt. After electrolysis, the pellet was raised and cooled in Ar flow. All the electrochemical experiments were operated under dry high-purity argon atmosphere with a flow of 200 ml/min. The reduced pellets were manually ground into powders and then cleaned with distilled water in an ultrasonic cleaner to remove the residual molten salt in the reduced samples. The samples were analyzed after dried in vacuum at 353 K.

The surface morphology and the phase composition of the reduced pellets were observed with a scanning electron microscope (SEM) and x-ray diffraction (XRD), respectively. The samples were analyzed by XRD (D/Max-2200 model) with Cu-Kα radiation at a scan rate of 10°/min in the range of 10°–90°. SEM (XL 30 ESEM TMP model) was used to characterize the morphology.

RESULTS AND DISCUSSION

Theoretical Considerations

To determine the thermodynamics of the electrolysis process, the theoretical decomposition potentials of the possible reactions are calculated from Eq. 1.

$$E_T^{\theta} = -\frac{\Delta G_T^{\theta}}{nF} \quad (1)$$

ΔE_T^{θ} theoretical decomposition potential;

ΔG_T^{θ} standard Gibbs free energy;

n transferred number of electrons;

F Faraday constant.

ΔG_T^{θ} is obtained from the known thermodynamic data at different temperature in HSC chemistry 6.0. The Gibbs free energy ΔG_T^{θ} of the possible reactions is shown in Table I. According to Table I and Eq. 1, the theoretical decomposition potentials of pure LiCl, KCl and CaCl₂, and the theoretical electro-reduction potentials of the possible reactions to produce metal or ferrotitanium alloy at cathode and CO gas at graphite anode were calculated, as shown in Fig. 2.

Table I reveals that the potentials and decrease gradually with temperature. For each reaction, the electrochemical potentials are lower by 0.2–0.4 V at 1073 K than those at 673 K. This suggests that the reaction becomes easier at a higher temperature.

From Fig. 2, it can be seen that the theoretical decomposition potential of CaCl₂ is lower than that of LiCl and KCl, and that the theoretical decomposition potentials of the molten salt electrolytes are much higher than those of the metal oxides.

Both in LiCl-KCl and LiCl-KCl-CaCl₂ molten salts, the potential for the reduction of ilmenite to metallic Fe is the lowest. This is in agreement with the previous study that metallic Fe is the easiest to obtain from FeTiO₃.^{19,20} From the Gibbs free energy changes for reactions (14), (15) and (16), it can be seen that the reduction of iron from ilmenite with

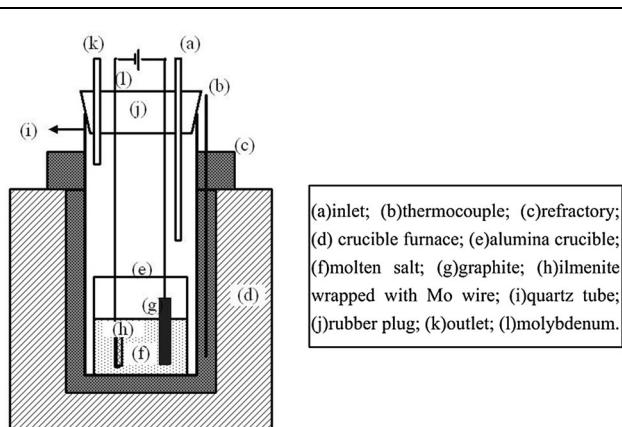


Fig. 1. Experimental apparatus for the electro-reduction of ilmenite.

Table I. Possible reactions and their Gibbs free energy

Reaction	$\Delta G_T^\theta / \text{kJ mol}^{-1}$			
	$\Delta G_T^\theta = a \pm bT$	673 K	873 K	1073 K
$2 \text{KCl} = 2 \text{K} + \text{Cl}_2$	$\Delta G_T^\theta = 867.78 - 0.18T$	744.39	706.53	671.40
$2\text{LiCl} = 2\text{Li} + \text{Cl}_2$	$\Delta G_T^\theta = 806.95 - 0.15T$	706.12	673.55	650.85
$\text{CaCl}_2 = \text{Ca} + \text{Cl}_2$	$\Delta G_T^\theta = 789.32 - 0.19T$	692.44	663.31	635.34
$(\text{CaO}) + \text{C} = \text{Ca} + \text{CO}$	$\Delta G_T^\theta = 523.87 - 0.19T$	393.14	354.52	315.98
$(\text{Li}_2\text{O}) + \text{C} = 2\text{Li} + \text{CO}$	$\Delta G_T^\theta = 492.45 - 0.23T$	339.73	293.68	248.24
$\text{Li}_2\text{TiO}_3 + \text{C} = (\text{Li}_2\text{O}) + \text{TiO} + \text{CO}$	$\Delta G_T^\theta = 419.26 - 0.17T$	303.43	269.18	234.90
$1/2\text{Fe} + 1/2\text{Li}_2\text{TiO}_3 + \text{C} = 1/2\text{FeTi} + 1/2(\text{Li}_2\text{O}) + \text{CO}$	$\Delta G_T^\theta = 403.73 - 0.17T$	286.29	251.64	217.62
$\text{Fe} + \text{TiO} + \text{C} = \text{FeTi} + \text{CO}$	$\Delta G_T^\theta = 387.47 - 0.17$	269.16	234.11	200.34
$\text{Fe} + 1/2\text{Li}_2\text{TiO}_3 + \text{C} = 1/2\text{Fe}_2\text{Ti} + 1/2(\text{Li}_2\text{O}) + \text{CO}$	$\Delta G_T^\theta = 379.21 - 0.17T$	264.82	230.96	197.77
$1/2\text{Fe} + 1/2\text{CaTiO}_3 + \text{C} = 1/2\text{FeTi} + 1/2(\text{CaO}) + \text{CO}$	$\Delta G_T^\theta = 379.43 - 0.17T$	263.30	228.91	195.35
$\text{CaTiO}_3 + \text{C} = (\text{CaO}) + \text{TiO} + \text{CO}$	$\Delta G_T^\theta = 371.39 - 0.17T$	257.44	223.70	190.35
$\text{Fe} + 1/2\text{CaTiO}_3 + \text{C} = 1/2\text{Fe}_2\text{Ti} + 1/2(\text{CaO}) + \text{CO}$	$\Delta G_T^\theta = 355.27 - 0.17T$	241.82	208.19	175.65
$2\text{Fe} + \text{TiO} + \text{C} = \text{Fe}_2\text{Ti} + \text{CO}$	$\Delta G_T^\theta = 339.16 - 0.17T$	226.20	192.69	161.04
$\text{FeTiO}_3 + \text{C} = \text{Fe} + \text{TiO}_2 + \text{CO}$	$\Delta G_T^\theta = 232.62 - 0.26T$	62.38	8.49	-51.36
$\text{FeTiO}_3 + \text{CaO} + \text{C} = \text{Fe} + \text{CaTiO}_3 + \text{CO}$	$\Delta G_T^\theta = 151.74 - 0.27T$	-22.23	-77.21	-138.30
$\text{FeTiO}_3 + \text{Li}_2\text{O} + \text{C} = \text{Fe} + \text{Li}_2\text{TiO}_3 + \text{CO}$	$\Delta G_T^\theta = 103.87 - 0.27T$	-68.21	-122.69	-182.84

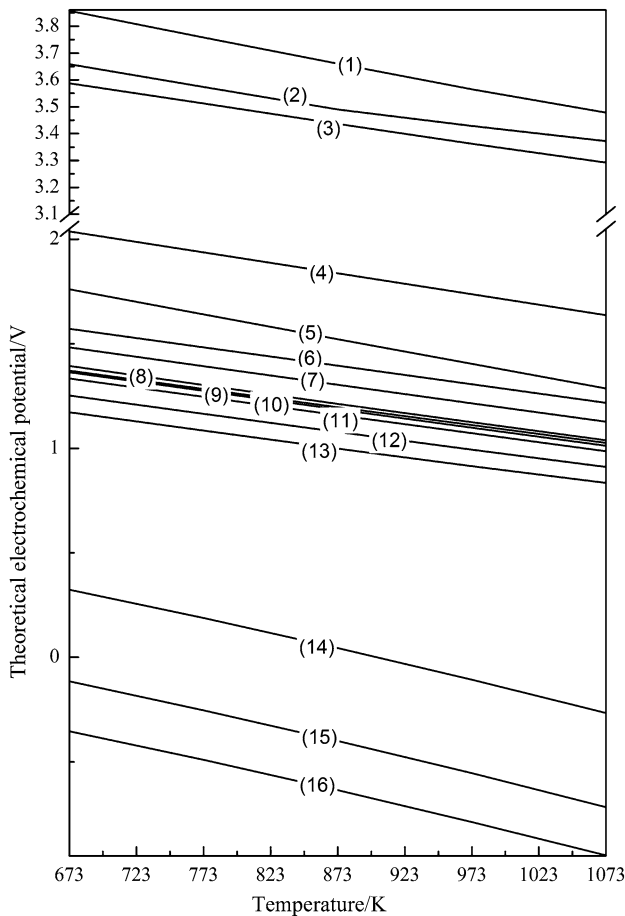


Fig. 2. Possible reactions and their potentials.

participation of Li_2O and CaO is thermodynamically more favorable than without them because reactions (15) and (16) require lower potentials

compared to reaction (14). Li_2O and CaO are normally formed by Ca^{2+} and Li^+ with O^{2-} dissolved in the molten salt during the deoxidation of oxides. In addition, reactions (15) and (16) can proceed spontaneously at 673 K, while reaction (14) cannot be achieved until the temperature rises to 1073 K.

According to the theoretical electrochemical potentials of reactions (7), (9), (10) and (12) in Fig. 2, it is revealed that the formation of Fe_2Ti requires a lower potential than that of FeTi . Hence, Fe_2Ti rather than FeTi would be preferentially formed at low temperatures.

No titanium oxides were observed in the products in the present experiments. Li_2TiO_3 and CaTiO_3 are the major oxide phases formed during the electrolysis. Reactions (15) and (16) are responsible for the formation of CaTiO_3 and Li_2TiO_3 . The electroreduction potential of CaTiO_3 is 0.25 V lower than that of Li_2TiO_3 . This indicates that CaTiO_3 is easier to reduce than Li_2TiO_3 . Therefore, the deoxidation of ilmenite in LiCl-KCl-CaCl_2 ternary molten salt is easier than that in the LiCl-KCl binary system.

Influence of Temperature

To confirm the influence of the temperature on the phase changes occurring during the electroreduction process in LiCl-KCl molten salt, experiments were performed at different temperatures (673 K, 873 K and 1073 K) with a constant cell voltage of 3.2 V.

The current–time plots during the reduction process of ilmenite pellets at different temperatures for 28 h are illustrated in Fig. 3. This indicates that a higher temperature can contribute to a faster reduction rate. In addition, it is shown that all the current curves have the similar features. The current rises rapidly in the first 2–3 min to a peak.

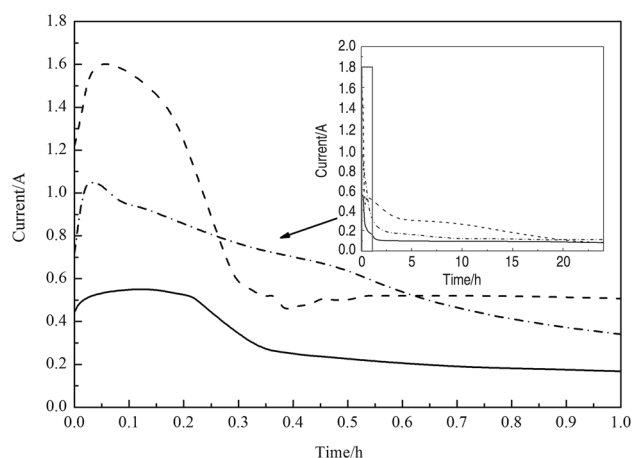


Fig. 3. Electrolytic current-time plots of FeTiO_3 pellets in $\text{KCl-LiCl}(0.4:0.6)$ at different temperatures. Cell voltage: 3.2 V. Solid: 673 K; dash: 873 K; dash-dot: 1073 K.

After 0.4 h electrolysis, the current declines gradually to a stable level until the electrolysis is terminated.

The XRD patterns of synthetic FeTiO_3 and partially reduced samples obtained from electrolysis at different temperatures for 20 h are shown in Fig. 4 and the phase compositions detected are shown in Table II, and are arranged in decreasing order of relative diffraction peak intensities.

It can be seen from Fig. 4 and Table II that Fe and Li_2TiO_3 are the main phases in the products at 673 K, which indicates that metallic Fe can be easily reduced from FeTiO_3 . Li_2TiO_3 is the only oxide phase, whereas phases of TiO_2 , titanium sub-oxides and titanium metal are not detected in the products at 673 K and 873 K. Chemical reaction (16) in Table I may be responsible for the formation of Li_2TiO_3 .

The main phases have no significant changes at 873 K compared with that at 673 K. No ferrotitanium alloy is observed at 673 K and 873 K, which implies that the ferrotitanium alloy cannot be obtained from FeTiO_3 at low temperatures. When the temperature rises to 1073 K, Fe_2Ti and TiO are the main phases. This suggests that some Li_2TiO_3 are reduced to TiO. Thus, the current is higher than those at 673 K and 873 K. Ferrotitanium alloy cannot be prepared from FeTiO_3 by electro-reduction until the temperature is as high as 1073 K. There is no metallic Ti observed in the products, since metallic Fe can combine with Ti to form ferrotitanium alloy (Fe_2Ti) as soon as the metallic Ti is reduced from TiO.

The experiments suggest that Li_2TiO_3 cannot be reduced to titanium sub-oxide or metallic Ti when the temperature is low. High temperature favors the reduction of Li_2TiO_3 . From the experiments, we can conjecture that the reduction of Li_2TiO_3 and TiO is the limiting step for the forming of ferrotitanium alloy in LiCl-KCl .

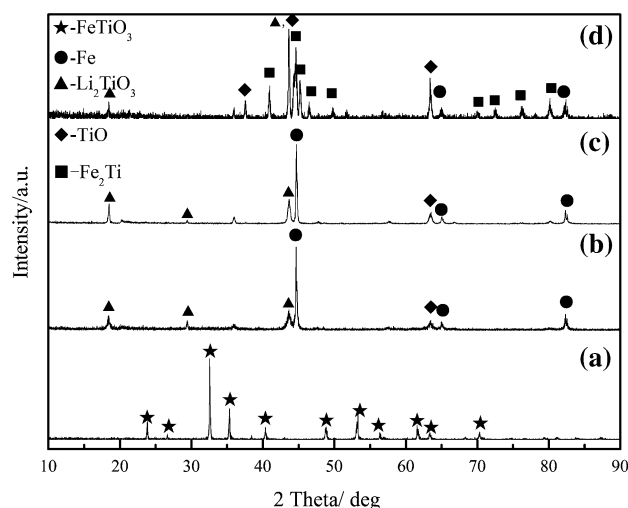


Fig. 4. XRD patterns of synthetic FeTiO_3 and reduced products obtained from electrolysis under different temperatures at 3.2 V, $t = 20$ h: (a) Synthetic FeTiO_3 ; (b) $T = 673$ K; (c) $T = 873$ K; (d) $T = 1073$ K.

According to Figs. 3 and 4, it can be predicted that the reduction stages are probably explained as follows: (1) Fe is firstly produced; thus, the electrical conductivity of the whole pellet was improved and the current increases to a peak; and (2) with the time increasing, the current declines gradually to a stable level. This indicates that the reactions became difficult.^{12,21–23} This is in agreement with the fact that Li_2TiO_3 and TiO are difficult to reduce, as shown in Fig. 2.

The Influence of Reaction Time

The measured XRD patterns of the synthetic FeTiO_3 and partially reduced samples are illustrated in Fig. 5b–e and the corresponding phase compositions are shown in Table III.

As shown in Fig. 5b and Table III, the sample is mainly composed of Fe and Li_2TiO_3 after being electrolyzed for 20 min. This indicates that the reduction rate of iron from ilmenite is rapid. The sample electrolyzed after 3 h is composed of Fe and Li_2TiO_3 . With the time increasing to 12 h, Li_2TiO_3 can be reduced to TiO and Fe_2Ti is obtained. There is still an amount of metallic Fe in the products. After 20 h, TiO and Fe_2Ti are the prevailing phases.

For all the products obtained from the interrupted experiments, the electro-reduction of ilmenite can be divided into the following steps: Fe is firstly produced with the removal of amounts of oxygen, which makes the FeTiO_3 pellet become a highly conducting cathode. Secondly, the oxygen removed from FeTiO_3 pellet dissolves in the molten salt. As more and more O^{2-} dissolves in the molten salt, it may react with Li^+ and TiO_2 to form Li_2TiO_3 . In the further electrolysis process, Li_2TiO_3 will be deoxidized to form titanium sub-oxide, TiO. At the same time, Li^+ ions are liberated from the Li_2TiO_3 .

Table II. Phases observed before and after electrolysis at different temperature for 20 h

	Before electrolysis	673 K	873 K	1073 K
Main phases	FeTiO ₃	Fe, Li ₂ TiO ₃	Fe, Li ₂ TiO ₃	Fe ₂ Ti, TiO, Fe

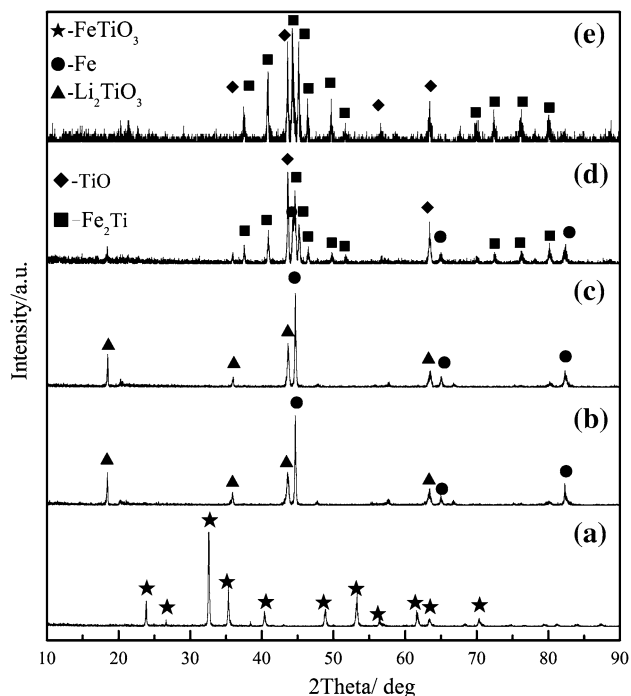


Fig. 5. XRD patterns of synthetic FeTiO₃ and reduced samples obtained from electrolysis in KCl-LiCl with different times at 3.2 V, T = 1073 K: (a) Synthetic FeTiO₃; (b) 20 min; (c) 3 h; (d) 12 h; (e) 20 h.

Finally, metallic titanium is reduced from the TiO and combines with metallic Fe to form ferrotitanium alloy.

The Influence of Ca²⁺

There is no FeTi obtained in the KCl-LiCl molten salt; however, FeTi has been successfully prepared in CaCl₂-containing molten salts (CaCl₂ and CaCl₂-NaCl molten salts). To investigate the influence of the Ca²⁺ on the electro-reduction of ilmenite, some CaCl₂ was added into the KCl-LiCl molten salt. The synthetic FeTiO₃ was electrolyzed in KCl-LiCl-CaCl₂ (0.45:0.30:0.25) molten salt for various times. XRD patterns of the synthetic FeTiO₃ and the products reduced by electrolysis in KCl-LiCl-CaCl₂ molten salt with different times at 3.2 V are shown in Fig. 6. The main phase compositions are shown in Table IV, and are arranged in decreasing order of relative diffraction peak intensities. The experiments indicate that the deoxidation rate of oxides in KCl-LiCl-CaCl₂ molten salt is faster than that without CaCl₂, suggesting that CaCl₂ plays an important role in the electro-reduction.

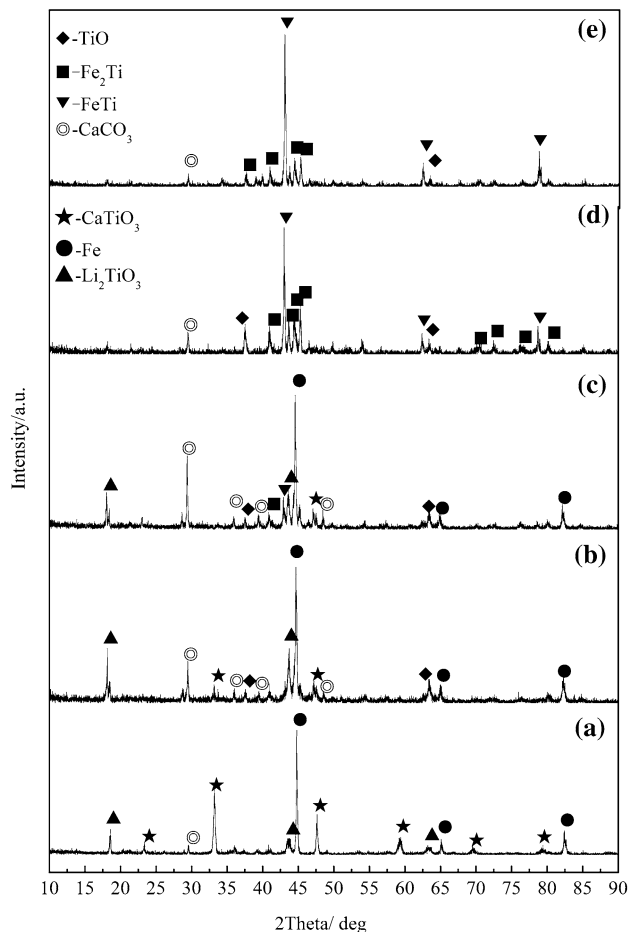


Fig. 6. XRD patterns of synthetic FeTiO₃ and reduced samples obtained from electrolysis in KCl-LiCl-CaCl₂ (0.45:0.30:0.25) with different times at 3.2 V, T = 1073 K: (a) 10 min; (b) 1 h; (c) 5 h; (d) 12 h; (e) 20 h.

As shown in Fig. 6 and Table IV, Fe is first obtained in 10 min. CaTiO₃ and Li₂TiO₃ are intermediate products during the electrolysis. In addition, CaCO₃ is also detected in the products. This may be attributed to the fact that CO₂ can dissolve in KCl-LiCl-CaCl₂ molten salt as CO₃²⁻, which can react with the Ca²⁺ present in the molten salt to form CaCO₃.

With time increasing to 1 h, the phases observed in the sample includes Li₂TiO₃, CaCO₃, CaTiO₃ and TiO, as shown in Fig. 6b. As compared with Fig. 6a, the relative diffraction peak intensity of Li₂TiO₃ and CaCO₃ in Fig. 6b increases and that of CaTiO₃ decreases. This indicates that Li₂TiO₃ is more difficult to reduce than CaTiO₃. TiO observed in the sample may result from the reduction of CaTiO₃.

Table III. Phases observed before and after electrolysis in KCl-LiCl

	<u>Before electrolysis</u>	<u>20 min</u>	<u>3 h</u>	<u>12 h</u>	<u>20 h</u>
Main phases	FeTiO ₃	Fe, Li ₂ TiO ₃	Fe, Li ₂ TiO ₃	TiO, Fe ₂ Ti, Fe	Fe ₂ Ti, TiO

Table IV. Phases after electrolysis in KCl-LiCl-CaCl₂ at 1073 K

	<u>10 min</u>	<u>1 h</u>	<u>5 h</u>	<u>12 h</u>	<u>20 h</u>
Main phases	Fe, CaTiO ₃ , CaCO ₃ , Li ₂ TiO ₃	Fe, Li ₂ TiO ₃ , CaCO ₃ , CaTiO ₃ , TiO	Fe, CaCO ₃ , Li ₂ TiO ₃ , FeTi, Fe ₂ Ti, TiO	FeTi, Fe ₂ Ti, TiO, CaCO ₃	FeTi, Fe ₂ Ti, CaCO ₃ , TiO

Table V. Solubility of O²⁻ in various molten salts^{21,24,25}

<u>Molten salt</u>	<u>X_{O²⁻}/mol.%</u>	<u>T/K</u>
LiCl-KCl (0.585:0.415)	0.71–1.32	673–823
CaCl ₂ -NaCl (1:1)	6.94–7.82	923–1123
CaCl ₂	26.10–27.76	1123–1223

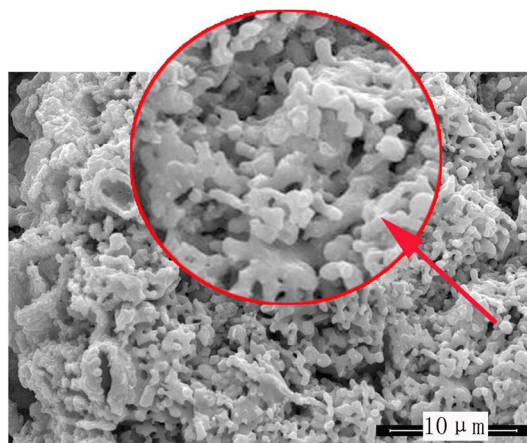
After 5 h, FeTi and Fe₂Ti are present in the samples. This result indicates that TiO has been reduced to titanium metal, which reacts with metallic Fe to form ferrotitanium alloy. In addition, the relative diffraction peak intensity of CaCO₃ increases.

By 12 h, FeTi and Fe₂Ti are the main phases and Li₂TiO₃ disappears. There is a little TiO and CaCO₃. The XRD analysis shows that the FeTiO₃ is almost completely reduced to FeTi after electrolysis for 20 h in KCl-LiCl-CaCl₂ molten salt.

The influence of Ca²⁺ on the electrochemical reduction process of ilmenite is related to its effect on the solubility of O²⁻ in the chloride molten salts. The solubility of O²⁻ in different molten salts is given in Table V, where *T* is the absolute temperature and X_{O²⁻} is the mol fraction of O²⁻ in molten salt.

It can be seen from Table V that the solubility of O²⁻ in LiCl-KCl molten salt is much lower than that of CaCl₂-containing ones. The solubility of O²⁻ appreciably increases with an increase in the CaCl₂ mol fraction of the molten salts. Hence, the addition of CaCl₂ into LiCl-KCl molten salt will result in a high concentration of O²⁻ in the salt, which is beneficial to the transportation and discharge of O²⁻. Accordingly, the electrochemical reduction rate of ilmenite will be accelerated due to the presence of CaCl₂ in LiCl-KCl molten salt.

In addition, the metallic Ca may be deposited from Ca²⁺ in the electrolyte on the cathode and dissolved in the electrolyte during the electrolysis process. The metallic calcium dissolved may also

Fig. 7. SEM of the reduced product obtained after electrolysis for 20 h in KCl-LiCl-CaCl₂ molten salt.

reduce the titanium oxides in the cathode and promote the overall electrochemical reduction of the ilmenite.

Micrograph Analysis

The micrograph of reduced sample obtained after electrolysis for 20 h in KCl-LiCl-CaCl₂ molten salt is shown in Fig. 7. It can be seen that the particles of the reduced product are uniformly shaped. This shows that the reduced product is porous.

CONCLUSION

In the current work, a study was carried out on the electro-reduction of synthetic FeTiO₃ in LiCl-KCl and LiCl-KCl-CaCl₂ molten salts at a voltage of 3.2 V. The study has shown that metallic Fe is obtained at low temperatures and Fe₂Ti is obtained at 1073 K. FeTi can be prepared in LiCl-KCl-CaCl₂ molten salt under the same conditions.

From the interrupt experiments both in LiCl-KCl and LiCl-KCl-CaCl₂ molten salts, the electro-reduction process can be included as follows. According to XRD patterns, Fe(II) in ilmenite is firstly reduced to metallic Fe. Then, the intermediate Li₂TiO₃ or

CaTiO₃ is reduced to TiO. Finally, metallic Fe combines with Ti partially reduced from TiO to form Fe₂Ti or FeTi.

The electrochemical reduction rate of ilmenite in LiCl-KCl-CaCl₂ molten salt is faster than that in LiCl-KCl, which indicates that the Ca²⁺ in the electrolyte favors the electro-reduction of ilmenite. The influence of Ca²⁺ can be drawn from the present work: (1) the electro-reduction of intermediate CaTiO₃ is much easier than that of Li₂TiO₃; (2) Ca²⁺ contributes to the dissolution of O²⁻ in molten salt and is beneficial to the removal of O²⁻; and (3) Ca²⁺ may be reduced to metallic Ca, which will cause the calcium thermal reduction of oxides and thus promote the electro-reduction of the ilmenite.

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REFERENCES

1. D.J. Fray, T.W. Farthing, G.Z. Chen, World Patent WO9964638.
2. G.Z. Chen, D.J. Fray, and T.M. Farthing, *Nature* 407, 361 (2000).
3. T. Nohira, K. Yasuda, and Y. Ito, *Nat. Mater.* 2, 397 (2003).
4. G.Z. Chen, E. Gordo, and D.J. Fray, *Metall. Mater. Trans. B* 35, 223 (2004).
5. X.Y. Yan and D.J. Fray, *Metall. Mater. Trans. B* 33, 685 (2002).
6. P. Kim, H.W. Xie, Y.H. Zhai, X.Y. Zou, and X.C. Lang, *Appl. Electrochem.* 42, 257 (2012).
7. M. Panigrahi, R. Paramguru, R. Gupta, E. Shibata, and T. Nakamura, *High Temp. Mater. Process.* 29, 495 (2010).
8. M. Panigrahi, E. Shibata, A. Iizuka, and T. Nakamura, *Electrochim. Acta* 93, 143 (2013).
9. Y. Zhu, D.H. Wang, X.H. Hu, X.B. Jin, and G.Z. Chen, *Chem. Commun.* 24, 2515 (2007).
10. X. Kang, Q. Xu, X.M. Yang, and Q.S. Song, *Mater. Lett.* 64, 2258 (2010).
11. J.J. Peng, Y. Zhu, D.H. Wang, X.B. Jin, and G.Z. Chen, *J. Mater. Chem.* 19, 2803 (2009).
12. W. Bin, K.R. Liu, and J.S. Chen, *Trans. Nonferrous Met. Soc. China* 21, 2327 (2011).
13. M. Ma, D.H. Wang, W.G. Wang, X.H. Hu, X.B. Jin, and G.Z. Chen, *Alloys Compd.* 420, 37 (2006).
14. K. Yasuda, T. Nohira, Y.H. Ogata, and Y. Ito, *Electrochem. Soc.* 152, D208 (2005).
15. Y.C. Zhai, P. Kim, H.W. Xie, and S.H. Ji, *Adv. Mater. Res.* 284, 2114 (2011).
16. Y. Katayama, B. Friedrich, in *Proceedings-206th Meeting of The Electrochemical Society*, Honolulu, American (2004).
17. K. Yasuda, T. Nohira, R. Hagiwara, and Y.H. Ogata, *Electrochim. Acta* 53, 106 (2007).
18. J.J. Ru, Y.X. Hua, C.Y. Xu, J. Li, Y. Li, D. Wang, K. Gong, R. Wang, and Z.R. Zhou, *Ceram. Int.* 40, 6799 (2014).
19. A.M. Abdelkader, K.T. Kilby, A. Cox, and D.J. Fray, *Chem. Rev.* 113, 2863 (2013).
20. M. Ma, D.H. Wang, W.G. Wang, X.H. Hu, X.B. Jin, and G.Z. Chen, *Chemistry* 12, 5075 (2006).
21. S.L. Wang and F.S. Zhang, *J. Northeast. Univ.* 31, 92 (2010).
22. M. Panigrahi, A. Iizuka, E. Shibata, and T. Nakamura, *Alloys Compd.* 550, 545 (2013).
23. P.K. Tripathy, M. Gauthier, and D.J. Fray, *Metall. Mater. Trans. B* 38, 893 (2007).
24. Y. Kado, T. Goto, and R. Hagiwara, *J. Chem. Eng. Data* 53, 2816 (2008).
25. T. Goto, Y. Kado, R. Hagiwara, *Molten Salts Chem.*, p.187 (2013).