JOM, Vol. 72, No. 11, 2020
https://doi.org/10.1007/s11837-020-04366-3

ELECTROMETALLURGICAL PROCESSING

Roles of SiO_2 Additive on Preparation of Ferrotitanium from Ilmenite Concentrate by Electrochemical Reduction in $CaCl_2$ Molten Salt

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The effect of the content of an SiO_2 additive on the electrochemical reduction of ilmenite concentrate to prepare ferrotitanium is investigated in $CaCl_2$ molten salt. A thermodynamic analysis of the Ti-Fe system and possible reactions has been carried out, and it demonstrated that SiO_2 and $FeTiO_3$ can be readily reduced to Si and intermediates (Fe and $CaTiO_3$), respectively. The experimental results demonstrated that the optimal molar ratio of Ti:Fe:Si in the cathode mixtures is 1.2:1:0.2. The porous ferrotitanium with uniform particle sizes were successfully obtained by electrolysis at 1173 K with a cell voltage of 3.2 V for 2 h. The SiO_2 additive plays an important role during the formation process of ferrotitanium, which is first reduced to Si and then serves as a reductant to catalyze $CaTiO_3$ and Fe to form FeTi alloys.

INTRODUCTION

Ferrotitanium, one of the best ferroalloys, has been widely employed as hydrogen storage material or has served as a deoxidizer in the steel-making industry. Generally, ferrotitanium is produced either by aluminothermic reduction of ilmenite concentrate as well as from titanium slag, or by re-melting iron and titanium scraps together at high temperatures.[1,2] However, these two methods have obvious disadvantages, such as high residual oxygen content, high impurities in products, and high energy consumption.[3,4] In recent decades, many efforts have been made to modify the refinement process for the production of ferrotitanium.

The direct electrolysis of a solid oxide in molten salt, known as the Fray–Farthing–Chen Cambridge (FFC) process with the merits of short-flow course and lower energy consumption, has been applied widely since 1998.[5,6] Numerous metals (e.g., Cr,[7] Ti,[8] Nb,[9] Ta,[10] Zr[11]), and alloys (e.g., LaNi,[12] TiC/SiC,[13] FeTi,[14] and TiSi[15]) have been prepared from corresponding oxides via the FFC method. Panigrahi et al. reported the preparation of ferrotitanium alloys from the direct electrolysis of TiO_2 and Fe_2O_3 mixtures in $CaCl_2$ molten salt.[16] However, a relative slower deoxidization rate and higher energy consumption were observed on account of the difficult reduction of TiO_2 and the multi-intermediates formed, such as $CaTiO_3$ and TiO. It has become imperative to develop an effective way to promote the reduction process. A great number of endeavors, including lowering the cathode mold pressure, and improving the cathode sintering temperature and cathode porosity, have been put into practice.[11,17] As a result, shorter electrolytic times and elevated electrolytic currents have been achieved. However, the intrinsic reduction routes have not been changed. Besides, our previous work suggests that the addition of CaO into $CaCl_2$-based molten salts can accelerate the transmission of O^{2-} and introduce the calciothermic reduction of cathodic oxides, leading to favorable cathodic reaction kinetics.[18] The only fly in the ointment could be that the CaO additive will result in the easy formation of intermediate $CaTiO_3$, so that the subsequent reaction is difficult.[19]

Recently, an acid oxide, SiO_2, was introduced in our work to accelerate the reduction of ilmenite. Here, the influence of the content of the SiO_2

(Received November 30, 2019; accepted August 28, 2020;

additive on the electrochemical reduction of ilmenite concentrate to prepare ferrotitanium was investigated. The thermodynamic analysis of the Ti-Fe system and possible reactions were performed by Outokumpu HSC Chemistry. A variety of techniques, including XRD, SEM, and EDS, were utilized to characterize the samples. The roles of the SiO_2 additive in the reduction process have also been proposed.

EXPERIMENTAL

Chemicals

The chemicals of analytical grade used in present work were purchased commercially from Aisinaladdin-e.com, Shanghai, China. The x-ray diffraction (XRD) pattern of the ilmenite concentrate sample in this experiment is shown in Fig. 1a, and the main phases are $FeTiO_3$ and TiO_2. The chemical composition of the ilmenite concentrate is also given in the inset. The molar ratio of the main elements in ilmenite concentrate is Ti:Fe:Si = 1.2:1:0.076.

Preparation of Cathode

Before electrolysis, the crushed ilmenite concentrate with an average particle size of $\sim 50\ \mu m$ was blended with the SiO_2 at different molar ratios of Ti:Fe:Si (1.2:1:0.076, 1.2:1:0.1, 1.2:1:0.2, 1.2:1:0.3, and 1.2:1:0.4). Then, the powders (1.5 g) were mixed with 10 wt.% polyvinyl alcohol and 25 wt.% NH_4HCO_3, and pressed into a cylindrical pellet (13 mm in diameter and 2.0 mm in thickness) under a pressure of 15 MPa. Finally, the pellets were sintered in an argon inert atmosphere at 1373 K for 4 h to obtain sufficient strength and the desired porosity.

Electrolysis Experiments

The electrolytic experiments were operated in a crucible furnace. A schematic of the experimental apparatus is shown in Fig. 1b. Before electrolysis, the sintered pellet was assembled by a molybdenum rod (99.95% in purity, 3 mm in diameter and 200 mm in length) to serve as the cathode. The graphite rod (99.9% in purity, 6 mm in diameter and 100 mm in length) tied by a molybdenum rod served as the anode. The electrolytic experiment was performed at 1173 K for 0.5–2.0 h in an Al_2O_3 crucible (Φ70 mm × 70 mm, 99.9% in purity) and a constant cell voltage of 3.2 V was supplied by a DPS-305BF DC voltage-stabilized power source (Zhejiang Yueqing Yizhan Electronics, China). As the furnace was heated to 1173 K, the electrodes were immersed in the $CaCl_2$ molten salt under an inert atmosphere. After the electrolysis, the cathode pellet was cooled to room temperature in the molten salt, then washed with distilled water to remove excessive molten salt, and dried in vacuum.

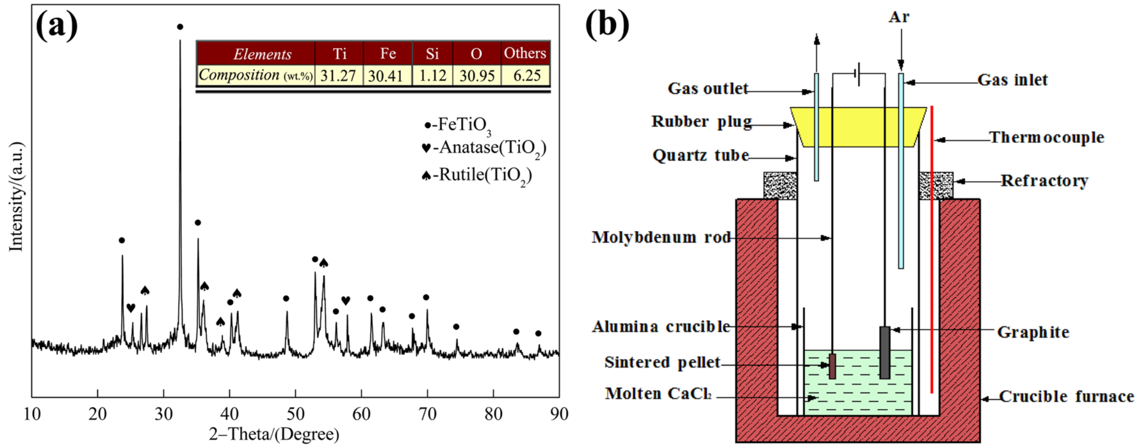
Characterization Analysis

The phases of sample were analyzed by XRD (Version D/Max-2200pc model with Cu-Kα radiation) at a scan rate of 8°/min in the range of 10°–90°. The morphology and element constituents of samples were characterized by SEM equipped with EDS (LEO-FEGSEM model).

RESULTS AND DISCUSSION

Thermodynamic Analysis

According to existing reports,[18,19] the electrochemical reduction of ilmenite concentrate is a complex process which involves the formation of intermediates, such as Fe, $CaTiO_3$, TiO, et al. It can be seen from the Ti-Fe binary phase diagram (Fig. 2a) that ferrotitanium alloys (Fe_2Ti and FeTi) exist in this system.[20] As a result, Fe_2Ti and FeTi can be formed during the electrolysis of $FeTiO_3$. When SiO_2 is added into the system, the reduction process will be more complicated. Here, possible



Elements	Ti	Fe	Si	O	Others
Composition (wt.%)	31.27	30.41	1.12	30.95	6.25

Fig. 1. (a) XRD pattern of ilmenite concentrate, (b) schematic of the electrolytic apparatus. Inset chemical composition of the ilmenite concentrate (wt.%).

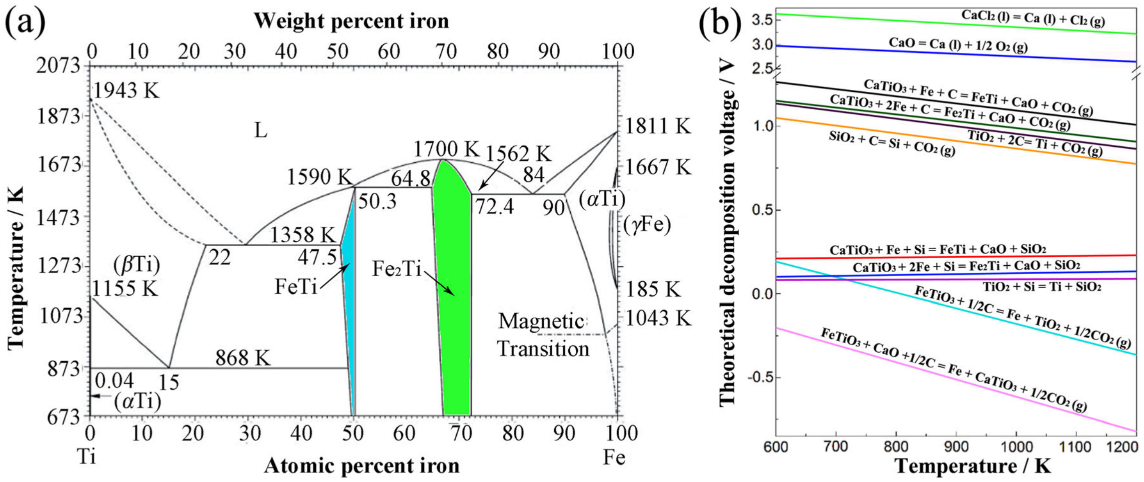


Fig. 2. (a) Ti–Fe binary phase diagram, (b) relationships between the theoretical decomposition voltage and temperature.

Table I. Possible reactions and relationships between Gibbs free energy, decomposition potentials and temperature

No.	Reaction	$\Delta G_T^\theta - T$	ΔG_T^θ/kJ (T=1173 K)	E^θ/V (T=1173 K)
(1)	$CaCl_2(l) = Ca(l) + Cl_2(g)$	772.98–0.09T	667.41	3.46
(2)	$CaO = Ca(l) + 1/2O_2(g)$	648.23–0.138T	486.36	2.52
(3)	$FeTiO_3 + 1/2C = Fe + TiO_2 + 1/2CO_2(g)$	145.36–0.180T	− 65.78	–
(4)	$FeTiO_3 + CaO + 1/2C = Fe + CaTiO_3 + 1/2CO_2(g)$	82.36–0.201T	− 153.41	–
(5)	$SiO_2 + C=Si + CO_2(g)$	511.81–0.177T	304.28	0.79
(6)	$TiO_2 + C=Ti + CO_2(g)$	545.64–0.178T	336.09	0.87
(7)	$TiO_2 + Si = Ti + SiO_2$	33.44–0.0014T	31.80	0.08
(8)	$CaTiO_3 + 2Fe + C=Fe_2Ti + CaO + CO_2(g)$	538.93–0.157T	354.76	0.92
(9)	$CaTiO_3 + 2Fe + Si = Fe_2Ti + CaO + SiO_2$	24.64 + 0.022T	50.45	0.13
(10)	$CaTiO_3 + Fe + C=FeTi + CaO + CO_2(g)$	587.44–0.166T	392.72	1.02
(11)	$CaTiO_3 + Fe + Si = FeTi + CaO + SiO_2$	72.02 + 0.014T	88.44	0.23

reactions during the electrochemical reduction of $FeTiO_3$ and TiO_2 are illustrated in Table I. The relationships between the standard Gibbs free energy, ΔG_T^θ, the theoretical decomposition voltage, E^θ, and temperature, T, have been calculated by HSC Chemistry 6.0, as presented in Fig. 2b. Based on the calculation, this demonstrates that the theoretical decomposition voltage, E^θ, of $CaCl_2$ (3.46 V at 1173 K) is the highest, implying that all the oxides can be reduced before the decomposition of the electrolyte. The Gibbs free energy values, ΔG_T^θ, of reactions (3) and (4) are negative at 1173 K, and thus $FeTiO_3$ can be easily reduced to Fe and TiO_2 or $CaTiO_3$. However, the Gibbs free energy change of reaction (4) is more negative than that of reaction (3), suggesting that $FeTiO_3$ can be easily reduced to Fe and $CaTiO_3$ via reaction (4).

From the calculation results, the decomposition voltage E^θ of reaction (5) is 0.79 V, indicating that SiO_2 can be readily reduced to Si. Moreover, the value of the theoretical decomposition voltage, E^θ, of reaction (5) is much lower than that of reactions (8) and (10), which implies that Si is preferentially formed before the reduction of $CaTiO_3$. Looking further at the thermodynamic calculations, comparing reactions (8–11), $CaTiO_3$ can be reduced to ferrotitanium alloys via reactions (9) and (11) due to their low theoretical decomposition voltages, E^θ. In addition, the theoretical decomposition voltage, E^θ, of reaction (7) is much lower than that of reaction (6), which means that the reduction of TiO_2 is significantly promoted by the formation of Si. Therefore, the participant of SiO_2 is thermodynamically favorable for the formation of ferrotitanium from ilmenite concentrate.

Time–Current Curves

The current as a function of time was recorded during the electrolysis of ilmenite concentrate with different SiO_2 contents, as shown in Fig. 3. All the values of the current decrease remarkably in the initial 30 min and then decay slightly later. The decline of the current value reflects the change of the reaction rate. At the beginning of electrolysis, the rapid reduction rate is put down to the large three-phase reaction interface between the cathodic oxide reactant, the metallic product, and the molten salt. As the reaction is performed inside the pellet, the reduction rate becomes slow because of the lessened three-phase interface.

In addition, from Fig. 3, it can be seen that the increase of SiO_2 content has a significant effect on the current values. In the initial 10 min, the current value decreases remarkably when the SiO_2 content is high. For example, the current value at 10 min decreases from 1.8 A to 1.76 A, 1.7 A, 1.55 A, and 1.45 A as the Ti:Fe:Si molar ratio varies from 1.2:1:0.076 to 1.2:1:0.1, 1.2:1:0.2, 1.2:1:0.3, and 1.2:1:0.4, respectively. However, in the subsequent electrolysis from 20 min to 120 min, the current values reduce slightly at high SiO_2 content. For instance, the current values at 60 min increase from 0.63 A to 0.75 A, 1.0 A, 1.13 A, and 1.83 A, respectively. According to thermodynamic analysis mentioned above, $FeTiO_3$ will be preferentially reduced to Fe and $CaTiO_3$ via reaction (4), and the intermediate $CaTiO_3$ will be deoxidized via reactions (8–11). Thus, the electrochemical reduction of ilmenite concentrate is suggested to be divided into two steps. $FeTiO_3$ is first reduced in the initial period and then $CaTiO_3$ is deoxidized. Moreover, it should be pointed out that the addition of SiO_2 into the cathode pellet might reduce the effective interface area of $FeTiO_3$ as the cathode weight is a constant, and the electrolysis of SiO_2 will consume more electricity. As a result, the reduction rate of $FeTiO_3$ decreases with an increase in the SiO_2 content of the cathode in the initial period. In contrast, with the participation of SiO_2, the further reduction of $CaTiO_3$ can be enhanced in thermodynamics, leading to the increase of the current value.

Phase Characterization

The ilmenite concentrate with different SiO_2 contents was electrochemically reduced at 3.2 V and 1173 K for 0.5 h, 1 h, and 2 h, respectively. The XRD patterns of the products are illustrated in Fig. 4 and the observed phases are listed in Table II.

As shown in Fig. 4 and Table II, when the samples are electrolyzed for 0.5 h, the $FeTiO_3$ can be completely reduced to form the dominant phases, Fe-Ti-O and $CaTiO_3$, and the minor phases, FeTi, Fe_2Ti, and SiO_2. This result reveals that $FeTiO_3$ can be preferentially reduced to intermediates Fe-Ti-O and $CaTiO_3$ in the initial period of 0.5 h. Looking further at the results in Fig. 4a and Table II, a small amount of SiO_2 can be detected, except in the sample with the Ti:Fe:Si molar ratio of 1.2:1:0.076, indicating that the SiO_2 is stable. Therefore, this suggests that the addition of SiO_2 has little impact on the initial electrochemical conversion of $FeTiO_3$ to $CaTiO_3$ and Fe via reaction (4). After 1 h (Fig. 4b), Si is observed in the product, which implies that SiO_2 can be reduced to Si at the middle stage from 0.5 h to 1 h. Meanwhile, the relative intensity of $CaTiO_3$ decreases with the increase of SiO_2 content. When the molar ratio of Si is higher than 0.3, $CaTiO_3$ is completely electrolyzed because the dominant phase is Fe-Ti-O, and the minor phases include FeTi, Fe_2Ti, and Si. This result shows that the further reduction process of $CaTiO_3$ can be accelerated by the addition of SiO_2, which is in good agreement with the thermodynamic analysis in “Thermodynamic Analysis” section.

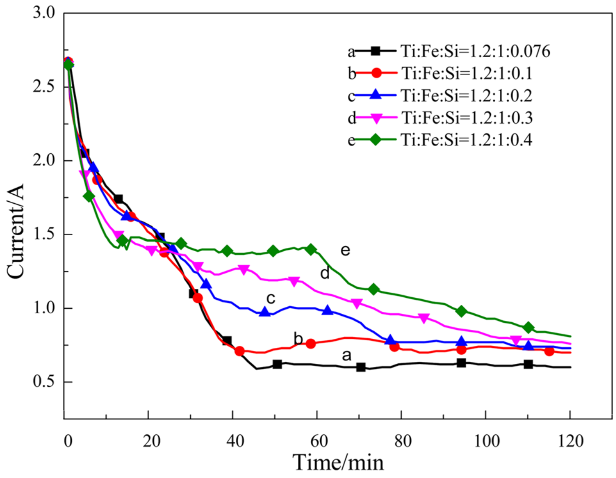


Fig. 3. Time–current curves during the electrolysis of samples with different SiO_2 contents.

When the electrolytic time is prolonged to 2 h (Fig. 4c), a small amount of $CaTiO_3$ is detected in the sample with the Ti:Fe:Si molar ratio of 1.2:1:0.076. However, the residual $CaTiO_3$ has been completely deoxidized to produce the dominant FeTi phase and other minor phases such as Fe_2Ti, Fe-Ti-O, TiSi, Ti_5Si_3, and $TiSi_2$ as the SiO_2 content increased. This means that the addition of SiO_2 can enhance the reduction process of $CaTiO_3$ and so plays a positive role in the electrolysis process. In addition, a small number of Ti-Si (TiSi, Ti_5Si_3, and $TiSi_2$) by-products are also formed with the addition of SiO_2. This may lead to a higher content of silicon impurities in the ferrotitanium. Thus, it is necessary to optimize the addition of SiO_2 content. Based on present research, the optimal Ti:Fe:Si molar ratio in the samples is 1.2:1:0.2, because ilmenite can be completely reduced to ferrotitanium alloys (FeTi, Fe_2Ti) for 2 h, as shown in Table II.

Micrograph of Products

The SEM images of the ilmenite concentrate and the products obtained after electrolysis of the samples with different SiO_2 contents under constant cell voltage of 3.2 V at 1173 K for 2 h are shown in Fig. 5. The ilmenite concentrate powders are of dense blocky-shaped particles with inhomogeneous

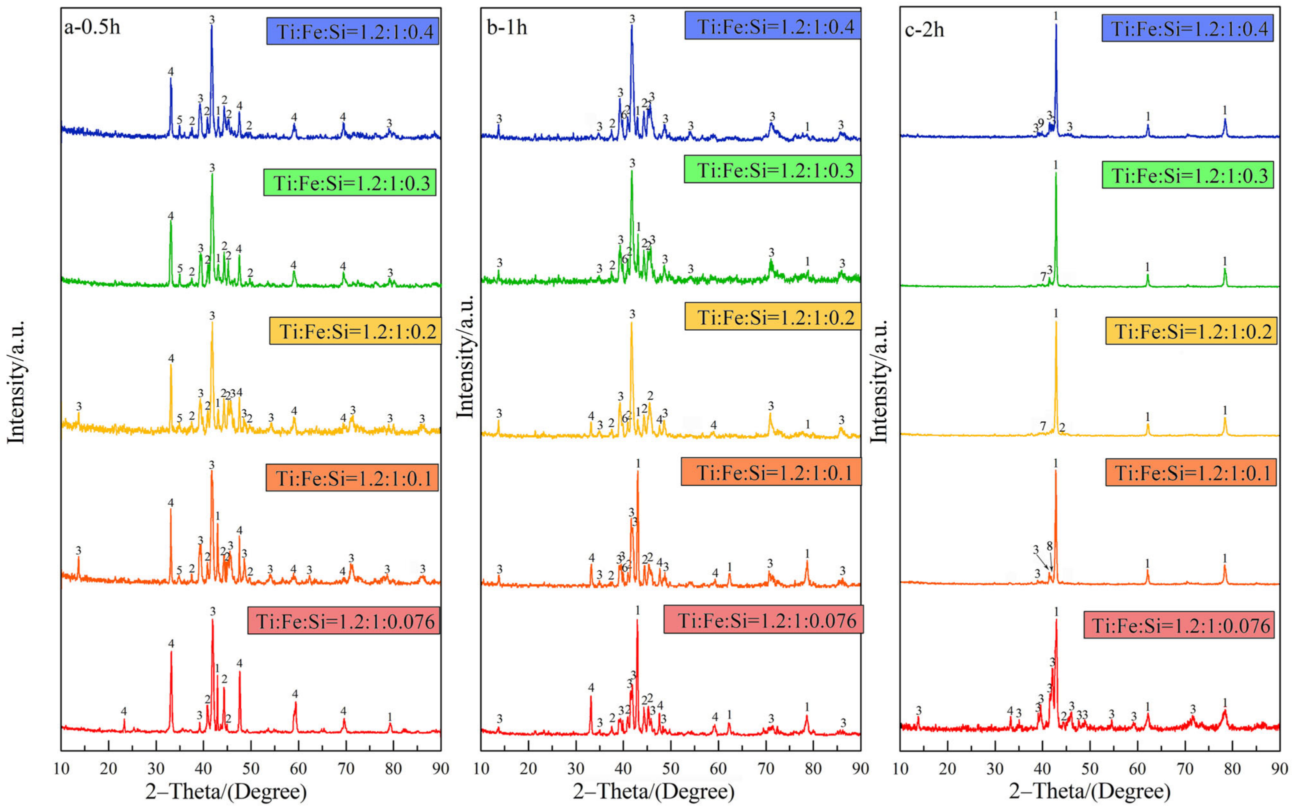


Fig. 4. XRD patterns of the products obtained after electrolysis of samples with different SiO_2 contents under 3.2 V at 1173 K for different times (a) 0.5 h, (b) 1 h, (c) 2 h. (*1* FeTi, *2* Fe_2Ti, *3* Fe–Ti–O, *4* $CaTiO_3$, *5* SiO_2, *6* Si, *7* Ti_5Si_3, *8* TiSi, *9* $TiSi_2$).

Table II. Phase observationd after electrolysis of the samples with different SiO_2 contents for various periods

	Time (h)					
	0.5		1		2	
Stoichiometric ratio	**Dominant phase**	**Minority phase**	**Dominant phase**	**Minority phase**	**Dominant phase**	**Minority phase**
Ti:Fe:Si = 1.2:1:0.076	Fe-Ti-O $CaTiO_3$	FeTi, Fe_2Ti	FeTi, Fe-Ti-O	Fe_2Ti, $CaTiO_3$	FeTi, Fe-Ti-O	Fe_2Ti, $CaTiO_3$
Ti:Fe:Si = 1.2:1:0.1	Fe-Ti-O $CaTiO_3$	FeTi, Fe_2Ti, SiO_2	FeTi, Fe-Ti-O	Fe_2Ti, $CaTiO_3$, Si	FeTi	Fe-Ti-O, TiSi
Ti:Fe:Si = 1.2:1:0.2	Fe-Ti-O $CaTiO_3$	FeTi, Fe_2Ti, SiO_2	Fe-Ti-O	Fe_2Ti, FeTi, $CaTiO_3$, Si	FeTi	Fe_2Ti, Ti_5Si_3
Ti:Fe:Si = 1.2:1:0.3	Fe-Ti-O $CaTiO_3$	FeTi, Fe_2Ti, SiO_2	Fe-Ti-O	FeTi, Fe_2Ti, Si	FeTi	Fe-Ti-O, Ti_5Si_3
Ti:Fe:Si = 1.2:1:0.4	Fe-Ti-O $CaTiO_3$	FeTi, Fe_2Ti, SiO_2	Fe-Ti-O	Fe_2Ti, FeTi, Si	FeTi	Fe-Ti-O, $TiSi_2$

structures in a size of about 2–10 μm (Fig. 5a). After electrolysis, products with a porous structure are obtained, as illustrated in Fig. 5b–f. In addition, it can be seen that the size of the newly formed particles decreases with the increase of SiO_2 content. Therefore, with the addition of SiO_2 into the sample, the ilmenite concentrate can be constantly electrolyzed to produce ferrotitanium powder with a smaller particle size. In addition, the products obtained after electrolysis of the sample with the Ti:Fe:Si molar ratio of 1.2:1:0.2 was further analyzed by EDS, as shown in Fig. 5g. It can be seen that the obtained particles are composed of the enriched elements, Fe and Ti, and that the Si

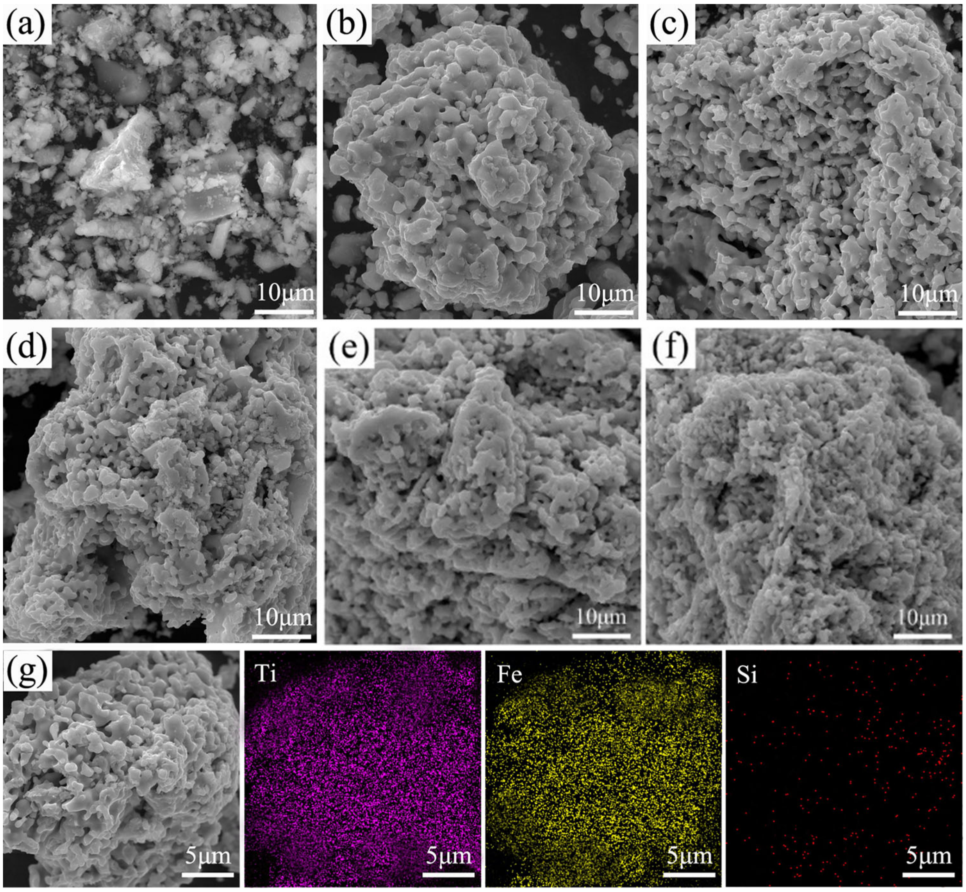


Fig. 5. (a–f) SEM images and (g) EDS analysis of the electrolytic products with different SiO_2 additions. (a) Ilmenite concentrate, (b) Ti:Fe:Si = 1.2:1:0.076, (c) Ti:Fe:Si = 1.2:1:0.1, (d, g) Ti:Fe:Si = 1.2:1:0.2, (e) Ti:Fe:Si = 1.2:1:0.3, (f) Ti:Fe:Si = 1.2:1:0.4.

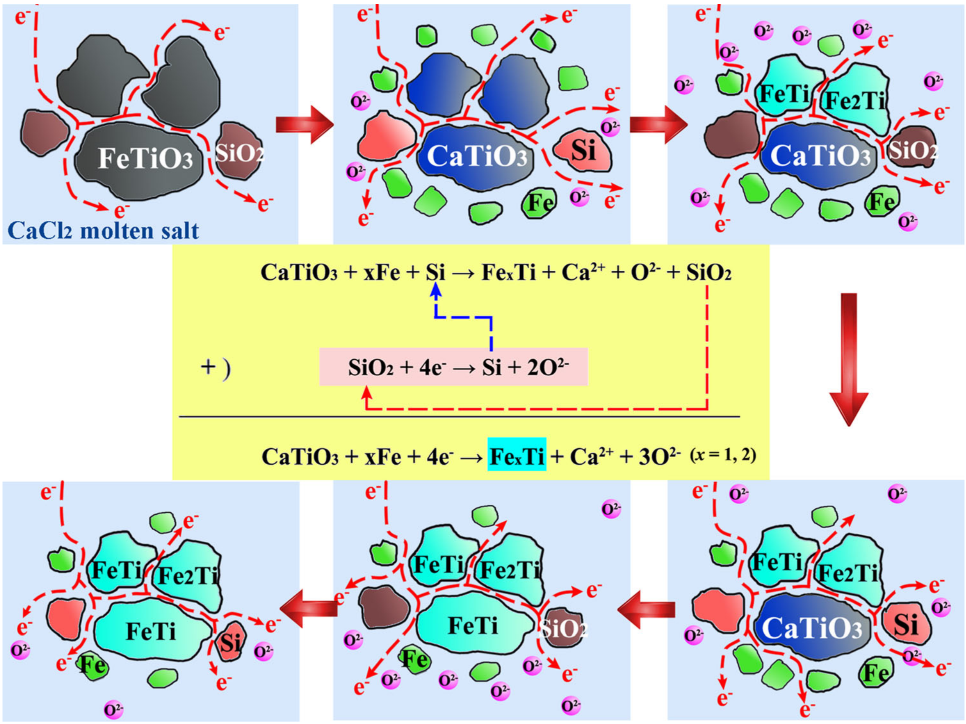


Fig. 6. Schematic of the roles of SiO_2 during the electrochemical reduction of ilmenite concentrate in $CaCl_2$ molten salt.

content is much lower. Moreover, the Si is dispersedthroughout these particles, which mainly include FeTi.

Role of SiO_2 Additive

Based on the above analysis, the preparation of FeTi from ilmenite concentrate by electrochemical reduction in $CaCl_2$ molten salt is a complex multistep process. First, $FeTiO_3$ is preferentially reduced to intermediates Fe and $CaTiO_3$ via reaction (4). In the second step, the intermediate $CaTiO_3$ is further reduced to ferrotitanium alloys through reactions (8) and (10). The further reduction of $CaTiO_3$ can be accelerated via reactions (9) and (11) with the addition of SiO_2, which demonstrates that the addition of SiO_2 into the sample during the electrochemical process can significantly promote the reduction of the intermediate $CaTiO_3$. The detailed roles of SiO_2 in the electrochemical reduction process can be proposed, as shown in Fig. 6. SiO_2 is first electrolyzed to produce Si, and the newly formed Si will act as the reductant to reduce $CaTiO_3$. Finally, the reduced Ti and Fe form FeTi alloys.

CONCLUSION

Ferrotitanium alloys were successfully prepared from ilmenite concentrate by electrochemical reduction with the addition of SiO_2 in $CaCl_2$ molten salt. SiO_2 plays an important role during the reduction process, and the optimal molar ratio in the cathode mixtures is Ti:Fe:Si = 1.2:1:0.2. Thermodynamic analysis of the Ti-Fe system and possible reactions indicate that SiO_2 can be readily reduced to Si, and that $FeTiO_3$ can be first transformed into intermediates, such as Fe and $CaTiO_3$. Electrolysis experiments demonstrated that SiO_2 is first reduced to Si and then serves as the reductant to participate in the reduction of $CaTiO_3$ and Fe to form FeTi alloys. The further reduction process of $CaTiO_3$ is promoted by the increase of SiO_2 content. The micromorphology of the ferrotitanium exhibits a porous structure and uniform particle size with the addition of SiO_2 into the ilmenite concentrate.

ACKNOWLEDGEMENT

The authors acknowledge the financial support of the National Natural Science Foundation of China (Project Nos. 51604136, 51274108).

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