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EXPERIMENTAL INVESTIGATION ON THE FORMATION MECHANISM OF THE TIFE ALLOY BY THE MOLTEN-SALT ELECTROLYTIC TITANIUM CONCENTRATE

R. Shi*, C. Bai*,#, M. Hu*, X. Liu* and J. Du**

*College of Materials Science and Engineering, Chongqing University, Chongqing, 400044, China.
**North West Insititute for Nonferrous Metal Research, Xian,710016, China

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Abstract

The ferrotitanium alloy was prepared in the molten $CaCl_2$ system, in which resolidified ilmenite and the graphite crucible were used as cathode and anode. In this study, the electrolytic voltage was fixed at 3.1V, and three different temperatures were applied: 850°C, 875°C and 900°C. Finally, the product was examined by SEM and XRD to determine the phase transformation after the electrolysis. The results show that the ilmenite was firstly reduced to Fe, and finally the TiFe alloy was formed. The intermediate products include $CaTiO_3$, TiO_2, Ti_2O_3, TiO, Fe, $TiFe_2$, and Ti. Different product and structure can be obtained by changing temperature. According to thermodynamic calculation, the principal electroreduction products are Ti and $TiFe_2$ and then Ti and $TiFe_2$ are formed by interdiffusion which is governed by temperature.

Key words: Ilmenite; Electroreduction; TiFe; $TiFe_2$; Inter-diffusion.

1. Introduction

As an attractive functional material, ferrotitanium alloy has been gotten more and more attention since it is developed [1, 2]. It has excellent hydrogen storage ability as well as low expansion rate so that can be potentially used as hydrogen storage material [3~5]. Excepting for conventional production method, VAR [6, 7], PAM [8, 9],

Corresponding author: bguang@cqu.edu.cn

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EBM [10-12], EBCHM [13], FFC based method comes into active using TiO_2 and Fe_2O_3 mixture as electrolyte material with advantages of short procedure, low energy cost and small pollution [1, 14]. There are some reports show ferrotitanium alloy can be produced by this method [1, 14, 15, 16, 17, 18, 19, 20], however, few study can be found about the formation mechanism of TiFe.

In the present study, ferrotitanium alloy was prepared in the molten $CaCl_2$ system by using ilmenite as cathode. Different temperatures were applied for the electrolysis process. The phases and microstructure of product were examined and formation mechanism of TiFe was analyzed as well.

2. Materials and Methods

The composition of Ilmenite from Pan Zhihua used in the study is shown in Tab.1. The main phase of ilmenite is $FeTiO_3$ and atom ratio of titanium and iron is roughly 1.08.

Initially, the cathode was prepared by melting-solidification process under protection atmosphere of argon, since Fe^{2+} in ilmenite is easy to be oxidized to form Fe^{3+} at high temperature, which is unacceptable for electrolytic reduction. Fig.1 presents the schematic of experimental facility. The $CaCl_2$ and graphite rod were used as electrolyte and anode. The reaction was processed in graphite crucible at three different temperatures: 850ºC, 875ºC and 900ºC. The constant voltage DC power was supplied by PARSTAT2273 electrochemical workstation, and the electrolytic voltage was set at 3.1V.

After electrolysis, the cathode was fully

Table 1 Element analysis of titanium 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

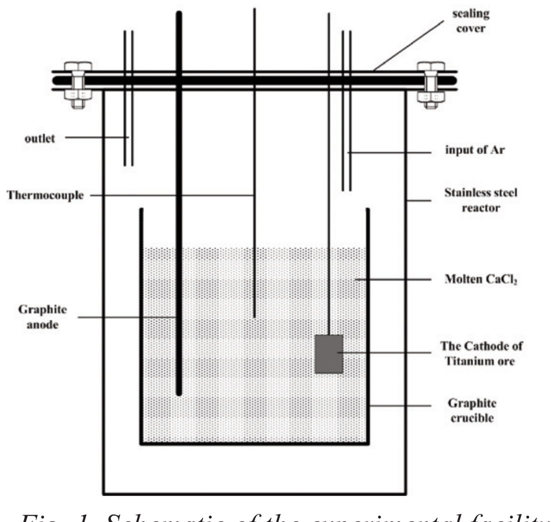


Fig. 1. Schematic of the experimental facility

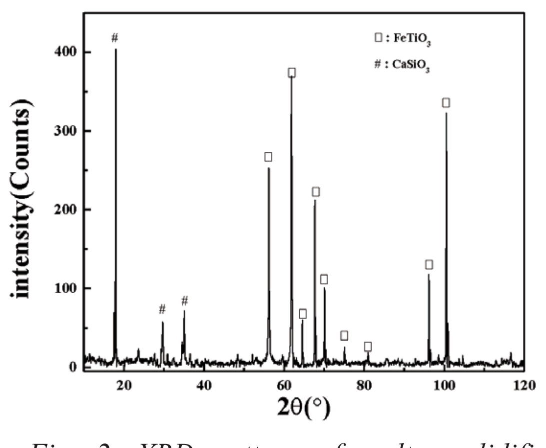


Fig. 2. XRD pattern of molten-solidified cathode

cleaned by Q2200E ultrasonic cleaner and then heat treated at low temperature to remove the water. The morphology was observed by SEM (scanning electron microscopy) and phase composition was also analyzed by XRD.

3. Results and Discussions

3.1 Phase and morphology of the ilmenite cathode

Figure 2 shows the XRD spectrum of ilmenite. According to the XRD analysis, the main phase in the cathode is $FeTiO_3$ which is the same as in the raw material. The result indicates that argon is very useful for maintaining Fe^{2+}. Besides, presence of $CaSiO_3$ in the material is due to silicate enrichment after melting-solidification process. From XRD data, no other phases can be recognized.

SEM image of the cathode, prepared by the method of resolidification is presented in Figure 3.

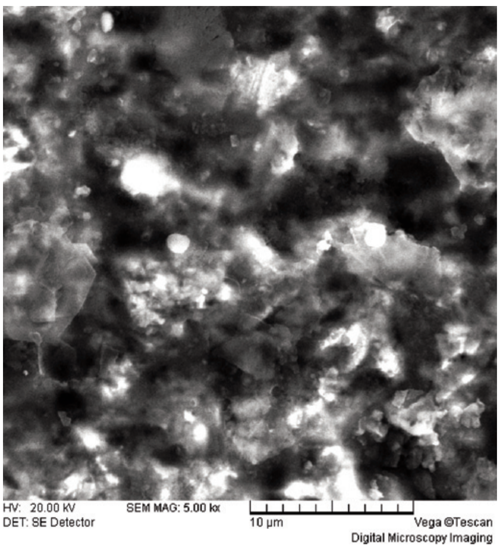


Fig. 3. SEM image of cathode

3.2 Electrolytic products after reaction at 900°C

After reaction at 900°C for 10 min and 30 min, the composition of cathode was analyzed by XRD. Fig.4 shows the diffraction pattern of XRD. We can find that after 10 min of electrolytic reduction, original phase $FeTiO_3$ is replaced by the new phases Fe, $CaTiO_3$, Ti_2O_3 and TiO, while after a longer time (30 min), $TiFe_2$ and TiFe are formed at cathode. Series functions are proposed to explain the mechanism of the electrolytic reaction:

$$Ca^{2+} + TiO_2 + O^{2-} = CaTiO_3 \quad ...(1)$$

$$FeTiO_3 + 2e = Fe + TiO_2 + O^{2-} \quad ...(2)$$

$$2CaTiO_3 + 2e = Ti_2O_3 + 2Ca^{2+} + 3O^{2-} \quad ...(3)$$

$$2CaTiO_3 + 2e = Ti_2O_3 + 2Ca^{2+} + 3O^{2-} \quad ...(4)$$

$$2TiO_2 + 2e = Ti_2O_3 + O^{2-} \quad ...(5)$$

$$2Ti_2O_3 + 2e = 2TiO + O^{2-} \quad ...(6)$$

$$TiO + 2e = Ti + O^{2-} \quad ...(7)$$

$$2Fe + TiO + 2e = TiFe_2 + O^{2-} \quad ...(8)$$

$$Fe + TiO + 2e = TiFe + O^{2-}$$

$$TiFe_2 + TiO + 2e = 2TiFe + O^{2-} \quad ...(9)$$

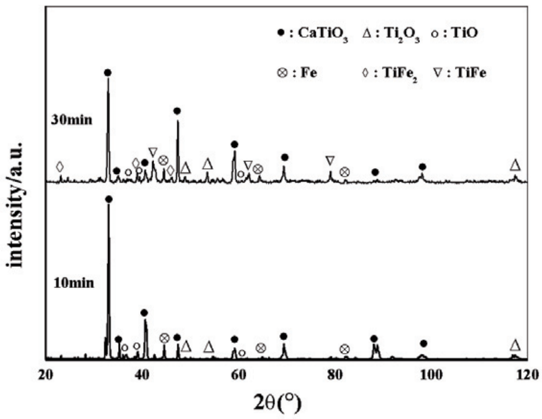


Fig. 4. XRD results of cathode electrolyzed after 10 and 30 mins

Theoretical electrolysis voltages of reactions (1) to (9) were calculated and temperature dependent E for different reactions is shown in Figure 5. It is found that the reduction potential of iron is lower than titanium, so the direct products from $FeTiO_3$ are iron, O^{2-} and TiO_2. In which TiO_2 reacts with CaO in molten salt and forms intermediate product $CaTiO_3$. In fact, CaO is formed by $CaCl_2$ hydrolysis because $CaCl_2$ has good hydrophilic ability.

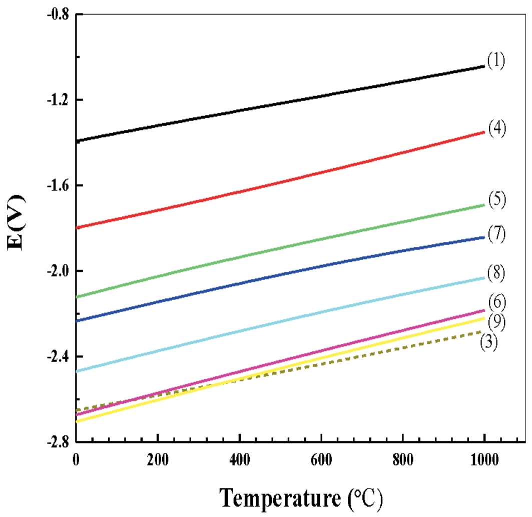


Fig. 5. Theoretical decomposition voltage of electrode reaction at 0~1000°C

Following the initial reaction, intermediate product $CaTiO_3$ is reduced to suboxide, like Ti_2O_3 and TiO. By comparing equations (6) to (8), it is found that the electrolytic voltage of TiO is higher than that of reaction between TiO and iron, which means that it is easier for this reaction to take place in the system. Therefore, if there is iron in the system, TiO will attach on the iron and will be reduced. Finally, $TiFe_2$ will be formed without pure titanium.

3.3 Analysis of the electrolytic products phase at different temperatures

From previous analysis, we can know that Ti and $TiFe_2$ were produced after electrolysis process. However, TiFe can be found under certain conditions, so it's meaningful to understand its formation mechanism. Further experiments are introduced with relative longer time (20h) but at different temperatures: 850°C, 875°C and 900°C. Then the products are investigated by XRD and SEM. Fig.6 and Fig.7 present the results from XRD and SEM.

From Fig. 6 it can be seen that electrolysis products are $TiFe_2$ and Ti at 850°C, which is coincident with thermodynamic analysis. If temperature is increased up to 875°C, TiFe is formed and X-ray diffraction peaks of it become more significant than the other two phases. With the further increase of temperature to 900°C, there is only TiFe left.

The result from 850 °C confirmed thermodynamic analysis which predicts $TiFe_2$ and Ti are the direct electrolysis

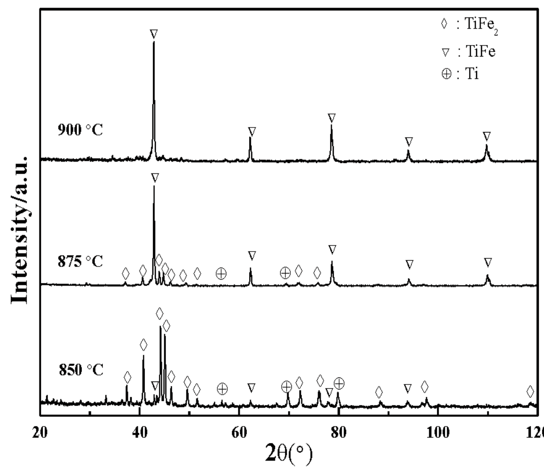
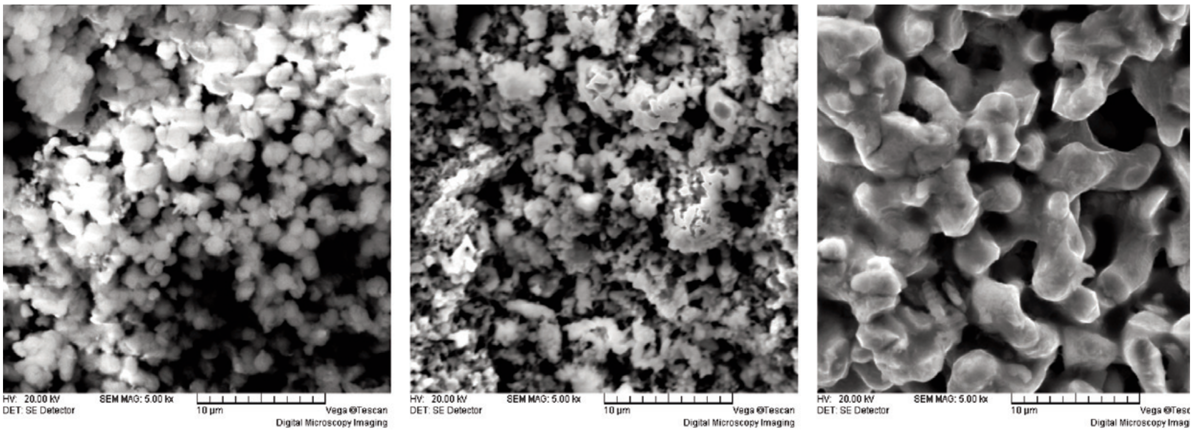


Fig. 6. XRD analysis of cathode electrolyzed at 850°C, 875°C, 900°C



a) 850ºC *b) 875ºC* *c) 900ºC*

Fig. 7. SEM images of cathode electrolyzed at 850ºC, 875ºC, 900ºC

products. From this point of view, TiFe is not formed during the electrolysis process but after that. With the increase of electrolysis temperature, the products change from $TiFe_2$ and Ti to TiFe. The higher temperature is, the more TiFe formed. It indicates that TiFe was generated from inter-diffusion of $TiFe_2$ and Ti on the cathode as expressed by equation 10. As we known, diffusion is a temperature dependent process, so it's not strange why there is only TiFe left after reaction at relatively high temperature. In conclusion, in the system $TiFe_2$ and Ti are formed by electrolytic reaction, while TiFe comes from inter-diffusion of electrolysis products.

$$TiFe_2 + Ti \rightarrow 2TiFe \quad ...(10)$$

Fig. 7 shows the SEM images of different samples. The structure looks like accumulated small spheres and sponge after electrolysis at 850ºC and 900ºC respectively, and the structure for 875ºC sample appearing somewhere in between. This provides useful insight for the temperature dependent process.

4. Conclusions

According to analysis of different electrolytic products from different experimental conditions: time and temperature, as well as thermodynamic calculation, the obtained conclusions can be summarized as follows:

1. Under applied experimental conditions TiFe alloy can be obtained successfully in the CaCl molten system.
2. The direct electroreduction products include Ti and $TiFe_2$ which can be recognized by experiment results and thermodynamic calculation.
3. TiFe alloy is formed by inter-diffusion between Ti and $TiFe_2$ rather than direct electroreduction.
4. The inter-diffusion process was influenced by temperature significantly so that different phases and structures can be formed at the different temperatures.

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