The Smelting Process of Titanium–Silicon Ferroalloy Using Blast Furnace Titaniferrous Slag

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In this paper the smelting process of titanium–silicon (Ti–Si) ferroalloy using waste blast furnace titaniferrous slag containing higher than 20% TiO_2 is introduced. Firstly the principle of smelting Ti–Si ferroalloy by electrosilicothermic method (ESTM) and the effects of DC on the reduction of TiO_2 in molten slag are studied. Ti–Si ferroalloy containing about 20% Ti can be produced by ESTM, and Ti recovery is less than 60%. And then, electrosilicoaluminothermic method (ESATM) is introduced. Ti–Si ferroalloy containing higher than 30% Ti and less than 35% Si can be produced by ESATM, and Ti recovery is higher than 80%. Studies on application of products (Ti–Si ferroalloy and residue slag) of the smelting process have been carried out, and the results show that the electrothermic smelting process can make the waste blast furnace titaniferrous slag be used perfectly.

KEY WORDS: smelting process; electrothermic reduction; Ti–Si ferroalloy; blast furnace titaniferrous slag.

1. Introduction

In the southwest of China, vanadium titaniferrous magnetite is abundant. When smelting it in blast furnace, a large amount of blast furnace titaniferrous slag containing 20–25% TiO_2 (BFTS) is obtained. BFTS is not used in a great quantity up to now, and discarded to slag pile. It contaminates the circumstance and influences production. So it has important realistic significance to study the comprehensive utilization of BFTS.

BFTS is very different from normal blast furnace slag in mineral compositions. BFTS can be used as additive of portland titanium slag cement through technical process, but titanium in BFTS is not recovered.

In this paper the electrothermic process for smelting Ti–Si ferroalloy using BFTS developed by us is introduced. In the smelting process BFTS is used as raw materials to produce Ti–Si ferroalloy, and the residue slag is used as additive for making cement. The process is different from traditional smelting process of Ti–Si ferroalloy in raw materials, smelting method and products. Titanium in BFTS can be recovered and residue slag can be used rationally.

A large scale hydroelectric power station is being constructed in the southwest of China, and so, the power to produce Ti–Si ferroalloy has reliable guarantee.

In the point of comprehensive utilization of resources and in the light of plentiful hydroelectric resources in the southwest of China, the smelting process of Ti–Si ferroalloy using BFTS is a method having a great future to utilize BFTS effectively.

First try and middle try of the smelting process have been conducted, and it is about to be put into industrial production.

2. Electrosilicothermic Method (ESTM) for Smelting Ti–Si Ferroalloy

2.1. The Principle of ESTM

The reduction reaction of TiO_2 by silicon is given as Eq. (1):

From the Gibbs free energy change in the standard state, the reaction can not take place. Under practical conditions, the activity of Ti in alloy melt is very lower and Ti combines with Si into titanium–silicide. So under practical conditions the reaction can take place perfectly. Under experimental conditions, when BFTS and metal reductant are mixed to smelt Ti–Si ferroalloy, and the metal particles are dispersed into molten slag, the overall reduction rate of TiO_2 in molten slag by metal reductant can be obtained from the microkinetics at the single metal particle and the macrokinetics between the sum of the metal particles and the slag.^{1,2)}

Assuming that A is the surface area of the metal particle, and V is the volume of the metal particle, at a time the Ti concentration change in metal particle is:

$$\frac{d[\text{Ti}]}{dt} = \bar{k} \cdot \frac{A}{V} \cdot ((\text{Ti}) - [\text{Ti}]/K) \quad \dots\dots\dots(2)$$

$$K = [\text{Ti}]^*/(\text{Ti})^* \quad \dots\dots\dots(3)$$

$$\frac{1}{\bar{k}} = \frac{1}{\beta_s} + \frac{1}{K\beta_m} + \frac{1}{k'} \quad \dots\dots\dots(4)$$

where $\bar{k}$ is the overall reduction rate constant of TiO_2 , β_s is mass-transfer coefficients in slag phase, β_m is mass-transfer coefficients in metal phase, k' is reduction rate constant of TiO_2 at the interface, K is the equilibrium concentration ratio at the interface when the interface reaction is at equilibrium. The star denotes the concentration at the interface. $[\text{Ti}]$ and (Ti) is Ti concentration in metal particles and in molten slag.

Assuming that the average residence time of the metal particles in molten slag is $\bar{t}$. During the average residence time Ti concentration in molten slag around a metal particle changes very little, and (Ti) is treated as constant.^{1,2)} With the boundary conditions:

$$\begin{aligned} [\text{Ti}] &= [\text{Ti}]_0 & \text{at } t=0 \\ [\text{Ti}] &= [\bar{\text{Ti}}] & \text{at } t=\bar{t} \end{aligned}$$

the integration of Eq. (2) gives

$$\begin{aligned} [\bar{\text{Ti}}] &= [\text{Ti}]_0 \cdot \exp\left(-\frac{k}{K} \cdot \frac{A}{V} \cdot \bar{t}\right) \\ &+ k \cdot (\text{Ti}) \cdot \left(1 - \exp\left(-\frac{k}{K} \cdot \frac{A}{V} \cdot \bar{t}\right)\right) \quad \dots\dots\dots(5) \end{aligned}$$

Equation (5) describes the change of Ti concentration in the metal particle when it is settled from slag to the bottom. In the process of the experiments W_m gram FeSi_{75} reductant is added to W_s gram BFTS. During the average residence time the increase of Ti in metal phase equals to the decrease of Ti in the molten slag phase, and with Eq. (5) it follows:

$$\begin{aligned} -\frac{d(\text{Ti})}{dt} &= \frac{1}{\bar{t}} \frac{W_m}{W_s} \left(1 - \exp\left(-\frac{\bar{k}}{K} \cdot \frac{A}{V} \cdot \bar{t}\right)\right) \\ &\cdot (K(\text{Ti}) - [\text{Ti}]_0) \quad \dots\dots\dots(6) \end{aligned}$$

with $[\text{Ti}]_0 = 0$, it follows:

$$-\frac{d(\text{Ti})}{dt} = \frac{K}{\bar{t}} \frac{W_m}{W_s} \left(1 - \exp\left(-\frac{\bar{k}}{K} \cdot \frac{A}{V} \cdot \bar{t}\right)\right) \cdot (\text{Ti}) \quad \dots\dots\dots(7)$$

With boundary conditions:

$$\begin{aligned} (\text{Ti}) &= (\text{Ti})_0 & \text{at } t=0 \\ (\text{Ti}) &= (\text{Ti})_t & \text{at } t=t \end{aligned}$$

the integration of Eq. (7) gives (using (TiO_2) instead of (Ti))

$$\ln \frac{(\text{TiO}_2)_t}{(\text{TiO}_2)_0} = -\frac{K}{\bar{t}} \frac{W_m}{W_s} \left(1 - \exp\left(-\frac{\bar{k}}{K} \cdot \frac{A}{V} \cdot \bar{t}\right)\right) t \quad \dots\dots\dots(8)$$

Equation (8) describes the overall reduction rate of TiO_2 in molten slag in the smelting process of Ti-Si ferroalloy.

In the smelting experiments of Ti-Si ferroalloy by ESTM, the compositions of BFTS used are: 22.57% TiO_2 , 23.04% SiO_2 , 26.18% CaO , 13.43% Al_2O_3 and 8.41% MgO . The reductant is ferrosilicon containing 73.65% Si. The quantity of ferrosilicon used is 33.0 gms/100 gms BFTS. The initial basicity of the slag (CaO/SiO_2)

is adjusted to 1.6 using calcium oxide. The burden is ground to finer than -80 mesh (the diameter of the particles is 0.2 mm), and mixed evenly before smelting. The experiments are conducted at 1570°C in the atmosphere of N_2 . The laboratorial experimental apparatus is presented in Fig. 1.

From Eq. (1), it follows

$$K_{\text{Ti}} = \frac{a_{[\text{Ti}]}^* \times a_{(\text{SiO}_2)}^*}{a_{[\text{Si}]}^* \times a_{(\text{TiO}_2)}^*} \quad \dots\dots\dots(9)$$

$$K = \frac{[\text{Ti}]^*}{(\text{Ti})^*} = K_{\text{Ti}} \times \frac{\gamma_{(\text{Ti})}^* \times a_{[\text{Si}]}^*}{\gamma_{[\text{Ti}]}^* \times a_{(\text{SiO}_2)}^*} \quad \dots\dots\dots(10)$$

where K_{Ti} is the equilibrium constant of the TiO_2 reduction reaction by silicon. The activity coefficients of elements in molten slag are calculated using regular ionic solution theory.⁴⁾ The activity coefficients of elements in metal melt are calculated using Bonnier formula.⁵⁾ It follows $K=0.0970$. And the following data are used for numerical calculation: $\bar{t}=1.5$ min, $W_m/W_s=0.33$, $r=0.0001$ m²) (here r is the average radius of reductant particle. To the spherical particle that its average radius is r , $A/V=3/r$), and the overall reduction rate of TiO_2 by Si is controlled by the step that (Ti^{4+}) diffuses in molten slag. So $\bar{k} \approx \beta_s = 10^{-5}$ m/sec.³⁾ The above data lead to $\exp(-\bar{k}/K \cdot A/V \cdot \bar{t})=0$, and at 1570°C

$$\ln \frac{(\text{TiO}_2)_t}{(\text{TiO}_2)_0} = -0.0214t \quad \dots\dots\dots(11)$$

The result of experiments is given as Eq. (12):

$$\begin{aligned} \ln \frac{(\text{TiO}_2)_t}{(\text{TiO}_2)_0} &= -0.0224t - 0.1210 \\ \gamma &= 0.9892 \quad \sigma = 0.3709 \quad \dots\dots\dots(12) \end{aligned}$$

Where γ is correlation coefficient, σ is standard deviation.

From the comparison of the above equations, one can

Fig. 1. The scheme of experimental apparatus.
1 - graphite crucible, 2 - slag and metal, 3 - alumina crucible, 4 - MoSi_2 heating elements, 5 - temperature controlling meter, 6 - temperature controlling thermocouple, 7 - temperature measuring meter, 8 - temperature measuring thermocouple.

see that the reduction rate calculated from Eq. (11) is in good agreement with that determined experimentally (shown in Eq. (12)). The results are also presented in Fig. 2.

2.2. The Effects of DC on the Reduction of TiO_2

When adding DC to the bath in the smelting process of Ti-Si ferroalloy by ESTM, the reduction of TiO_2 in molten slag is achieved by following ways: silicothermic reduction, electrolysis reduction, carbothermic reduction, electrophoresis of metal particles, gravity settling and the convection of the bath (see Fig. 3). The electrolysis reduction and electrophoresis of metal particles are characteristic of DC smelting. Comparing with ESTM without DC, the physicochemical conditions of TiO_2 reduction with DC are more advantageous.

In the laboratory, when experimental conditions is the same as that of ESTM, and adding 3.0 and 5.0 V/cm DC to the bath (the apparatus can be seen in Fig. 4), the reduction rate of TiO_2 in molten slag are presented in Fig. 5 and Eqs. (13) and (14).

3.0 V/cm DC ($t < 50$ min)

Fig. 2. TiO_2 concentration in molten slag versus the smelting time.

○ experimental points
 - - - experimental regression curve
 — theoretical curve

Fig. 3. The scheme of reduction of TiO_2 of BFTS by DC electric furnace.

A. Silicothermic reduction; B. electrophoresis; C. electrolysis; D. carbothermic reduction; E. gravity settling; F. convection

$$\ln \frac{(\text{TiO}_2)_t}{(\text{TiO}_2)_0} = -0.0549t - 0.0776$$

$$\gamma = 0.9822 \quad \sigma = 0.2445 \quad \dots\dots\dots(13)$$

5.0 V/cm DC ($t < 30$ min)

$$\ln \frac{(\text{TiO}_2)_t}{(\text{TiO}_2)_0} = -0.090t - 0.033$$

$$\gamma = 0.9991 \quad \sigma = 0.0067 \quad \dots\dots\dots(14)$$

Equations (12), (13), and (14) describe that when adding DC to the bath the rate of TiO_2 reduction increases greatly, Ti content of Ti-Si ferroalloy increases, Si content of Ti-Si ferroalloy decreases and the grade of Ti-Si ferroalloy is increased. The results are presented in Table 1.

Fig. 4. The scheme of experimental apparatus for studying the effects of DC. 1. graphite electrode (anode); 2. graphite electrode (cathode); 3. screw jack; 4. electrode holder; 5. DC powder; 6. temperature controlling meter; 7. temperature controlling thermocouple; 8. potentiometer; 9. temperature measuring thermocouple; 10. MoSi_2 heating elements; 11. graphite crucible; 12. alumina crucible; 13. molten slag; 14. metal

Fig. 5. The effects of DC on the reduction of TiO_2 in molten slag.

○ — with ferrosilicon, 0.0 V/cm DC
 × — with ferrosilicon, 3.0 V/cm DC
 ▲ — with ferrosilicon, 5.0 V/cm DC

Table 1. The effects of DC on Ti and Si content of Ti-Si ferroalloy under laboratory conditions.

Experimental conditions	Ti content in alloy (%)	Si content in alloy (%)	(TiO ₂) content in slag (%)	Ti recovery (%)
ESTM no DC	29.87	40.43	1.86	87.69
ESTM 3.0 V/cm DC	30.37	39.53	1.20	90.63
ESTM 5.0 V/cm DC	30.41	39.59	0.83	92.92

Table 2. Semi-industrial experiments conditions and results for smelting Ti-Si ferroalloy by ESTM.

Furnace type	(TiO ₂) (%)	Slag type	Reductant (g/100 g slag)	Smelting time (min)	[Ti] (%)	[Si] (%)	(TiO ₂) (%)	η_{Ti} (%)
50 KVA AC(1)	47	Compound	60	110	24.29	48.0	12.71	53.0
50 KVA AC(2)	30	Compound	45	110	18.40	36.80	5.44	51.0
650 KVA AC	41.70	Compound	55	110	22.25	41.89	12.10	55.50
100 KVA AC	22.57	BFTS	30	75	19.11	50.83	9.22	50.23
200 KVA DC	22.57	BFTS	30	65	21.49	44.44	7.90	59.32

η_{Ti} , %: Ti recovery

2.3. Semi-industrial Experiments for Smelting Ti-Si Ferroalloy by ESTM

Conditions and results for semi-industrial experiments are presented in **Table 2**. (η_{Ti} , %, expresses Ti recovery.)

From the results of semi-industrial experiments, one can see that Ti-Si ferroalloy containing about 20% Ti can be produced by ESTM using BFTS or compounded titanium-bearing slag (its compositions are: 41.70% TiO₂, 19.60% SiO₂, 12.63% CaO, 12.92% Al₂O₃ and 6.98% MgO.). To add DC to the bath, Ti content of Ti-Si ferroalloy and Ti recovery can be increased, Si content of Ti-Si ferroalloy and TiO₂ content in residue slag can be reduced.

3. Electrosilicoaluminothermic Method (ESATM) for Smelting Ti-Si Ferroalloy

When ferrosilicon is used as reductant, Ti recovery is lower than 60%, and a considerable amount of TiO₂ remains still in the residue slag. If the quantity of the ferrosilicon exceeds too much, Ti recovery cannot be increased, and Si content of Ti-Si ferroalloy will be increased only. To increase Ti content of Ti-Si ferroalloy and Ti recovery, and to reduce Si content of Ti-Si ferroalloy and TiO₂ content in residue slag, strong reductant must be used. Silicoaluminium ferroalloy (Si-Al-Fe) is cheaper than aluminium powder in price, and stronger than ferrosilicon in reduction ability. So to use Si-Al-Fe alloy is beneficial to reduce Si content of Ti-Si ferroalloy and to increase the Ti content. Under laboratorial and semi-industrial conditions, Si-Al-Fe alloy is used as reductant to smelt Ti-Si ferroalloy. The experimental conditions in laboratory are as follows: the smelting temperature is 1 550–1 570°C, the initial basicity of burden is 1.80, the quantity of reductant is 31.0 g/100 g BFTS, the smelting time is 100 min. The semi-industrial experiments are conducted in 200 KVA DC furnace, the smelting temperature is 1 560–1 670°C, the initial basicity is 1.80, the quantity of reductant is 30.0 g/100 g BFTS, the smelting time is 70 min. The

Table 3. The results of smelting Ti-Si ferroalloy using Si-Al-Fe reductant.

Experimental conditions	[Ti] (%)	[Si] (%)	(TiO ₂) (%)	η_{Ti} (%)
Laboratory	33.57	25.05	2.20	89.13
200 KVA DC	31.63	32.79	4.50	84.30

compositions of Si-Al-Fe alloy are: 49.11% Al, 21.46% Si, 29.50% Fe. The results are presented in **Table 3**.

Table 3 shows that by ESATM Ti-Si ferroalloy containing higher than 30% Ti and less than 35% Si can be produced, Ti recovery is higher than 80%, and TiO₂ content in the residue slag can be reduced to below 5%.

4. Application of Products

The electrothermic smelting process produces two types of products: Ti-Si ferroalloy and residue slag containing less than 10% TiO₂. Studies on application of Ti-Si ferroalloy in steelmaking are carried out in LD, EAF, and open hearth furnace in Chongqing Iron and Steel Company. The compositions of Ti-Si ferroalloy used are: 20% Ti, 44% Si. Ti-Si ferroalloy is used to replace TiFe for smelting steel grades of 16MnR, 20g, 20R, 15MnTi, etc. The results give that it is feasible to use Ti-Si ferroalloy to conduct titanium-treatment to steel. There are no influences on the process of smelting and casting of steel. There are no harmful influences on the quality of steel and properties of steel products. Ti-Si ferroalloy can be used to replace TiFe, and at the same time can save the quantity of ferrosilicon added. The product cost of unit steel can be also reduced. At the same time, if Ti content of Ti-Si ferroalloy can be increased to above 25% and the Si content can be reduced to less than 35% (by ESATM), Ti-Si ferroalloy can be used in smelting steel containing Ti in a great range, and can be used to replace TiFe overall in steel-making.

The results of the experiments to use the residue slag for making cement show that the residue slag is mainly composed of Gehlenite, its basic index is higher than 2.0, it is active additive and fit for making portland cement. The strength grade of cement clinker is above 525 grade when the quantity of residue slag is 20 %, The strength grade of portland cement is above 425 grade when the residue slag is used as additive of cement and the quantity added is 20–50 %.

The results of application of products shows that the electrothermic process for smelting Ti–Si ferroalloy using BFTS can make the waste BFTS be used perfectly.

5. Conclusions

(1) To smelt Ti–Si ferroalloy by ESTM, the overall reduction rate of TiO_2 in molten slag is given as:

$$\ln \frac{(\text{TiO}_2)_t}{(\text{TiO}_2)_0} = k'' t$$

where k'' is a constant. The results of theoretical study is in good agreement with that of experiments.

(2) Adding DC to the bath, Ti content of alloy and Ti recovery can be increased, Si content of alloy and TiO_2 content of the residue slag can be reduced, the reduction rate of TiO_2 can be increased greatly.

(3) By ESATM, Ti–Si ferroalloy containing higher than 30 % Ti and less than 35 % Si can be produced, TiO_2 in residue slag can be reduced to less than 5 % and Ti recovery can be increased to higher than 80 %.

(4) The electrothermic smelting process of Ti–Si ferroalloy using BFTS can make the waste BFTS be used perfectly.

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