Optimization of Medium-and Low-Carbon Ferromanganese Process by Silicothermic Reduction

Ding Weizhong, Xu Weiwei, Tang Kai and Jiang Guochang

Shanghai University, Shanghai Enhanced Laboratory of Ferrometallurgy
149 Yanchang Road, Shanghai 200072, China

Abstract

According to the knowledge of chemical reaction and stoichiometry, a fundamental framework has been developed for equilibrium relations in the medium- and low-carbon ferromanganese process by silicothermic reduction. Compositions of carbon unsaturated alloys in equilibrium with slags have been determined experimentally and calculated based on a thermodynamic solution model. The obtained result may be numerically described and dealt with for optimizing the silicothermic process.

1. Introduction

The production of medium- and low-carbon ferromanganese consists of two processes: the manganese oxygen refining (MOR) process and the silicothermic process with reduction of MnO in MnO-rich slags or manganese ores. The basic equilibrium data concerning silicothermic reduction are seldom. Process control and regulation depend mainly on producer's experience accumulated from their practices.

In the early eighties some metallurgists[1,2] attempted to optimize silicothermic reduction process by means of industrial data and laboratory results. But there was poor understanding of the process at that time. Any attempting, therefore, seems apparent and statistic. Recently reaction equilibrium for the system Mn-Si-C-O has been analyzed thermodynamically[3]. Equilibrium relations were then constructed to show the quantitative effects of different operating parameters in smelting processes. Also equilibrium compositions for carbon saturated systems have been measured successfully[4-7]. In this case it is possible to investigate the optimization of silicothermic process for medium- and low-carbon ferromanganese.

2. Thermodynamic Analysis of the Process

2.1. Reaction equilibrium

The principle reaction of the process taking place in the interface between slag and metal is the following

$$\underline{Si} + 2(MnO) = 2\underline{Mn} + (SiO_2) \qquad (1)$$

The equilibrium constant for reaction (1) is given by

$$\frac{a_{Mn}^2}{a_{Si}} = K\frac{a_{MnO}^2}{a_{SiO_2}} \qquad (2)$$

Medium- and low-carbon ferromanganese may be considered as a quaternary system Mn-Si-Fe-C. As their carbon and iron contents are fixed by an alloy specification, according to the phase rule the activity ratio (a_{Mn}^2/a_{Si}) of an alloy has a unique relation to its silicon content. Fig. 1 illustrates the inferred relationship between the activity ratio and the silicon content in different alloys.

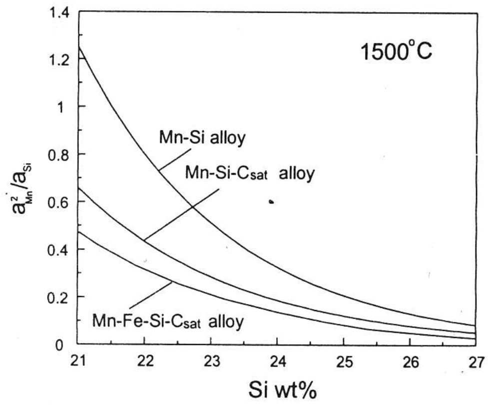

Figure 1. Inferred relationship between activity ratio and silicon content in different alloys.

It is found from Fig. 1 that at a certain temperature the silicon contents are quite different for alloys with the same activity ratio (a_{Mn}^2/a_{Si}). The highest silicon content appears for Mn-Si alloy and the lowest for Mn-Fe-Si-C_{sat} alloy. The line position for Mn-Fe-Si-C alloy is believed to be between them.

The left term of equation (2) is thought to be a function of the silicon content of an alloy, and the right term concerns temperature and slag composition. Presentation of equilibrium composition can use a pseudo-ternary diagram for all slags. In such a diagram silica and manganese oxide occupy two apexes of the triangle, respectively. The other oxides, which are not reduced in the process and called as "unreducible oxides", can be represented by the left bottom apex. They are CaO, Al_2O_3, MgO and BaO etc., and may keep their mutual ratios during the reactions. After reaching slag/metal equilibrium the slag composition should satisfy the relation defined by equation (2). In other words, the equilibrium composition in the diagram actually indicates the relationship between the component concentration and the activity ratio (a^2_{MnO}/a_{SiO_2}). Fig. 2 shows such a hypothetical equilibrium diagram. The composition of slag in equilibrium with a certain alloy can be represented by a curve in the diagram, which in fact is a iso-activity ratio (a^2_{MnO}/a_{SiO_2}) line. To give a more clear indication, a quantity for each iso-activity curve may refer to Si content of the equilibrated alloy rather than the value of (a^2_{MnO}/a_{SiO_2}).

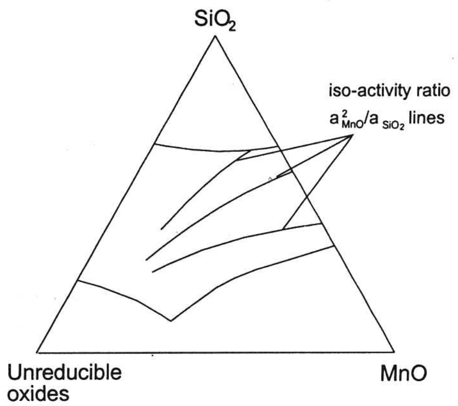

Figure 2. Illustration of slag/metal equilibrium.

2.2. Stoichiometric relation

In addition to chemical equilibrium conditions, the final state and amounts of slag and metal produced in a silicothermic process will be dependent on the stoichiomtry of the system. A quantitative relation between the initial raw material and the final product compositions has been derived from mass balance [4]. A change of slag composition duo to silicothermic reduction will be along the dashed lines, which are defined as "reaction paths", illustrated in Fig. 3. The direction of such a change is towards high silica content because manganese oxide is reduced during the reaction. The angle between the path and the MnO axis varies from 60°C to 30°C. As an example, the initial composition at point A in Fig. 3 will go to point B after reaction (1) conducts.

A similar result can also be obtained for the alloy system. Silicomanganese, used as a reducing agent, is normally manufactured in submerged arc furnaces by carbothermic reduction. Its carbon concentration should be in saturation. Then the carbon content of medium- and low-carbon ferromanganese produced by a silicothermic process depends on that of silicomanganese employed. Fig. 4 shows the path of alloy composition change(wt%) when silicothermic reduction takes place. The shaded area in the figure is a two-phase region of liquid alloy and solid carbon material (graphite or silicon carbide). Point A and B are the

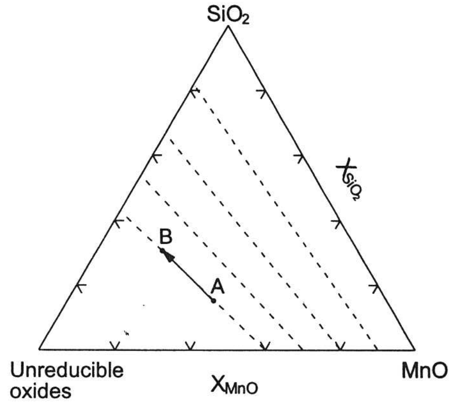

Figure 3. Slag composition changes due to silicothermic reduction.

compositions of silicomanganese and the final alloy, respectively In order to produce an alloy with lower carbon content, a low carbon reductive alloy is essentially required. As we know, carbon solubility of an alloy is a function of the silicon content. Therefore the silicon content of a reductive alloy for production of low-carbon ferromanganese has to be high enough.

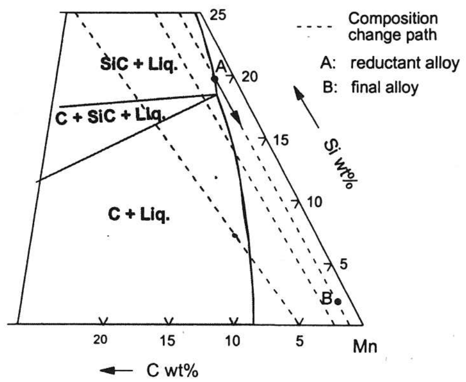

Figure 4. Path for alloy composition change during silicothermic reduction.

3. Numerical Description of Equilibrium and Optimization Model

3.1. Numerical description of slag/metal equilibrium relation

The equilibrium relation of the silicothermic reduction makes producers have an entire knowledge to understand the process. To optimize the process, many other relations must be considered simultaneously including reaction stoichiometry, available raw materials, possible production conditions and price of goods. It is so complicated that mathematical treatment and calculation by computer are necessary. All basic relations have to be dealt with by use of numerical expressions. Among them the most important work is to describe the slag/metal equilibrium mathematically.

On the basis of the equilibrium diagram in the forgoing section, numerical description of slag/metal equilibrium can be carried out by Pelton method [8]. A ternary may be regarded as a system possessing two degrees of freedom. Two new component variables, y and z, are therefore chosen after transformations as follows

$$y=1-x_1 \qquad (3)$$

$$z=\frac{x_3}{x_2+x_3} \qquad (4)$$

where x is the original oxide coordinate variable, which may be in mole fraction or weight percentage. The subscript *1*, *2* and *3* represent silica, unreducible oxides regarded as a whole and manganese oxide, respectively.

Under given conditions (temperature, mutual ratios of unreducible oxides, carbon and iron contents of an alloy), slag/metal equilibrium composition can be described by silicon content expressed as power series in y and z. For a ternary alloy Mn-Si-C_{sat} with less than 8 wt% of silicon and a quaternary slag MnO-SiO_2-CaO-Al_2O_3 (CaO/Al_2O_3=1.5), their slag/metal equilibrium at 1550 ℃ may be written as

$$\begin{aligned}\ln(Si\%)=&-2.328-9.208y+76.098y^2-183.010y^3\\&+141.526y^4+2.624z-10.031yz+8.348y^4z\\&+8.365z^2-54.059yz^3-2.045y^2z^3+62.152y^4z^3\\&-39.454z^4+543.735y^2z^4-882.930y^4z^4+89.752z^5\\&-1.105yz^5-1212.506y^2z^5+1412.129y^3z^5\\&-88.410z^6+327.492xy^6-244.729y^2z^6\end{aligned} \qquad (5)$$

3.2. Optimization model

Optimization of the process is based on thermodynamic equilibrium and stoichiometry. In the case of the production of a specified alloy the equilibrated slag composition varies within a wider region, as shown in Fig. 5. From an economic point of view, the lowest MnO content in the final slag does not mean the best choice. The objective of the production is to gain the maximum profit. Many economic parameters have to be taken into consideration, such as the price and amount of each manganese ore and MnO-rich slag, the price and composition of reductive alloys and their consumption, as well as the cost of smelting technology. These may be belong to the searching problem of nonlinear program [9]:

Target function:
S = the price of products − the sum price of raw materials − the sum cost of smelting = Maximum

Restrictions:
Slag/metal equilibrium relation
Stoichiometric relation
Energy balance of process
Kinds of available raw materials
Specification of products

The optimization of nonlinear program is a gigantic and complicated mathematics issue. After defining all boundary conditions the computer calculation can solve the problems to give a optimal result.

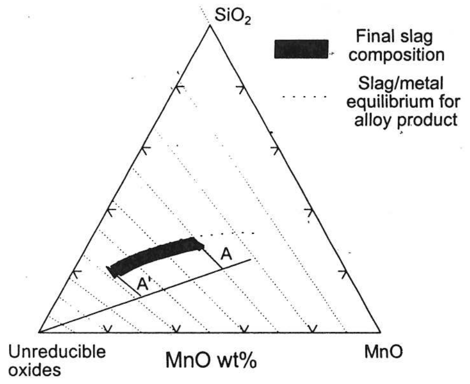

Figure 5. Region of slag composition in equilibrium with a fixed alloy.

4. Measurement and Calculation of Equilibrium Composition

The key to optimize the process is to get the basic data of related slag/metal equilibrium composition. Because of restriction of available crucible materials, the measurement for carbon unsaturated alloys in equilibrium with multi-component slags is difficult to be carried out. Laboratory work was done only under the condition of slags saturated with some oxides [10].

According to the conclusion of the thermodynamic analysis before, if the relationship between the Si content of carbon unsaturated alloy and its activity ratio is known, the slag/metal equilibrium composition published for carbon saturated alloys is equally applicable to carbon unsaturated system. Thus new measurement does not required. In this investigation, such a relationship was obtained by calculation through a thermodynamic solution model[11], which was designated as SELF-SReM model. Specially designed experiments were conducted to judge the calculated result.

4.1. Principle of experiment and procedure

The relationship between the Si content of carbon unsaturated alloy and its activity ratio (a^2_{Mn}/a_{Si}) was determined with a reference of carbon saturated alloy. Alloys with carbon saturation (as a reference) and unsaturation (detected alloys) equilibrated simultaneously with the same slag during the measurement. In accordance with reaction (1), the activity ratio (a^2_{Mn}/a_{Si}) of all alloys should be identical when equilibrium was established, namely

$$(a^2_{Mn}/a_{Si})\Big|_{Mn-Si-C_{sat}}=(a^2_{Mn}/a_{Si})\Big|_{Mn-Fe-Si-C} \qquad (6)$$

In fact the exact value of slag activity ratio (a^2_{MnO}/a_{SiO_2}) are not known. The activity ratio (a^2_{Mn}/a_{Si}) of equilibrated alloys are, therefore, not determined yet. But the experiment will give the mutual relation of the Si contents in carbon saturated and unsaturated alloys with the same activity ratio. The published result for carbon saturated system[5-7] may then be expanded to carbon unsaturated one.

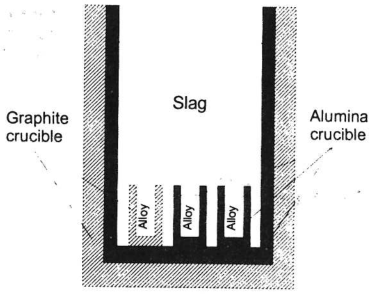

Figure 6. Schematic show of the crucible assembly.

Experiments were done in a vertical graphite resistance furnace. It comprised two working regions: a high temperature zone and a water cooling jacket. The latter ensured a crucible containing melts to be quenched fast when experiment ended. Fig. 6 illustrates a

4.2.2. Effect of carbon content

The carbon content of alloy changes remarkably the equilibrium composition. In equilibrium with the same slag, lower carbon content makes the silicon content of the alloy increase considerably whether iron is present or not [9-12], shown in Fig. 8-11. This means that the silicon content of low carbon alloy will be higher than that of carbon saturated alloy.

It is considered that the contribution of carbon towards the activity coefficient of silicon is approximately the same as that of silicon itself [4]. The silicon activity coefficient decreases with a drop of carbon. Carbon effect on the manganese activity coefficient seems to be not so strong [12,13]

4.2.3. Effect of iron

Presence of iron will affect the relationship between the silicon

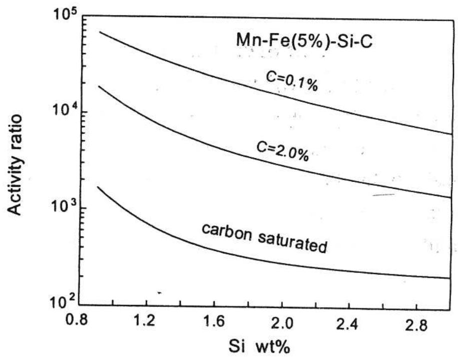

Figure 8. Calculation result for Mn-Fe(5%)-Si-C alloy at 1550 ℃.

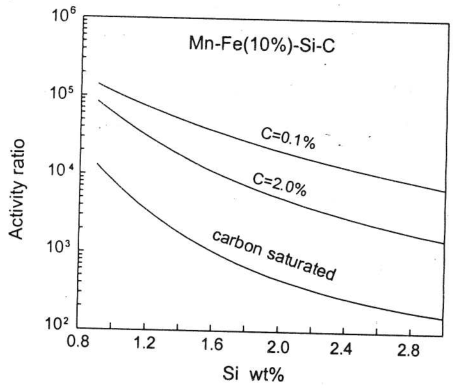

Figure 9. Calculation result for Mn-Fe(10%)-Si-C alloy at 1550 ℃.

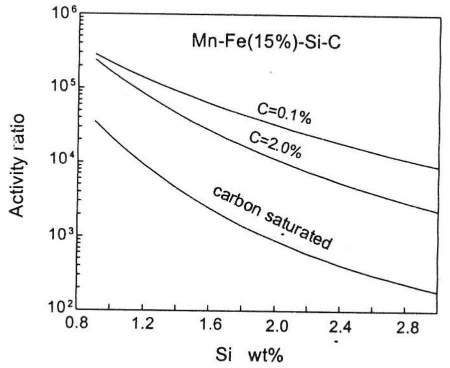

Figure 10. Calculation result for Mn-Fe(15%)-Si-C alloy at 1550 ℃.

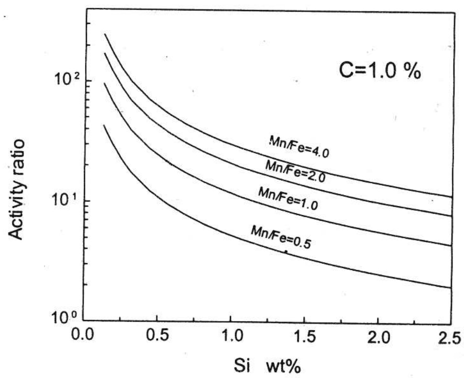

Figure 11. Effect of iron on activity ratio at 1550 ℃.

content and the activity ratio (a^2_{Mn}/a_{Si}). In the case of lower silicon content, the larger the value of (Mn/Fe) is, the smaller the activity ratio (a^2_{Mn}/a_{Si}) appears. When the silicon content rises to a certain level, this relation is probably inverted. Fig. 11 gives an image of activity ratio (a^2_{Mn}/a_{Si}) change with different of (Mn/Fe).

5. Conclusion

Optimization of the silicothermic process for medium- and carbon ferromanganese is based on thermodynamic analysis of chemical reactions. The relationship between the Si content and the activity ratio (a_{Mn}^2/a_{Si}) of carbon unsaturated alloys is determined experimentally and calculation by the solution model SELF-SReM. The available slag/metal equilibrium data are then applied to the low carbon system. After mathematical treatment, the optimal process can be realized by utilizing the optimization technology and computing methods.

Reference

1. N.A.Barcza and D.P.O'shaughnessy, "Optimum Slag-Alloy Relationships for the Production of Medium-to Low-Carbon Ferromanganese" , Can.Metall.Q., 20 (1981),285-294
2. J.Kr.Tuset, "Silicothermic Reduction of Manganese", 50th International Iron and Steel Congress Proceedings, (1986), 59-64
3. W.Ding and S.E.Olsen, "Thermodynamic Analysis of the Silicomanganese Process", 1991 Electric Furnace conference Proceedings. 259-264
4. W.Ding, "Equilibrium Relations in the Production of Manganese Alloy", Doctoral thesis, (NTH), 1993.2
5. W.Ding and S.E.Olsen, "Reaction Equilibria in the Production of Manganese Ferroalloys", Met.&Mater.Trans.B, 27B(1996), 5-17
6. S.E.Olsen and Ding, "Equilibrium in Production of High Carbon Ferromanganese", 7th International Ferroalloys Congress (INFACON 7) Proceedings , (1995), 591-600
7. W.Ding and S.E.Olsen, "Reactions between Malticomponent Slags and Mn-Fe-Si-C alloys—Equilibrium and stoichiometry " , Scand . J. Metall. , 25(1996), 232-243
8. A.D.Pelton and S.N.Flengas, "An Analytical Method of Calculating Thermodynamic Data in Trenary Systems", Can. J.Chen., 47(1969), 2283-2292
9. Fan and Y. Zhang, "Basis of Optimization", Qinghua University Press, 1982 (Chinese)
10. J.Kr.Tuset, J.Sandvik and K.Venas, "The Distribution of Manganese and silicon between Fe-Mn-Si-alloys and Ternary and Complex Slags", SINTEF Research Report 340420,1971.
11. Zhang, Ph.D. thesis, Shanghai University, 1996.6 (Chinese)
12. R.Gee and T.Rosenqvist, "The Vapour Pressure of Liquid Manganese and Activities in Liquid Mn-Si and Carbon-saturated Mn-Si alloy", Scand. J. Metallurgy, 5(1976), 57-62
13. R.Gee and T.Rosenqvist, "Activities in Liquid Fe-Mn-Si Alloys", Scand. J. Metallurgy, 7(1978), 38-41