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EQUILIBRIUM IN PRODUCTION OF HIGH CARBON FERROMANGANESE

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ABSTRACT

A laboratory investigation has been carried out to determine distribution equilibria relevant to industrial production of high carbon ferromanganese in submerged arc furnaces. Liquid synthetic slags in the system MnO-SiO_2-CaO-Al_2O_3-MgO and industrial ferromanganese slags were equilibrated with Mn-Fe-Si-C_{sat} alloys in graphite crucibles. The experiments were carried out in Ar and CO gas atmosphere at temperatures ranging from 1350 to 1450°C. The results are illustrated in equilibrium diagrams showing partial slag/metal equilibrium lines of constant alloy compositions and complete slag/metal/gas equilibrium lines giving slag compositions dependent on temperature and alloy composition. The effect of process temperature and slag basicity is discussed.

INTRODUCTION

High carbon ferromanganese (HC FeMn) is either produced in blast furnaces or in electric submerged arc furnaces. When produced in electric furnaces, the operating conditions are often set to obtain about 35% MnO in the slag and less than 1% Si in the alloy. The rich slag is reutilized for production of silicomanganese. This process route ensures a high manganese yield.

The main parameters which determine the manganese and silicon distribution between metal and slag are the process temperature and the chemistry of the slag. It is well known that the manganese content of the slag is decreased if a more basic slag is produced. Equilibrium composition of slag and process temperature are closely related. Increasing process temperature favors slag reduction to give a lower content of manganese in the slag and a higher content of silicon in the metal.

There have been some discussions whether equilibrium is reached or not in the ferromanganese process. Even if equilibrium is not reached, the knowledge of what

equilibrium should be is of interest. Equilibrium relations have previously been established for ternary and quaternary slags containing MnO, SiO_2, CaO and Al_2O_3 and iron-free Mn-Si-C_{sat} alloys with silicon contents ranging from about 1 to 30% [1]. The temperature range was from 1450 to 1600°C. The results gave a complete image of the equilibrium compositions for the system. However, in a real industrial system the alloys will always contain 10-15% Fe, and there will be some magnesia in the slag, coming from manganese ores and added fluxes. In addition, the existence of K_2O and BaO in the slag should not be ignored even if their sum is only 4-7%.

The purpose of this investigation was to study in more detail equilibrium relations relevant to industrial production of HC FeMn in submerged arc furnaces. The range of experimental temperatures was expanded down to 1350°C, which is considered to be in the area of real process temperatures. Industrial slag from Elkem PEA, synthetic multicomponent slags and low-Si (<1%) alloys with 10-14% Fe were the main materials for these experiments.

PROCESS CHEMISTRY

The main constituents of the ferromanganese slags are MnO, SiO_2, CaO, MgO and Al_2O_3. MnO and SiO_2 are partially reduced and the system is characterized by the distribution of Mn and Si between the slag and metal phases. Less SiO_2 is reduced because silica is more stable than MnO. More stable oxides, such as CaO, MgO and Al_2O_3, exist only in the slag phase. Even though these oxides do not take part in the chemical reactions, they are of great importance for the thermodynamic and physical properties of the slag phase. Any iron in the raw materials goes almost completely into the metal phase under the strongly reducing conditions prevailing at normal process temperatures.

The reactions of main interest for the ferromanganese process are the following:

$$(SiO_2) + 2\underline{C} = \underline{Si} + 2CO_{(g)} \quad (1)$$

$$(MnO) + \underline{C} = \underline{Mn} + CO_{(g)} \quad (2)$$

$$(SiO_2) + 2\underline{Mn} = \underline{Si} + 2(MnO) \quad (3)$$

$$(SiO_2) + \underline{Si} = 2SiO_{(g)} \quad (4)$$

$$\underline{Mn} = Mn_{(g)} \quad (5)$$

where parentheses denote the slag phase and underscored the metal phase.

In the temperature range of the process, say below 1450°C, both P_{SiO} and P_{Mn} are quite low and may be neglected. P_{CO} is therefore considered to be equal to the total gas pressure. Graphite is the stable phase coexisting with low-Si, carbon saturated Mn-Fe-Si melts of interest for HC FeMn production. Then the important reactions are (1), (2) and (3). Only two of these reactions are independent. The third will result from a combination of the other two. If only one reaction is brought to equilibrium, the situation is defined as *partial equilibrium* When two partial equilibria are simultaneously attained, *complete equilibrium* is established.

Slag composition triangles are used for graphic representation of partial and complete equilibria in the same diagram. Such a diagram is illustrated in Figure 1. The 'unreducible' oxides such as CaO, MgO and Al_2O_3 *etc*, which may be one single oxide or a combination of several oxides, are represented by the left bottom apex of the diagram. An industrial slag system with any number of unreducible oxides can then be treated in the same way as a ternary slag system because the unreducible oxides will maintain their mutual ratios during the reactions.

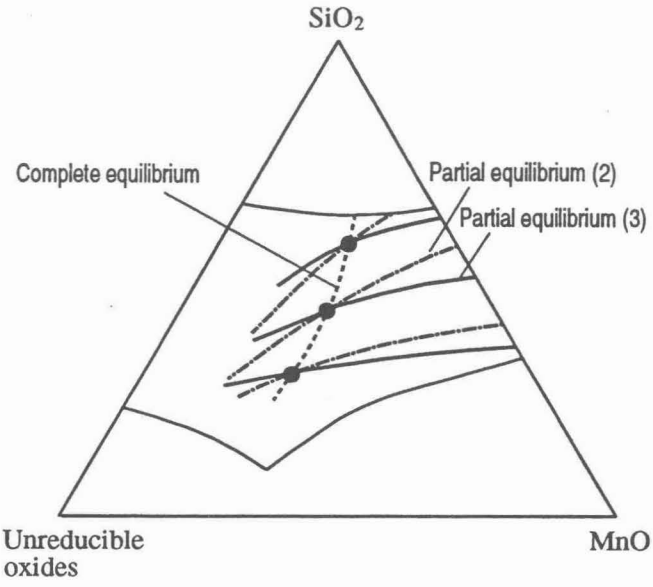

FIG.1. Illustration of partial and complete equilibria in a pseudo-ternary slag diagram.

The composition of slags in equilibrium with a certain alloy can be represented by an iso-activity curve of SiO_2 or MnO with respect to reaction (1) or (2), or an iso-activity ratio a_{MnO}^2/a_{SiO_2} curve with respect to reaction (3), see Figure 1. Two curves referring to different partial equilibria but representing the same alloy composition will intersect in a single point. Connecting such points gives a complete equilibrium line.

To describe both slag and alloy compositions in the same diagram, we need a certain quantity to characterize the equilibrated alloy. According to the phase rule, Mn-Fe-Si-C_{sat} alloys with constant Fe content is monovariant at a given temperature. In order to define it, only one composition variable needs to be designated. The Si content is usually selected as such a variable. Once its value is known, the alloy is exclusively defined.

EXPERIMENTAL

The experimental set up for the equilibrium study is shown schematically in Figure 2. A vertical furnace with a graphite heating element was used. The furnace assembly was designed for fast cooling of the crucible in a water cooling jacket. Detailed description of the experimental apparatus has been given elsewhere [1].

ARG graphite crucibles (18 mm ID) were used for measurement of equilibrium. For partial slag/metal equilibrium, the initial weight ratio of slag/metal was about 0.5, and the metal was fully covered with slag in the crucible. For complete equilibrium only a small amount of slag was added to form a ring of oxide melt along the crucible wall. This exposed both metal and slag to the surrounding atmosphere.

Five-component synthetic [MnO-SiO_2-CaO-Al_2O_3-MgO] slags with weight ratios CaO/Al_2O_3=1.5 and MgO/Al_2O_3=0.8, and carbon saturated metal with low Si (<1%) and 10-

14% Fe were used. Mixtures of reagent grade chemicals in desired ratios were premelted in graphite crucibles. The quality of these chemicals has been mentioned elsewhere [1].

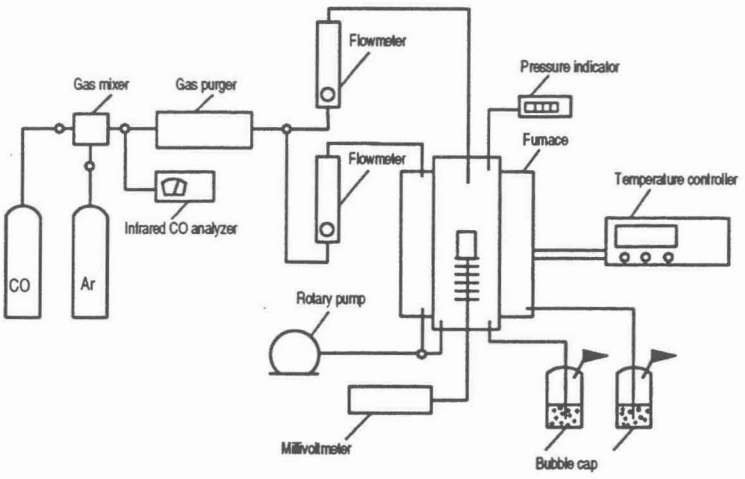

FIG.2. Schematic illustration of the experimental apparatus.

Moreover, industrial HC FeMn metal and slag from Elkem PEA were used as raw materials in the experiments. The composition of the PEA slag is shown in Table 1. The composition of the initial slag was adjusted as desired for each experiment by addition of MnO and SiO_2. However, the ratios between its unreducible oxides were kept unchanged.

TABLE 1 *Major components in industrial high carbon ferromanganese slag (%).*

	MnO	SiO_2	CaO	Al_2O_3	MgO	K_2O	BaO	(C+M)/S
PEA slag	34.7	25.2	16.7	9.6	7.7	2.5	1.6	0.97

All metal samples were analysed by a wet chemical method or the ICP method. Microanalysis, EPMA, was used to examine slag compositions.

The experimental arrangements were somewhat different for partial slag/metal and complete slag/metal/gas equilibrium studies:

Slag/metal equilibrium: 1400°C was chosen for these experiments, which is close to the HC FeMn process temperature. In principle, the gas phase does not participate in establishing partial slag/metal equilibrium. Therefore the ambient atmosphere was often Ar-gas. The holding time was normally 3 hours. 10 grams of metal and 5 grams of slag were used in each crucible.

Slag/metal/gas equilibrium: These experiments were carried out at four different temperatures: 1350, 1400, 1430 and 1450°C. The ambient atmosphere was CO-gas and the holding time between 13 and 24 hours, increasing with decreasing temperature. 12 grams of metal and 1 gram of slag were used in each crucible.

RESULTS AND DISCUSSION

Partial slag/metal equilibrium

Slag/metal equilibrium curves are shown in Figure 3 for synthetic [MnO-SiO_2-CaO-Al_2O_3-MgO] slags in equilibrium with [Mn-Fe(10-14%)-Si-C_{sat}] alloys at 1400°C. Figure 4 gives

slag/metal equilibrium curves at 1400°C for the same alloys in equilibrium with industrial slags. Each curve represents a fixed alloy composition, here characterized by its silicon content. To avoid cluttering due to a large number of experiments (≈100), only accommodated curves are shown.

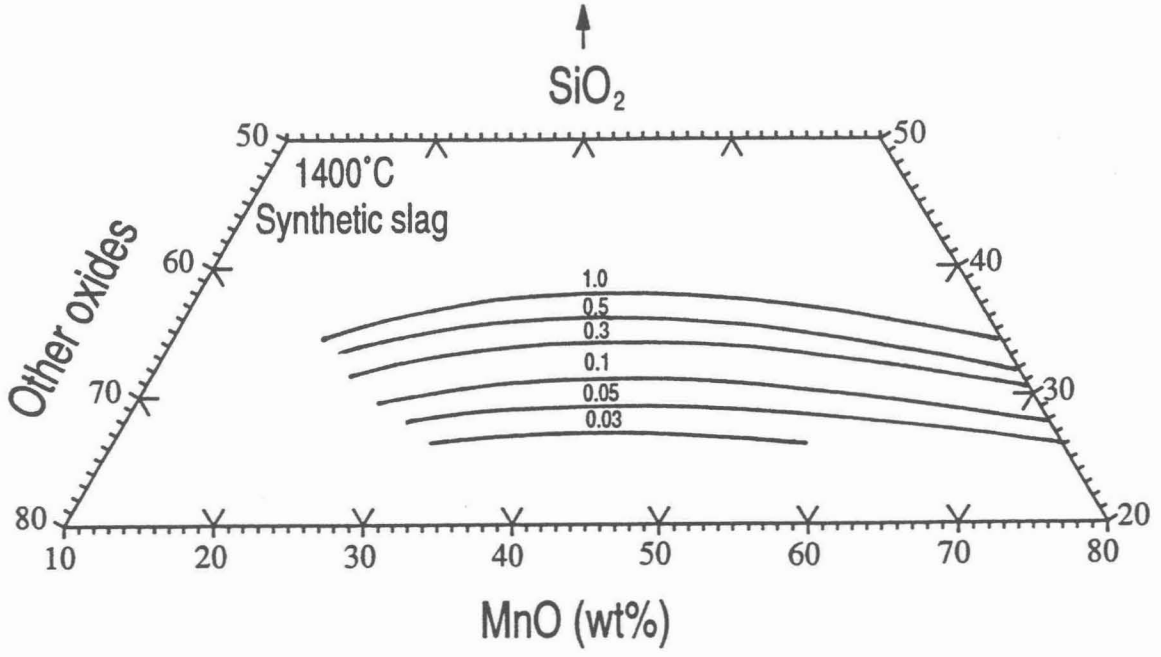

FIG.3. Partial slag/metal equilibria at 1400°C between Mn-Fe(10-14%)-Si-C_{sat} alloys and synthetic [MnO-SiO_2-CaO-Al_2O_3-MgO] slags with fixed wt-ratios CaO/Al_2O_3=1.5 and MgO/Al_2O_3=0.8.

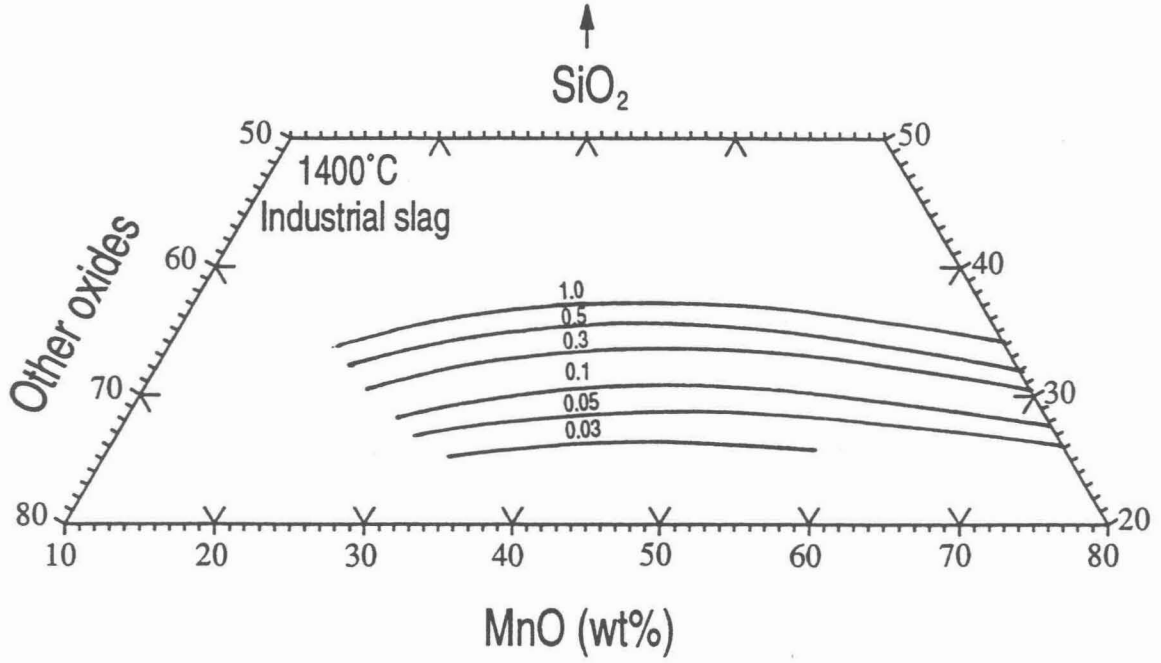

FIG.4. Partial slag/metal equilibria at 1400°C between Mn-Fe(10-14%)-Si-C_{sat} alloys and adjusted industrial PEA slags.

Comparison of related equilibrium curves for synthetic and industrial slags shows that the industrial slag contains less silica, when both slags are equilibrated with the same alloy. As mentioned, a partial slag/metal equilibrium curve is also an iso-activity ratio a^2_{MnO}/a_{SiO_2} line in the slag diagram. The difference between synthetic and industrial slags is caused by the different contents of unreducible oxides which influence the slag structure and thereby the activity relations for MnO and SiO_2. On the other hand, specially for low-silica slags, any factor which affect the melting temperature of the slags will change the 'distribution' of the iso-activity lines of SiO_2. It is well known from related phase diagrams that both Al_2O_3 and alkalies (K_2O) will lower the melting temperature of the slag.

The position of the partial slag/metal equilibrium curves is relatively little dependent on the temperature [2]. According to our experience, every 50 degrees increase in temperature will result in an increase of about 0.1% Si or less in equilibrated low-Si alloys (<1%), assuming a fixed slag composition.

Complete slag/metal/gas equilibrium

Series of experiments were carried out in CO gas atmosphere (P_{CO}=1 atm) at 1350 and 1400°C with both synthetic and industrial slags to measure complete slag/metal/gas equilibrium. The results are shown in Figures 5 and 6 respectively. Results obtained with synthetic slags at 1430 and 1450°C are shown in Figure 7.

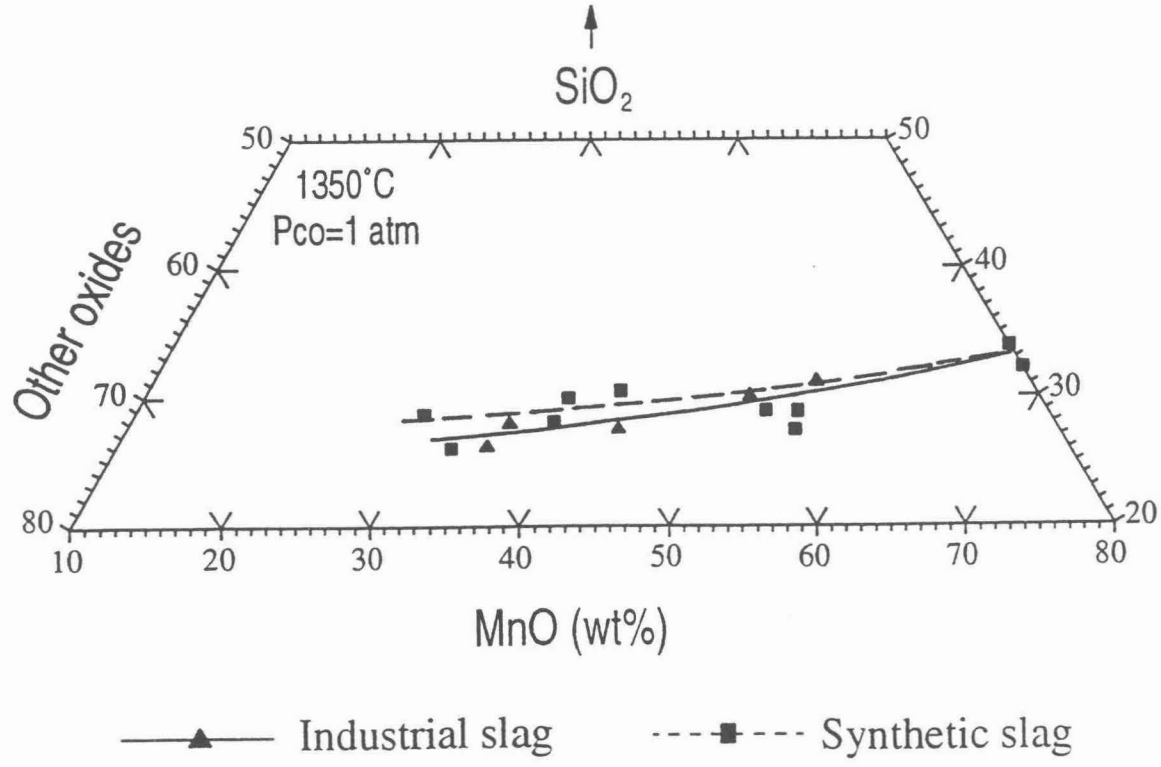

FIG.5. Complete slag/metal/gas equilibria at 1350°C and P_{CO}=1 atm for Mn-Fe(10-14%)-Si-C_{sat} alloys and the two different slag systems. The solid line represents adjusted industrial PEA slags and the dotted line synthetic [MnO-SiO_2-CaO-Al_2O_3-MgO] slags with fixed wt-ratios CaO/Al_2O_3=1.5 and MgO/Al_2O_3=0.8.

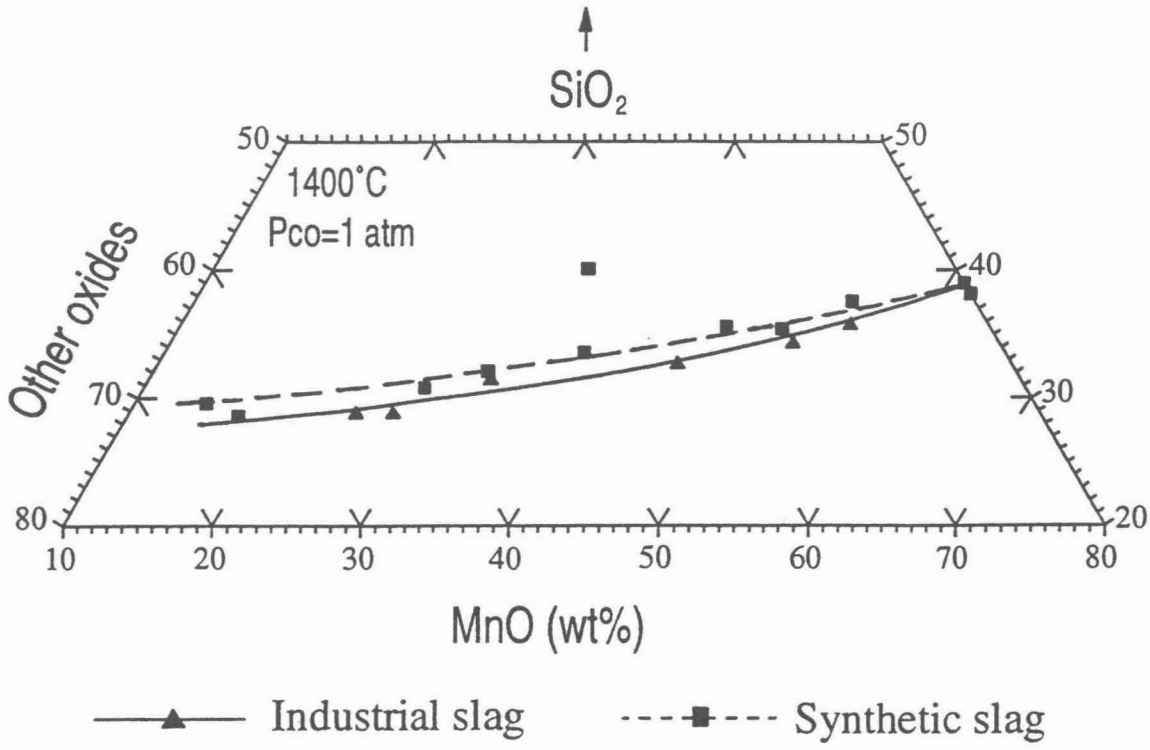

FIG.6. Complete slag/metal/gas equilibria at 1400°C and P_{CO}=1 atm for Mn-Fe(10-14%)-Si-C_{sat} alloys and the two different slag systems. The solid line represents adjusted industrial PEA slags and the dotted line synthetic [MnO-SiO_2-CaO-Al_2O_3-MgO] slags with fixed wt-ratios CaO/Al_2O_3=1.5 and MgO/Al_2O_3=0.8.

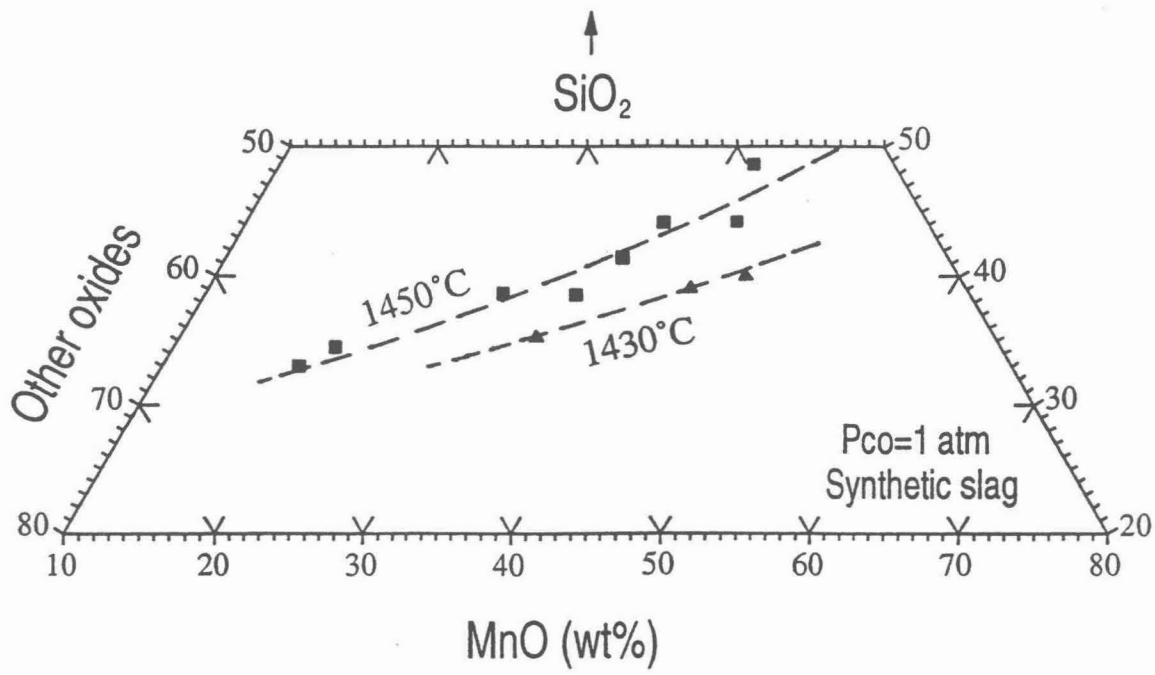

FIG.7. Complete slag/metal/gas equilibria at 1430 and 1450°C and P_{CO}=1 atm, for Mn-Fe(10-14%)-Si-C_{sat} alloys and synthetic [MnO-SiO_2-CaO-Al_2O_3-MgO] slags with fixed wt-ratios CaO/Al_2O_3=1.5 and MgO/Al_2O_3=0.8.

The solid lines in Figures 5 and 6 represent complete equilibrium with industrial slag and the dotted lines with synthetic slag. Equilibrated with the same alloy, the industrial slag contains less silica. Except for a small amount of K_2O and BaO in the industrial slag, the relative amounts of other unreducible oxides are quite similar in the two slag systems. The different compositions will probably not influence the activity coefficients of MnO and SiO_2 that much, but they will result in a lowering of the melting point of the slag. As discussed above, any factor which affect the position of the bottom liquidus line or activity relations of the slags, is considered to give contribution to a change in the position of the equilibrium lines.

In addition to temperature, the CO partial pressure will play an important role in establishing complete equilibrium. The CO pressure will be close to 1 atm for production of HC FeMn in electric furnaces, whereas P_{CO} is estimated to be about 0.35 atm in a blast furnace with normal air blast operation and somewhat higher for O_2 enriched operation. Decreasing the CO pressure by about two thirds is estimated to be equivalent to an increase in temperature by approximately 50-70 degrees.

Effect of process temperature and slag basicity

In addition to chemical equilibrium, the final state and the amounts of slag and metal will depend on the stoichiometry of the production system. Two different reduction paths, representing different slag basicities, are illustrated for industrial slag compositions in Figure 8. Because, practically speaking, only MnO is reduced, a reduction path will follow a straight line originating from the MnO-corner through the initial charge composition. The solid circles mark the initial charge compositions and the squares the final slag compositions.

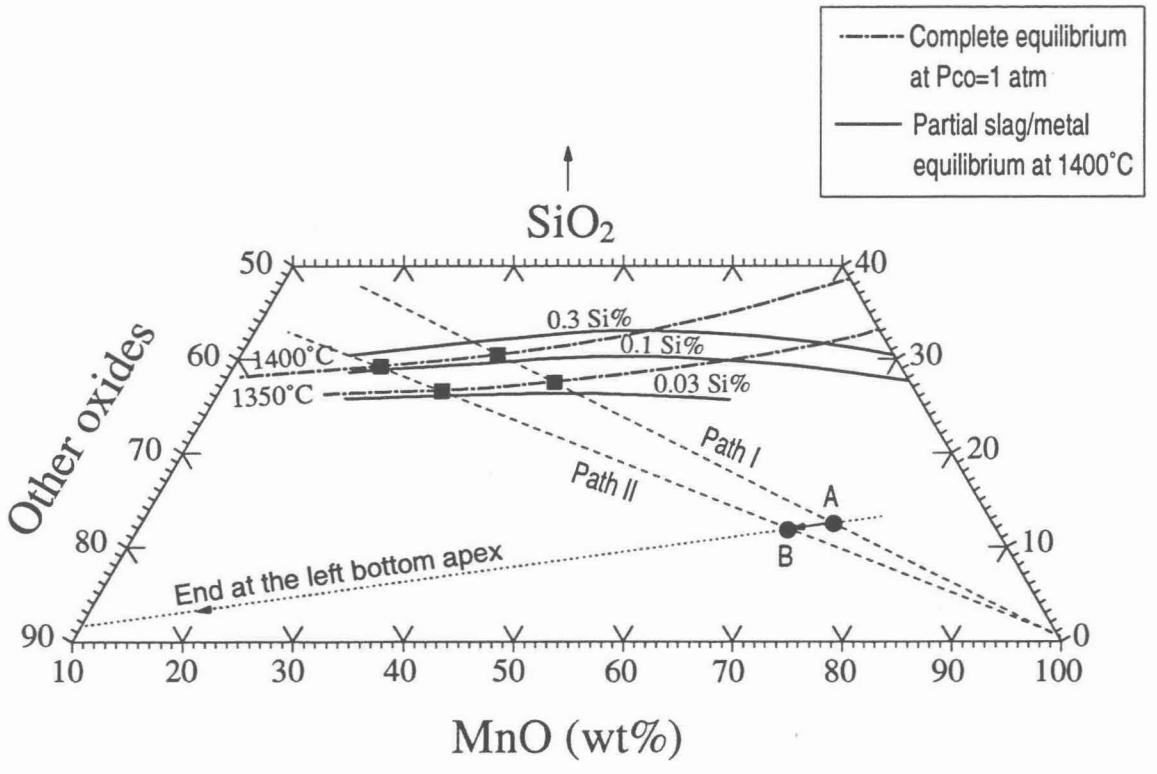

FIG.8. Reduction paths for production of high carbon ferromanganese. Adjusted industrial PEA slags in equilibrium with Mn-Fe(10-14%)-Si-C_{sat} alloys.

The system is fixed when the initial charge composition is given and in addition the process temperature or the final alloy composition. In practice, we are not free to control the process temperature.

Path I in Figure 8 represents slags with a lime basicity, LB=0.75, defined as the wt%-ratio (CaO+MgO)/SiO_2. If the process temperature is 1350° the equilibrium content of MnO in the slag is 40% and the silica content 27.7%. The silicon content of the metal is 0.035%. If the process temperature for some reason or other increases to 1400°C, the equilibrium MnO is reduced to 33.5% and the silica content is raised to 31.5%. The silicon content of the metal should be about 0.15%.

If the slag basicity is increased by addition of flux to the charge mixture, the initial charge composition is changed from circle A to B in Figure 8. The new basicity is LB=1.0. Now the reduction will take place according to path II. Again, if the process temperature is 1350°C, the equilibrium content of MnO in the slag is 30% and the silica content 27%. The silicon content of the metal is 0.03%. If the process temperature for some reason or other increases to 1400°C, the equilibrium MnO is reduced to 23.5% and the silica content is raised to 29.5%. The silicon content of the metal should be about 0.12%.

CONCLUSIONS

A laboratory investigation has been carried out to determine distribution equilibria relevant to industrial production of high carbon ferromanganese in electric submerged arc furnaces. Synthetic slags in the system [MnO-SiO_2-CaO-Al_2O_3-MgO] and industrial ferromanganese slags have been equilibrated with Mn-Fe-Si-C_{sat} alloys at temperatures ranging from 1350 to 1450°C. The results are illustrated in equilibrium diagrams showing partial slag/metal equilibrium lines of constant alloy compositions and complete slag/metal/gas equilibria at P_{CO}=1 atm, giving slag compositions dependent on temperature and alloy composition.

The slags are characterized by the kind and content of unreducible oxides being present, *e.g.*, CaO, MgO, Al_2O_3, BaO, K_2O *etc* and their mutual ratios. These oxides differ noticeably in their effect on the liquidus boundaries of the slag and on the activity coefficients of MnO and SiO_2. This explains the somewhat different results obtained with synthetic and industrial slags.

Process temperature and slag basicity are of vital importance for the equilibrium content of MnO in the slags, but have a relatively small effect on the equilibrium composition (Si-content) of the high carbon ferromanganese alloys.

ACKNOWLEDGMENT

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