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# Phosphide capacities of ferromanganese smelting slags

**Maramba, Blessing**

**2008-04-21T05:28:34Z**
http://hdl.handle.net/10539/4767

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# 1 INTRODUCTION

## 1.1 Manganese Ore Production in South Africa

Manganese ore production in South Africa is estimated to be the second largest in the world after that of the former USSR. The deposits of manganese ores in South Africa are found in the Northern Cape province near Postmasburg and at Kuruman and in Gauteng (Transvaal) near Krugersdorp. The major deposits in the Northern Cape are the Hotazel, Wessel and Mamatwan ores. The Mamatwan deposit has the largest ore reserves. Manganese ore minerals occur in several forms as oxides, silicates and carbonates. Typical ore minerals are braunite, braunite II, bixbyite, hausmannite and manganite[1,2,3].

## 1.2 Uses of Manganese and Ferromanganese Production

Manganese metal is readily available at a low price and is mostly used in the form of ferromanganese in steelmaking. The major use of manganese is as an alloying addition to steel, where it acts as a desulphuriser and a deoxidizer, a very important function in steelmaking. Manganese also provides improved rolling and forging characteristics, improved strength, toughness, hardenability and wear resistance by suppressing the hardening transformation of steel on quenching. It is also added to Al, Ag, Mg, Ni, Ti and Zn alloys as an alloying element. Manganese is added in the form of its ore during ironmaking or as ferromanganese alloy at the steelmaking stage. There are four main types of ferromanganese alloys; high carbon ferromanganese (HC-FeMn), ferromanganese silicide (FeMnSi), medium carbon ferromanganese (MC-FeMn) and low carbon ferromanganese (LC-FeMn). Table 1.1[1] gives the typical composition limits for the ferromanganese alloy grades. The major producers of high carbon ferromanganese alloy are the USA, the former USSR, Japan and South Africa[1]. The most commonly used ferromanganese alloy is high carbon ferromanganese (HC-FeMn) as an additive to steel. Ferromanganese silicide

(FeMnSi), medium carbon ferromanganese (MC–FeMn) and low carbon ferromanganese (LC–FeMn) constitute a fair proportion of alloying additives used to produce steel where low carbon is required.

**Table 1.1: The typical composition of Ferromanganese alloys[1]**

| ALLOY | COMPOSITION (wt. %) | | | |
|---|---|---|---|---|
| | **Mn** | **Fe** | **Si** | **C** |
| **High Carbon** | 74 – 80 | 12.2 | 0.1 – 0.8 | 6 – 7 |
| **Ferromanganese Silicide** | 65 - 75 | Balance | 15 – 32 | 0.4 – 2.3 |
| **Medium Carbon** | 80 - 85 | 11 – 18 | 1 – 2 | 1 – 2 |
| **Low Carbon** | 80 - 85 | 13.5 – 18.5 | 1.0 | 0.5 |

HC-FeMn is produced both in the blast furnace and in the submerged arc-furnace with the latter being more popular where low cost electric power is available. The electric arc furnace has advantages over the blast furnace, which are:

i. Easy and more flexible operation
ii. Low coke requirements
iii. Production of pure alloys with low contamination
iv. Consumption of lower grade ores and inferior reducing agents
v. Overall recovery of manganese on a ferromanganese smelter plant is higher when slag produced in the submerged arc furnace is reused to manufacture ferromanganese silicide

When HC-FeMn is produced in the electric arc furnace, two processes can be employed:

i) The rich slag practice and
ii) The discard slag practice

In the discard slag practice, the manganese content of the final slag is low (< 20% MnO) and thus these slags are discarded. In the rich slag practice, the slags which have at least 25% MnO content are used as raw material for the production of

ferromanganese silicide alloy. Total recovery of manganese is higher with the rich slag practice combined with production of ferromanganese silicide which lowers the production costs. The main constituents of HC-FeMn slags are MnO, MgO, CaO, $Al_2O_3$ and $SiO_2$. The slags contain between 15-20% MnO- for discard slags and between 30-45% MnO-for rich slags, between 10 - 25% MgO, between 10-45% CaO, between 20-40% $SiO_2$ and up to 25% $Al_2O_3$[4].

**Table 1.2: The composition ranges for the manganese oxide slags[2]**

| SLAG TYPE | COMPOSITION RANGE | | | |
|---|---|---|---|---|
| | **MnO** | **CaO** | **MgO** | **$SiO_2$** |
| **Lime – Ore melt** | 50 – 55 | 35 – 40 | 5 | 5 |
| **High grade Mn – Oxide slag** | 30 – 35 | 30 – 35 | 5 | 25 - 30 |
| **Low grade Mn – Oxide slag** | 20 – 25 | 25 – 30 | 5 | 35 |
| **Discard slag** | <15 | 30 – 35 | 5 | 40 – 55 |

## 1.3 Ferroalloy Usage in Steelmaking and the Associated Sulphur and Phosphorus Problems

The steelmaking industry is the major consumer of ferroalloys. The demand on steelmakers to improve the speed of working, yield and consistency of product quality has resulted in increased attention to the accuracy of analysis and quality of ferroalloys supplied. The consistency of analysis is important for easing the bulk handling of materials and for steelmaking quality control. The use of high sulphur and/ or high phosphorus ferroalloys requires extra time and special procedures to remove these impurities. In steelmaking it is still difficult to remove both sulphur and phosphorus from melts even when using the recently developed converters such as the Creusote Loire Uddeholm (CLU) converter. Present refining processes based on oxidation cannot achieve low phosphorus levels in chromium containing steels since

the chemical affinity of oxygen to phosphorus is weaker than that to chromium. High sulphur and phosphorus containing alloying agents, including ferroalloys cannot be used for high quality steel production processes because very low sulphur and phosphorus levels in these steels are a prerequisite for improved physical properties. Sulphur in the steel should be less than 0.01% (0.006 - 0.01%) because the sulphide and oxide inclusions adversely affect the mechanical properties of steel products. On the other hand for ferritic stainless steel with superior stress corrosion resistance the phosphorus level must be below 0.005% compared to the ordinary concentration of 0.01 to 0.03%[5].

The presence of sulphur and phosphorus lowers the quality of steel produced causing it to exhibit poor physical properties in the rolling and forming processes. In the steelmaking process, to ensure ultra low levels of sulphur and phosphorus in the final steel products all the input materials should have very little quantities of these elements. For the steel producers to meet their product chemical specification they use strict quality control methods on procurement of input materials including ferroalloy products. Steelmakers charge suppliers penalties in the form of discounts when critical elements agreed in the sales contract are out of specification. Elements normally included in the alloy specification section of such sales contracts are S, P, Mn, C and Si.

One of the major problems in ferroalloy production is the inconsistency of the chemical composition of ores used in terms of S, P, $Cr_2O_3$, MnO and FeO contents. Because of this problem, concerted effort is required to produce ferroalloy products of consistent quality especially on S and P content. The control of sulphur and phosphorus is considered in terms of:

i. Partitioning of sulphur and phosphorus in gaseous compounds and sulphur and phosphorus in solution at the gas-liquid interface.
ii. Partitioning of sulphur and phosphorus between the slag and metal phases at the slag-metal interface.

Of the two equilibrium processes, sulphur and phosphorus control is mainly achieved by the slag-metal partitioning process (ii).

The use of high-phosphorus and high-sulphur reductants and ores due to the depletion of good quality materials makes control of these elements even more difficult. There are limited ways of controlling the sulphur and phosphorus in the final ferroalloy, which are:

i) The use of low sulphur and phosphorus reductants and ores. However, this option is limited due to the depletion of good reductants and ores. Good quality ores and reductants are available at very high prices, thereby forcing ferroalloy producers to consume less expensive high-sulphur/ high-phosphorus materials.

ii) Increasing the level of carbon and silicon content in the alloy. This is also limited by the specifications of C and Si required in the final alloy.

iii) Down-stream refinement of ferroalloys can be conducted but this will result in increased production costs of the final product.

iv) The most feasible option to achieve low sulphur and phosphorus levels in ferroalloy production is to remove these elements during the primary smelting process by operating with an optimised slag composition (basicity) that will ensure maximum deportment of sulphur or phosphorus from the metal phase to the slag phase. Due to low costs involved, effective desulphurization and dephosphorisation in the primary smelting process is always lucrative.

Dephosphorisation of steel has been traditionally carried out under oxidizing conditions using basic slags. However, this conventional technique is not applicable to alloys which contain a large amount of elements less noble than iron such as chromium and manganese. A new dephosphorisation technique to serve this purpose was proposed in which dephosphorisation by $CaO\text{-}CaF_2$ or $CaC\text{-}CaF_2$ fluxes are applied. Because the underlying knowledge of dephosphorisation technique is still wanted, more research work needs to be conducted in this field.

## 1.4 Project Motivation

There has been a lot of work on ferroalloy desulphurisation and dephosphorisation in ladles outside the furnace (ladle treatment) but less work has been done to find ways of improving these processes inside the furnace, for example the significant influence of the oxygen partial pressure ($Po_2$) and temperature on dephosphorisation proved by various researchers has been neglected. As real prices of ferroalloys continue to fall in this highly competitive industry, new technologies must continually be developed for the industry to remain profitable and to ensure that raw materials feeding the steel industry and related industries are produced cost effectively thereby securing their future. For example the prices for HC-FeCr fell by 57% between 1970 and 1996[(6)]. With production costs escalating and selling prices on a downward trend due to a glut on the market, ferroalloy producers cannot afford to sell their products at discounted prices due to non-conformance because of high sulphur or phosphorus content.

This project was initiated to focus on the high phosphorus problem affecting ferromanganese producers and the need to satisfy steelmakers' requirements at reduced production costs and thus help both the ferromanganese smelters and steelmakers to maximise profit margins. The scope of this research work involved the determination through analysis of the equilibrium slag and metal phase compositions, factors that affect the equilibrium distribution ratio of phosphorus ($L_P$) between the two phases in high carbon ferromanganese smelting process. The slag phosphide capacity ($C_P^{3-}$) values were calculated from the equilibrium phosphorus distribution ratio ($L_P$) results and the factors affecting the slag phosphide capacities were established. The calculated slag phosphide capacities ($C_P^{3-}$) indicate the dephosphorisation ability or power of the respective slags. Ferroalloy smelters can use the results on $L_P$ and $C_P^{3-}$ to optimize their smelting slag compositions. It is hoped that knowledge gained from this project on optimisation of phosphide capacities of smelting slags will help ferroalloy producers to maximise partitioning of phosphorus

to the slag phase and minimise the amount of phosphorus reporting in the final alloy product. This will help to improve ferroalloy products conformance rate in terms of phosphorus and at the same time reduce the cost of down stream refining processes to remove this element. With this development ferromanganese producers will be able to realise the full value of their products, as they will not be penalized for phosphorus nonconformance. Adequate knowledge of the reaction equilibrium is a prerequisite to a better understanding of the smelting operations and to the development of methods of controlling phosphorus content in the alloy. In the development of ferroalloy smelting slags, slag phosphide capacity ($C_P^{3-}$) is a key property that must be taken into account. The $Cp^{3-}$ data available are still too few to meet the technological demands of the metallurgical industry.

The objective of this MSc research project was to determine the effect of slag and metal phase composition as well as the oxygen partial pressure ($Po_2$) on the equilibrium phosphorus distribution ratio ($L_P$) between the slag and metal phases and hence their effect on the phosphide capacities ($C_P^{3-}$) of ferromanganese smelting slags. The investigations involved equilibrating the slag and metal phases of varying composition in a graphite crucible under two different partial pressures of oxygen ($Po_2$).