

Thermodynamic Considerations in the Production of Bulk Ferro Alloys (Fe-Mn, Fe-Cr and Fe-Si)

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1. Introduction

The above mentioned ferro alloys are produced commercially by reduction smelting of their oxide minerals with coke or charcoal in a submerged arc furnace and, to a lesser extent, by a metallic reductant such as aluminium. In general, the overall reduction reactions are highly endothermic, thus, requiring large thermal energy inputs.

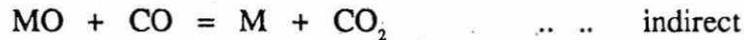
In this paper, the thermodynamic principles underlining reduction smelting of oxides are discussed with the help of free energy-temperature (Ellingham) diagram with a focus on the role of direct reduction, the smelting temperatures required for a given oxide mineral, the thermal energy requirements, the suitability of carbon as reductant, the alloy grade and impurity levels, the slag-metal equilibria and the formation of carbides.

2. Ellingham Diagram

Figure 1 is an Ellingham diagram which shows the standard Gibbs energy of formation of various oxides as a function of temperature, with respect to one mole of oxygen gas [1].

- a) When so formed, the more stable oxides appear on the lower part of the diagram in the order FeO, P_4O_{10} , Cr_2O_3 , MnO, SiO_2 , Al_2O_3 , MgO and CaO. Thus, if conditions are made favourable for the reduction of MnO, then the oxides of iron, phosphorus and chromium will also be reduced.
- b) For a given oxide mineral, the oxides below it on the Ellingham diagram are stabler and therefore, the elements of the latter (such as Al, Si and Ca) could readily act as reducing agents. This principle is utilized in metallothermic reduction processes.
- c) Whereas most lines in the Ellingham diagram slope upward, the CO line slopes downward because of entropy considerations. Thus, there is a temperature above which CO is more stable than the oxide mineral to be reduced. However, the actual operation may have to be conducted at temperatures higher than the temperature of intersection between MO and CO lines in order to enhance the reaction rates and facilitate metal-slag separation.
- d) All the lines plotted in the Ellingham diagram correspond to standard states (pure condensed substances). For impure oxides, the line would rotate clockwise (with respect to zero temperature) indicating greater ease of formation; conversely, for impure elements, the lines would rotate anti-clockwise.

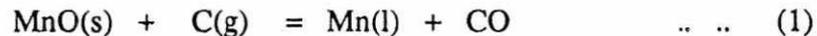
3. Direct vs Indirect Reduction



The indirect reduction is more exothermic (releases an extra 290 kJ/g.mole) relative to the direct reduction. Consequently, the energy efficiency of a process could be significantly enhanced by utilizing the CO formed by direct reduction for subsequent indirect reduction as accomplished in the iron-making blast furnace. However, the latter calls for a long stack and elaborate burden preparation so that descending charge could be preheated and reduced indirectly by the upward moving hot gases before getting directly reduced. However, the relatively small scale of ferro-alloy operations does not permit high shaft furnaces and consequently, most of the CO generated by direct reduction leaves the furnace without being utilized in any indirect reduction reaction.

4. Smelting Temperature

The final products are molten alloy and slag. The alloy composition should be within the specified/desired limits and their temperatures should be high enough (~100°C above the liquidus) to impart adequate fluidity for good separation. In the case of ferro-manganese, the equilibrium pressure of CO produced from the reaction.



$$\Delta G^0_1 = 290,350 - 173.25 T \text{ J/g.mole} \quad [2]$$

reaches 1 atm at about 1400°C (corresponding to the intersection of MnO and CO lines on the Ellingham diagram). This temperature allows good slag-metal separation and hence is the normal smelting temperature.

It should be noted, however, that even if an equilibrium pressure of 1 atm for CO could be achieved at somewhat low temperatures, the need for a clean metal-slag separation (if a slag is formed) may necessitate high smelting temperatures.

5. Thermal Energy Requirements

As stated earlier, production of ferro-alloys is generally an energy intensive operation mainly due to the endothermic reduction reactions as shown below:

	<u>Enthalpy Change ΔH^0_{298}</u> <u>kJ/g.Mol</u>	<u>Ref.[2-3]</u> <u>kWh/kg-metal</u>	
$\text{MnO}_2(\text{s}) + 2 \text{C} = \text{Mn}(\text{s}) + 2 \text{CO}$	300.0	1.52 (2)
$\text{Cr}_2\text{O}_3(\text{s}) + 3 \text{C} = 2\text{Cr}(\text{s}) + 3 \text{CO}$	803.1	2.15 (3)
$\text{SiO}_2(\text{s}) + 2 \text{C} = \text{Si}(\text{s}) + 2 \text{CO}$	689.8	6.82 (4)

Additional heat must be supplied for melting the metal and slag and raising their temperatures (for clean separation) as well as the gas temperature to the requisite values. Further, heat losses to surroundings and cooling water must be provided for. As a result, the heat requirement increases significantly; for manganese it was estimated to be 2.45 kWh/kg. (see Appendix A). Because of such large thermal requirements, it is a standard practice to produce ferro-alloys in submerged arc furnaces, wherein the arc provides the necessary heat thus maintaining the reaction zone at suitably high temperatures. The final state of the metal-slag bath is governed by the hearth temperature which should be reasonably high to effect metal-slag separation.

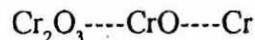
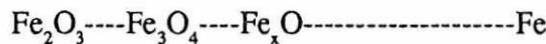
6. Alloys Grade and Impurity Levels

The Ellingham diagram suggests that all the oxides of iron and phosphorus would get reduced during reduction smelting of MnO , Cr_2O_3 as well as SiO_2 . As a result, the overall grade of the molten alloy is determined by the extent of oxide reduction and the burden of iron oxides and other easy-to-reduce oxides in the charge. The slag composition is determined by the total gangue from ore, fuel, flux, etc., besides the unreacted mineral oxide.

If the alloy specifications call for a maximum limit on phosphorous content, it must be adjusted in the burden itself (such as through mineral beneficiation) as there are no commercially established technologies available to remove phosphorous from the molten ferro alloys [4].

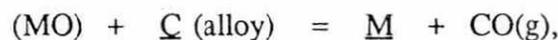
7. Slag Metal Equilibria

The reduction of oxide minerals of iron, manganese and chromium takes place in stages as shown below :



The reduction of Mn ores upto the stage of Mn_3O_4 occurs by thermal dissociation and indirect reduction (like that of iron ores to Fe_3O_4) and thereafter, by direct reduction.

In the last stage of direct reduction of oxides, the slag-metal phases are believed to approach thermodynamic equilibrium as follows :

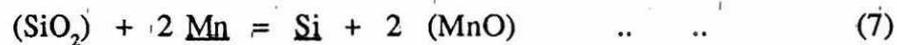
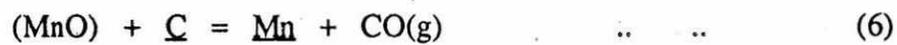
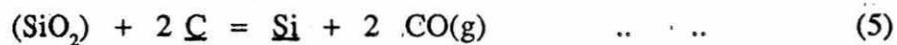


$$\Delta G^0 = -RT \ln K = -RT \ln [a_M p_{CO} / (a_{MO} \cdot a_C)]$$

Where parentheses for MO indicate the slag phase and underline for C, M indicates the liquid alloy phase. Thus, a knowledge of the equilibrium constant K, through standard Gibbs energy data, is useful in determining the ways to promote a reaction in the desired direction. Thanks to the extensive thermodynamic studies done on liquid iron solutions and oxide slags [5-7], the activities of various components can be estimated and used to assess the extent of equilibrium achieved in a given process.

The multiphase equilibria such as those pertaining to ferro alloy processes have been analyzed by several investigators [8-11] with the help of the phase rule and Gibbs energy minimising techniques for predicting the distribution of a metal between the slag and alloy phases for different charge compositions and operating conditions of temperature and pressure.

In a recent study, Ding and Olsen [12] have analyzed the silico manganese process by considering the main reactions as follows :



The carbothermic reduction of silica in slag (reaction 5) being very sluggish, they used only reactions (6) and (7) for describing the equilibria as shown in Figure 2 which indicates that, for a given alloy composition (%Si), the slag composition will shift to a lower (MnO) content in slag with increase in temperature. Another advantage of increasing the temperature will be to improve the slag/metal ratio significantly.

The slag produced in ferro-alloy process usually contains appreciable amounts of the valuable metal as shown below [13].

Alloy	Mn	Cr	C	Si
High C Ferro Chrome	-	65.5	7.0	4.5
Med C Ferro Manganese	72	-	2.0	0.8

	Slag Composition						Slag/ Metal Ratio
	MnO	Cr ₂ O ₃	CaO	MgO	SiO ₂	Al ₂ O ₃	
High C FeCr	-	6.2	-	37.2	30.6	26.0	0.83
Med C FeMn	14	-	38	5.0	28.0	3.0	?

If the metal loss is considered excessive, such as in the case of medium carbon ferro-manganese shown above, and if the process economics warrants then, in the opinion of this author, a proper control of slag composition should help lower the metal loss. In the case of ferromanganese, a slight increase in slag basicity will tend to increase the activity of MnO in slag as shown in Figure 3, thereby lowering the (MnO) content. Furthermore, a higher basicity should also help lower the phosphorus content of the alloy.

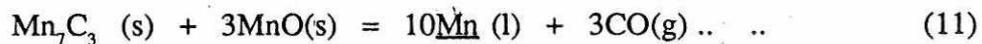
8. Carbide Formation

From an economic viewpoint, coke-carbon is considered a preferred reductant. However, the ferro-alloy thus produced contains high levels of carbon promoting formation (precipitation) of metal-carbides such as :



These carbides are refractory materials and the low temperature at the hearth bottom is likely to help precipitate Cr_7C_3 and SiC which may cause furnace bottom build up. It is to be noted that in the case of manganese and chromium, the equilibrium carbide phase after solidification will be mostly M_{23}C_6 ; at the smelting temperatures, however, the first carbide to precipitate is likely to be Mn_7C_3 or Cr_7C_3 [14].

From a thermodynamic view point, it should be possible to reduce these carbides and recover the metal into the alloy by reacting the former with metal oxide at relatively high temperatures, as shown below :



$$\Delta G_{11}^0 = + 937215 - 461.5 T, \text{ J/g. mole [2]}$$

For a molten bath saturated with Mn_7C_3 ($a_{\text{Mn}_7\text{C}_3} = 1$) and in contact with solid MnO, with $P_{\text{CO}} = 1$ atm and taking $a_{\text{Mn}} = 0.3$ for a 75% Mn in ferromanganese alloys [15], one finds that the above reaction becomes feasible (-ve Gibbs energy) at about 1400°C.

Similarly, for



$$\Delta G_{12}^0 = 941,192 - 442.1 T, \text{ J/g. mole [2]}$$

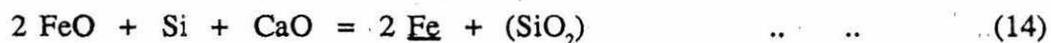
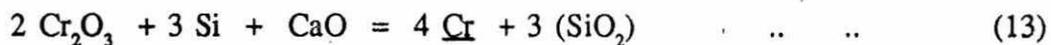
Using $a_{\text{SiC}} = 1$, $a_{\text{SiO}_2} = 1$, $P_{\text{CO}} = 1$ atm and $a_{\text{Si}} = 0.82$ for a 75% Si in ferrosilicon [2], it is found that ΔG equals zero at 1830°C. Thus, at temperatures above 1830°C, the above reaction will become feasible promoting dissolution of silicon carbide into the Fe-Si alloy.

9. Production of low Carbon Ferro Alloys

Low carbon alloys are usually produced by aluminothermic or silicothermic reduction smelting of the mineral and, to a smaller extent (for special purposes), by refining of a high carbon liquid alloy through oxidation (of carbon) by fluxes and/or oxygen, as illustrated below for the case of ferro chrome:

i) Silicothermic Reduction of Chrome Ore :

Using ferrochromic silicon (Si: 46-50%, C < 0.1%) as the reductant and lime as flux, low carbon ferro chrome can be and is produced by smelting of chrome ore as per the following reactions.



For given compositions of the chrome ore, flux and ferrochromic silicon [16], one can calculate charge requirements and product chemistries using mass balance equations along with simplifying assumptions as follows:

Chrome ore : (Cr₂O₃ : 53, FeO : 14, SiO₂ : 7, MgO : 12, Al₂O₃ : 11)
 Fe-Cr-Si : (Si : 52, Cr : 31, Fe : 16.9, C : 0.02)
 Lime : (CaO : 90)
 Alloy : (0.06% C, 0.70 Si) . . . aim composition

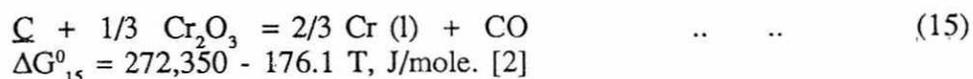
Assume : Cr recovery : 82%, Fe recovery : 90%
 Si efficiency : 70%, Slag basicity (CaO + MgO)/ SiO₂ = 2.2

For a 100 kg. of the chrome in the charge, mass balance for Si and CaO yields :

Alloy : 59.2 kg (Cr : 71.1, Fe : 28.0, Si : 0.7, C : 0.06)

Slag : 184.2 kg (SiO₂ : 27.5, CaO : 54.04, MgO : 6.5,
 Al₂O₃ : 5.98, Cr₂O₃ : 5.18, FeO : 0.76)

ii) Oxidation Refining by Oxide Fluxes/Oxygen.



To attain very low carbon levels in the alloy melt, it is necessary to increase temperatures (to ~ 1800°C) and/or reduce P_{CO} using vacuum.

10. Summary

This paper showed that a better understanding of the principles of thermodynamics and their application to ferro alloys processes can be very useful in :

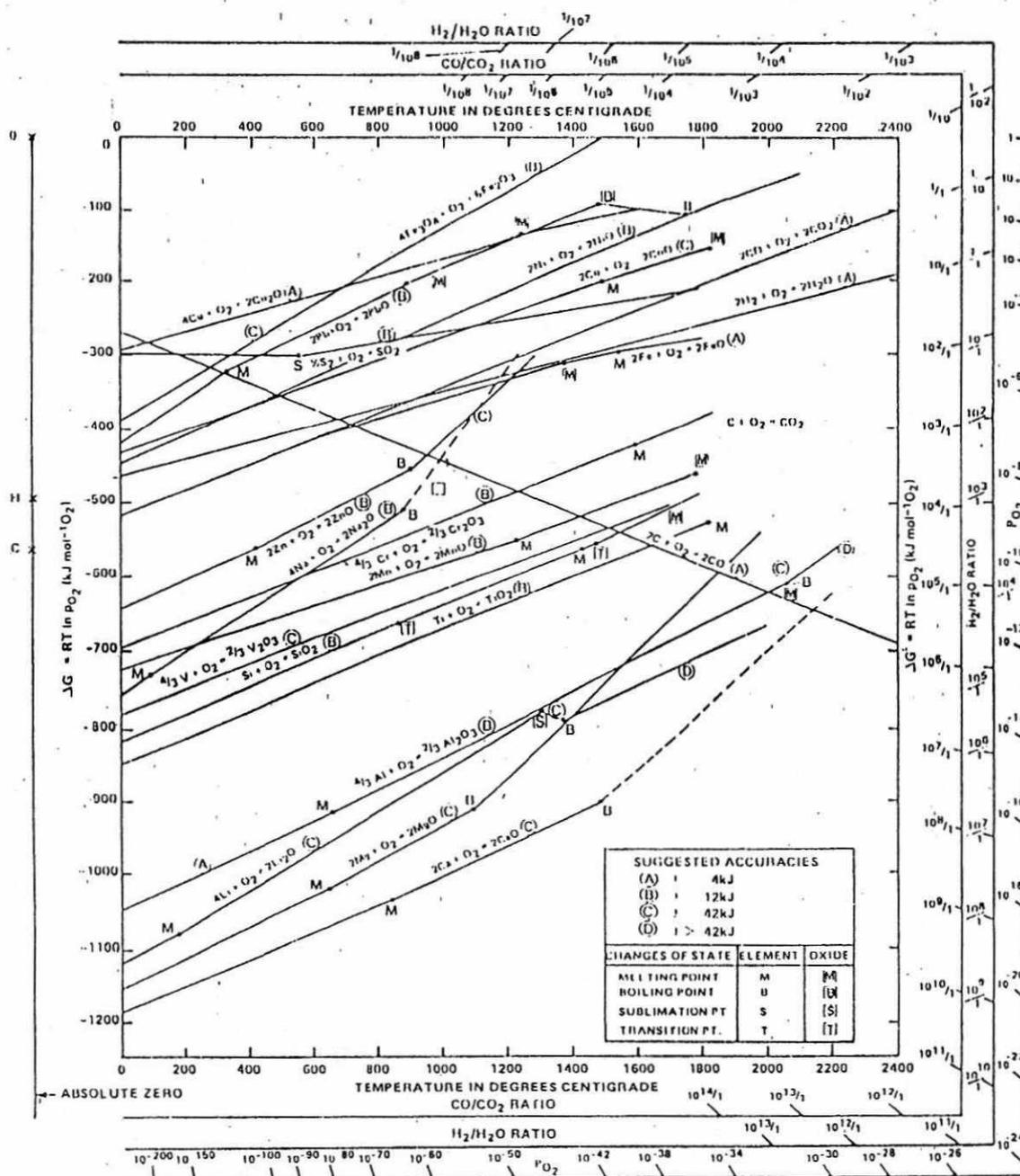
- promoting a smelting reaction in the desired direction,
- lowering metal losses into the slag phase
- improving the slag/metal volume
- lowering the impurity levels in the alloy, and
- preventing the formation of unwanted carbides.

There is a greater need to utilize such concepts for optimizing the furnace performance from a thermochemical standpoint.

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Figure 1. The standard Gibbs energies of formation of metal oxides as a function of temperature [1]



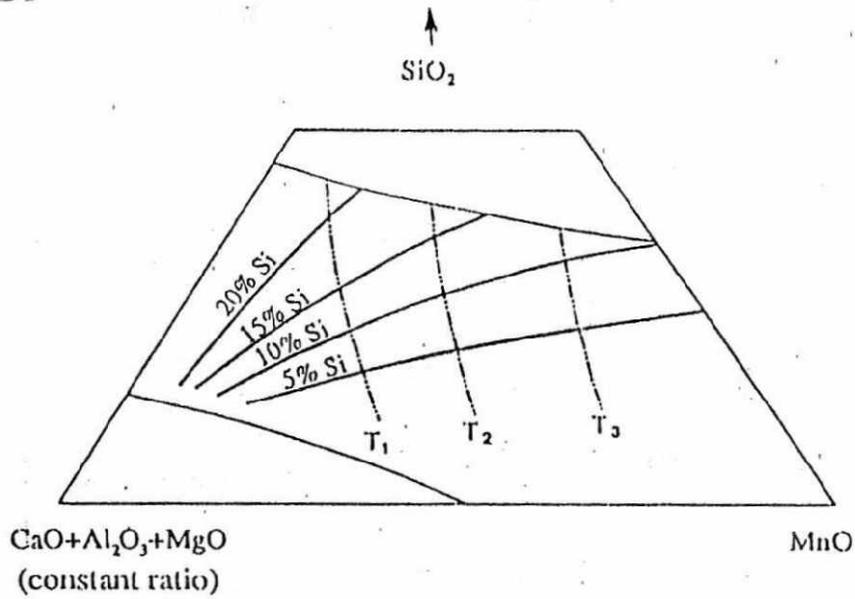
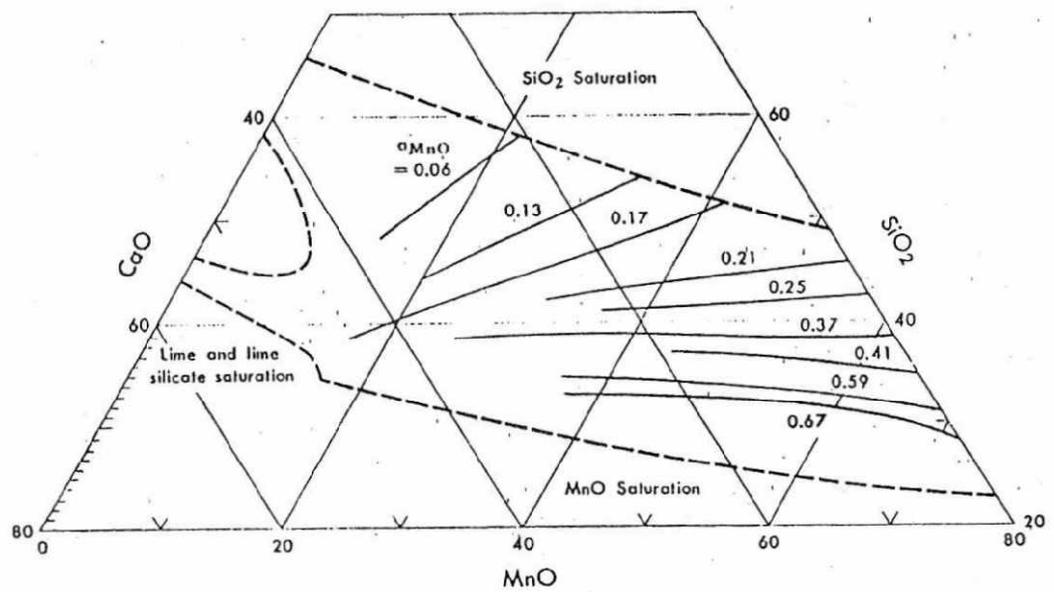


Figure 2. Slag-metal equilibria [reaction 7] at various silicon contents in the Si-Mn alloy along the solid lines [12]. Complete equilibria are drawn by dotted lines.

Figure 3. Iso-activity lines for MnO in the CaO-MnO-SiO₂ system at 1500°C [2].



(b) Compositions: w/o.

Standard state
MnO: Pure solid MnO in equilibrium with melt.

Appendix - A

Thermal Requirements for Smelting Manganese Ore

The overall smelting reaction can be represented as :

$$\text{MnO}_2(\text{s}) + 2 \text{C} + \text{Fluxes} = \text{Mn} (\text{l}) + 2 \text{CO} + \text{slag} (\text{l}) \dots (\text{A})$$

Assuming

Metal and slag temperature	:	1500°C
Gas exit temperature	:	1000°C
Slag volume	:	0.5 kg/metal

and using pertinent thermodynamic data

ΔH_{298}^0 for MnO_2	:	-521,050 J/g. mole	(a)
ΔH_{298}^0 for CO	:	-110,530 "	(b)
Heat content of Mn(l)	:	+ 75000 "	(c)
Heat content of CO	:	+ 31,000 "	(d)
Heat content of Slag	:	+ 1,780,000 J/kg.	(e)

The enthalpy change for reaction (A) is obtained as

$$\begin{aligned} \Delta H_A^0 &= -H_a + 2 H_b + H_c + 2H_d + H_e \\ &= [521,050 + 2 (-110,530) + 75,000 + 2 \times 31,000] \text{ J}/(0.055\text{kg Mn}) \\ &\quad + (1,780,000)/2 \text{ J/kg Mn.} \\ &= 8835 \text{ kJ/kg Mn} \\ &= 2.45 \text{ kWh/kg Mn.} \end{aligned}$$