DEOXIDISING OF STEEL

METALLURGICAL TREATMENTS

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CONTENT

1.   INTRODUCTION

Deoxidation is the removal of excess oxygen from molten metal.

Deoxidation is a metallurgical treatment for melted steel in order to improve the quality of the liquid metal to ensure that the solidified metal will meet all requirements.

The procedure involves adding materials with a high affinity for oxygen, the oxides of which are either gaseous or readily form slag.

The deoxidation of steel is usually performed by adding Mn, Si and Al, or rarely by adding Cr, V, Ti, Zr and B.

The deoxidation of molten steel exhibits a paradox. By increasing the concentration of deoxidizer in the melt over some critical value reoxidation of steel takes place.
A few examples of the reoxidation of steel by adding the usual deoxidizers (Si and Al) are examined in this article.

Deoxidation is the last stage in steelmaking.

2.   BOF STEEL

In the Basic Oxygen Furnace (BOF) and other similar steelmaking practices the steel bath as the time of tapping contains 400 to 800 ppm activity of oxygen.

Deoxidation is carried out during tapping by adding into the tap-ladle appropriate amounts of ferromanganese, ferrosilicon and/or aluminum or other special deoxidizers. If at the end of the blow the carbon content of the steel is below specifications, the metal is also recarburized in the ladle. However, large additions in the ladle are undesirable, because of the adverse effect on the temperature of the metal.

Eight typical conditions of commercial ingots, cast in identical bottle-top molds, in relation to the degree of suppression of gas evolution are shown schematically in Figure 1.

The dotted line indicates the height to which the steel originally was poured in each ingot mold. Depending on the carbon content and particularly of the oxygen content, the ingot structures range from that of a fully killed or dead-killed ingot N°1 to that of a violently rimmed ingot N°8. Included in the series are indicated in figure 1 i.e. killed steel N°1, semi-killed steel N°2, capped steel N°5, and rimmed steel N°7.

Figure 1: Series of typical ingot structures
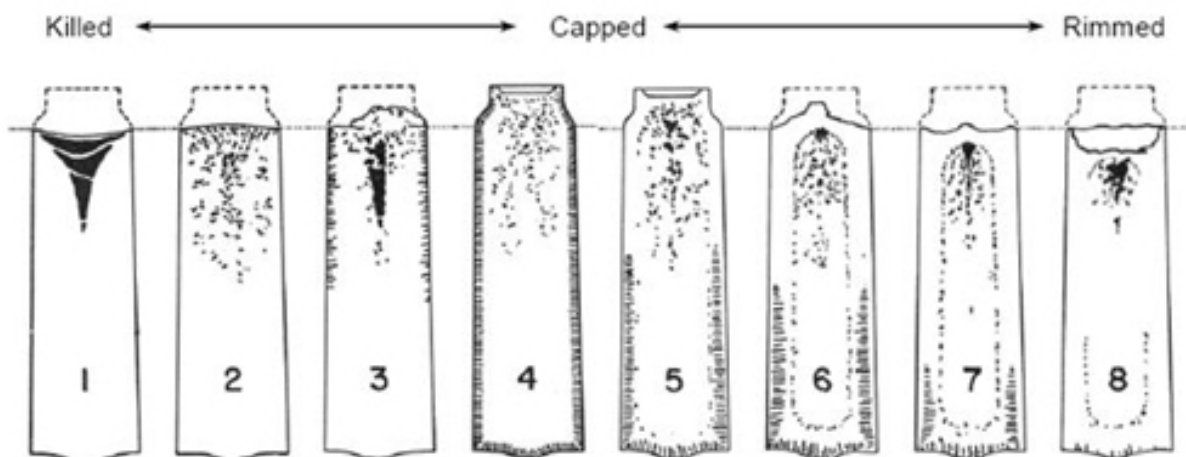
Rimmed steel usually is tapped without having made additions of deoxidizers to the steel in the furnace or only small additions to the molten steel in ladle, in order to have sufficient oxygen present to give the desired gas evolution by reacting in the mold with carbon.
The exact procedures followed depend upon whether the steel has a carbon content in the higher ranges i.e. %C = 0,12 – 0,15 or in the lower ranges, e.g. %C < 0,10. When the metal in the ingot mold begins to solidify, there is a brisk evolution of carbon monoxide, resulting in an outer ingot skin of relatively clean metal low in

carbon and other solutes. Such ingots are best suited for the manufacture of steel sheets.

Capped steel practice is a variation of rimmed steel practice.
The rimming action is allowed to begin normally, but is then terminated after a minute or more by sealing the mold with a cast-iron cap. In steels with a carbon content greater than 0,15 % the capped ingot practice is usually applied to sheet, strip, wire and bars.

Semi-killed steel is deoxidized less than killed steel and there is enough oxygen present in the molten steel to react with carbon forming sufficient carbon monoxide to counterbalance the solidification shrinkage. The steel generally has a carbon content within the range %C = 0,15 – 0,30 and finds wide application in structural shapes.

Killed steel is deoxidized to such an extent that there is no gas evolution during solidification.
Aluminum is used for deoxidation, together with ferro-alloys of manganese and silicon; in certain cases calcium silicide or other special strong deoxidizers are used.
In order to minimize piping, almost all killed steels are cast in hot-topped big-end up molds.
Killed steels are generally used when a homogeneous structure is required in the finished steels. Alloy steels, forging steels and steels for carburizing are of this type, when the essential quality is soundness. In producing certain extra-deep-drawing steels, a low-carbon (%C = < 0,12) steel is killed, usually with a substantial amount of aluminum that is added in the ladle, in the mold or both.

Remark

Although the deoxidation of steel by aluminum suppresses the formation of carbon monoxide during solidification, and hence suppresses blow holes, there are many steel processing operations where aluminum killing of steel is undesirable.

For example, it is widely recognized that certain alloy steels to be cast as large ingots should not be subject to aluminum killing, because of the piping and of deleterious effects of alumina inclusions on the subsequent processing of ingots for certain applications, e.g. generator-rotor shafts.

It has been recognized from the early days of the continuous-casting operation nearly two decades ago that casting difficulties and poor surface conditions are often experienced with aluminum-killed steels. It is for these reasons that other forms of deoxidation are often preferred in a number of steel-processing operations, e.g. silico-manganese deoxidation and / or vacuum carbon deoxidation.

3.   DEOXIDATION EQUILIBRIA

Deoxidation reactions can be described using the deoxidation equilibrium constant.

A wide spectrum of deoxidation equilibriums pertaining to the most common deoxidants for steel is summarized in Table 1 as a log-log plot of the concentration of oxygen in solution in liquid steel against that of the added elements.

Table 1: Solubility of the products of deoxidation in liquid iron.

Equilibrium constant K*	Composition range	K at 1600°C	log K
$[a_{Al}]^2[a_O]^4$	< 1 ppm Al	1.1×10^{-15}	-71600/T + 23.28
$[a_{Al}]^2[a_O]^3$	< 1 ppm Al	4.3×10^{-14}	-62780/T + 20.17
$[a_B]^2[a_O]^3$		1.3×10^{-8}	
$[a_C] [a_O]^3$	> 0.02% C	2.0×10^{-3}	-1168/T - 2.07
$[a_{Cr}]^2[a_O]^3$	> 3% Cr	1.1×10^{-4}	-40740/T + 17.78
$[a_{Mn}] [a_O]$	> 1% Mn	5.1×10^{-2}	-14450/T + 6.43
$[a_{Si}] [a_O]^2$	> 20 ppm Si	2.2×10^{-5}	-30410/T + 11.59
$[a_{Ti}] [a_O]^2$	< 0.3% Ti	2.8×10^{-6}	
$[a_{Ti}] [a_O]$	> 5% Ti	1.9×10^{-3}	
$[a_V]^2[a_O]^4$	< 0.10 V	8.9×10^{-8}	-48060/T + 18.61
$[a_V]^2[a_O]^3$	> 0.3% V	2.9×10^{-6}	-43200/T + 17.52

- Activities are chosen such that $a_{Mn} \equiv$ %Mn and $a_O \equiv$ %O when %M→O
- Square brackets [ ] denote component present in molten steel
- Temperature (T) is on the Kelvin scale.

In all cases, the oxygen and the alloying element in solution are in equilibrium with the appropriate gas, liquid or solid oxide phases at 1600°C, e.g. 1 atm CO, pure B_2O_3, pure Al_2O_3 etc.
The curves for **Mn**, **Si** and **C** are from compiled data.
The curves for **Cr**, **V**, **B**, **Ti** and **Al** are based on the recent work done in this laboratory by Fruehan using the oxygen galvanic cell previously described in measuring the equilibrium oxygen potentials.

Deoxidation reactions can be described using the deoxidation equilibrium constant.

The reaction when the alloying element (M) is added to the steel can be represented by:

$$M_xO_y = xM + Yo \ .....(1)$$

The deoxidation constant assuming pure M_xO_y forms (i.e. unit activity for M_xO_y) is given by:

$$K = (h_M)^x (h_O)^y \ .....(2)$$

Where h_M and h_O are the Henrian activities defined such that activity of the components is equal to its weight percent at infinite dilution in iron.

$$H_i = f_i(wt.\% \ i) \ .....(3)$$

The activity coefficient f_i can be corrected for alloying elements by use of the interaction parameter e^j_i

$$(d \log f_i / d \log wt\%j) = e^j_i \ .....(4)$$

Table 2 shows the coefficients of interaction for the common elements of carbon and stainless steels at 1600°C.

Table 2: The coefficients of interaction for the common elements of carbon and stainless steels at 1600°C

Metal		Al	C	Mn	P	S	Si	Ti	H	N	O	Cr	Ni
Carbon steel 1600°C	$\%_i$		0.05	0.45	0.02	0.01	0.3	0.05					
	f_i	1.05	1.06	1.0	1.1	1.0	1.15	0.93	1.0	0.97	0.85		
	a_i		0.053	0.45	0.022	0.01	0.345	0.046					
Stainless steel 1600°C	$\%_i$		0.05	0.45	0.02	0.01	0.3	0.05				18	8
	f_i	3.6	0.49	1.0	0.32	0.66	1.24	9.4	0.93	0.17	0.21	0.97	1.0
	a_i		0.025	0.45	0.006	0.007	0.372	0.47				17.5	8.0

For most low alloy steels encountered in ladle metallurgy the activity coefficient can be taken as unity and equation 2 reduces to:

$$K_M = (\%M)^x (\%O)^y \ .....(5)$$

To illustrate how to use these constants consider a steel containing 0,1 %Si at 1600°C (2912°F) in equilibrium with SiO_2. The value of K_{Si} is given by:

$$K_{Si} = (\%Si)(\%O)^2 \ .....(6)$$
$$K_{Si} = 2.2 \times 10^{-5}$$

Therefore:

$$(\%O)^2 = 2.2 \times 10^{-4}$$
$$(\%O) \approx 0.015 \text{ or } 150 \text{ ppm.}$$

==It is important to remember that these calculations are for soluble oxygen content; the total oxygen content which includes both the soluble oxygen and the oxygen associated with inclusions could be much higher.==

For single element deoxidation, the solubility of oxygen in liquid iron at 1600°C (2912°F) is given as a function of the concentration of the alloying element.

In each case, the melt is in equilibrium with the respective pure oxide; e.g. SiO_2, Al_2O_3 etc.

It can be clearly seen that aluminum is the strongest of the common deoxidisers followed by titanium.

Rare earths are about as strong aluminum as deoxidizers and will be discussed later in detail.

4. TYPES OF DEOXIDATION

In all steelmaking processes, except for the acid silicon reducing process, the steel must be deoxidized after having been brought to the specified carbon content to make the dissolved oxygen inactive and prevent further oxidation of carbon.

There are primarily three elements used in steel deoxidation:

1. Manganese and silicon as low and high carbon ferro alloy
2. Silico-manganese alloy and
3. Aluminum, about 98% of purity.

4.1 DEOXIDATION WITH Fe-Mn

When the steel is partially deoxidized with **Mn**, the iron also participates in the reactions, forming liquid or solid Mn (Fe)O as the deoxidation product.

$$[Mn] + [O] \rightarrow MnO$$
$$[Fe] + [O] \rightarrow FeO$$
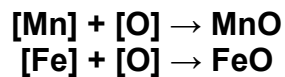
The state of equilibrium of steel with the deoxidation product Mn(Fe)O is shown in Figure 1 on next page.

Figure 1

Manganese and oxygen contents of iron in equilibrium with FeO-MnO liquid or solid solution.
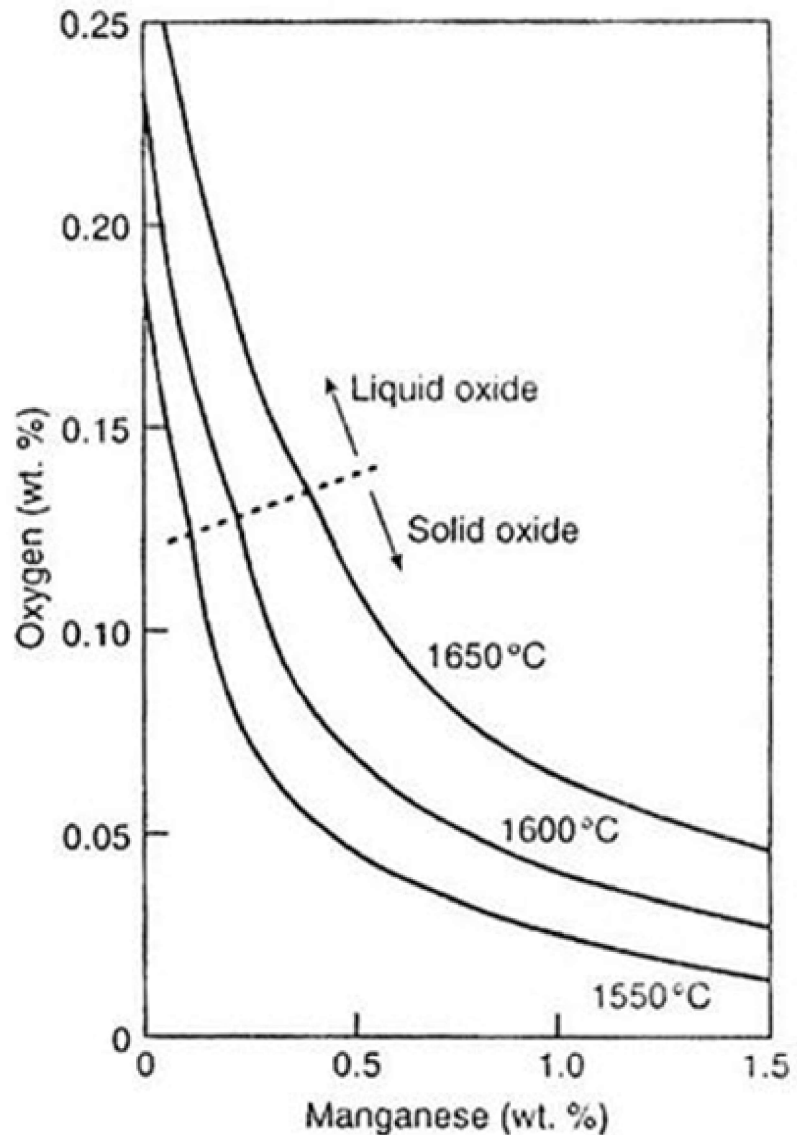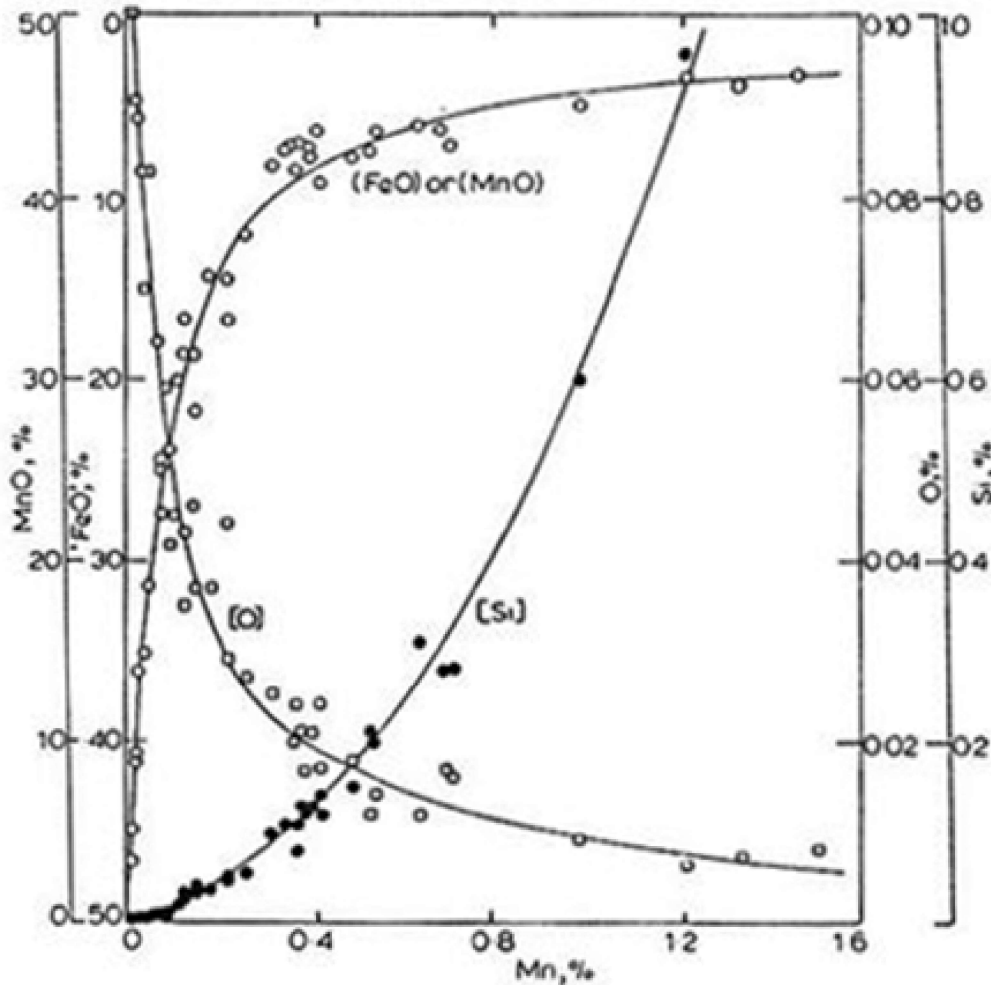
4.2 DEOXIDATION WITH Si-Mn

==The deoxidation by silicon is much more complete than that by manganese and simultaneous deoxidation by these two elements gives much lower residual oxygen in solution, because of reduced silica activity.==

Depending on the concentration of Si and Mn added to steel in the tap ladle, the deoxidation product will be either molten manganese silicate $MnO\ SiO_2$ or solid silica SiO_2.

$$[Si] + 2[O] \rightarrow SiO_2 \quad (1)$$
$$[Mn] + [O] \rightarrow MnO \quad (2)$$
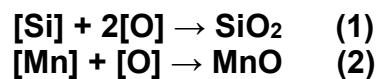
One of the early pioneering studies of slag-metal reaction equilibriums is that attributed to Korber and Oelsen for their measurement of the equilibrium distribution of manganese and silicon between liquid iron and MnO-FeO-SiO$_2$ slag saturated with silica.

The results of their experiments at 1600 ±10°C are shown in Figure 2.

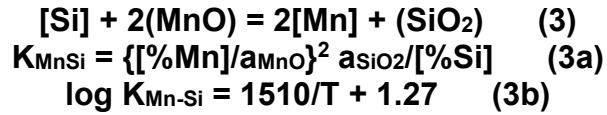**Figure 2:** Concentration of Mn, Si and O in liquid iron equilibrated with SiO$_2$.

Saturated manganese silicate melts at 1600 ±10°C.

Value of the equilibrium constant for **Si** deoxidation is already given in equation (1). The following equilibrium relation is obtained for the Si-Mn deoxidation reaction.

$$K_{Si}= a_{SiO2} / [\%Si] [\%O]^2 \qquad (1a)$$

where the silica activity **a**$_{SiO2}$ is with respect to solid SiO$_2$ as the standard state.

The sum of the deoxidation reactions by silicon and manganese gives following equilibrium relation

$$[Si] + 2(MnO) = 2[Mn] + (SiO_2) \qquad (3)$$
$$K_{MnSi} = \{[\%Mn]/a_{MnO}\}^2 \, a_{SiO2}/[\%Si] \qquad (3a)$$
$$\log K_{Mn\text{-}Si} = 1510/T + 1.27 \qquad (3b)$$

where a_{SiO2} and a_{MnO} are relative to pure solid oxides.
For high concentration of silicon (Si > 0,4 %) the activity coefficient f_{Si} = 0,11 x [%Si].

The activities of MnO in manganese silicate melts have been measured by Rao and Gaskell. Their results are in substantial agreement with the results of the earlier work by Abraham et all. The activity coefficient of the oxides (relative to solid oxides) are plotted in Figure 3.
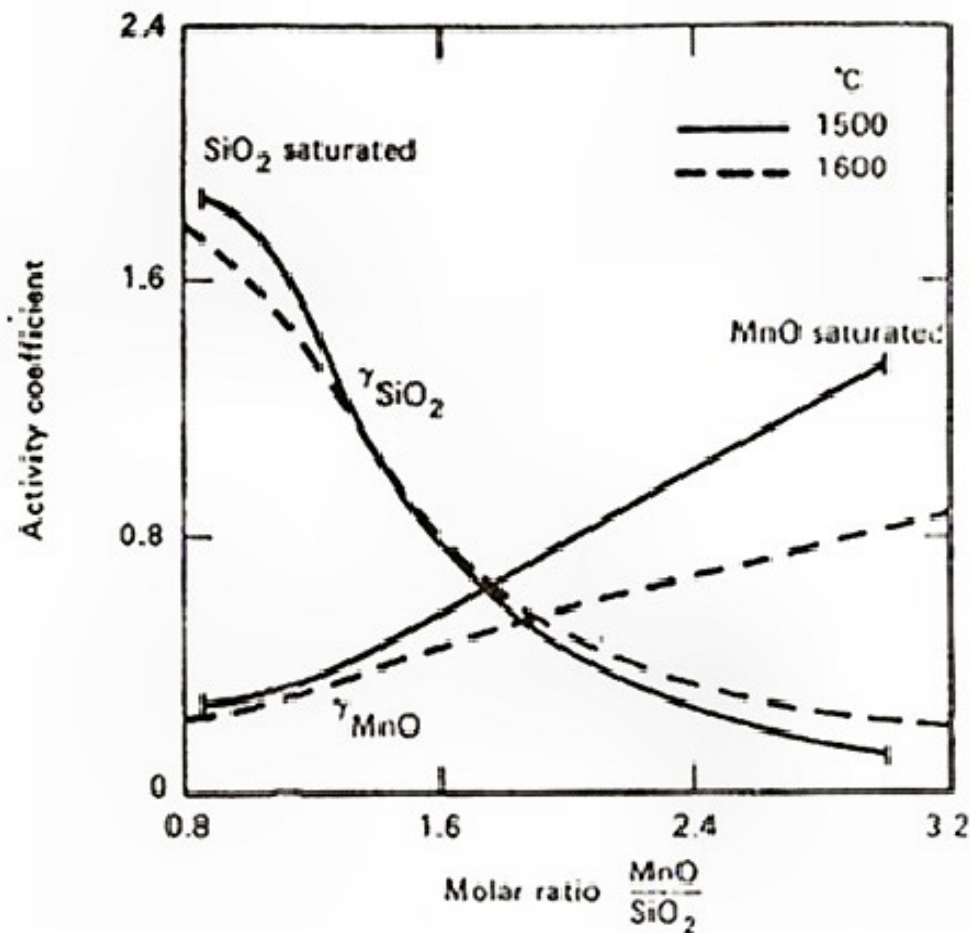
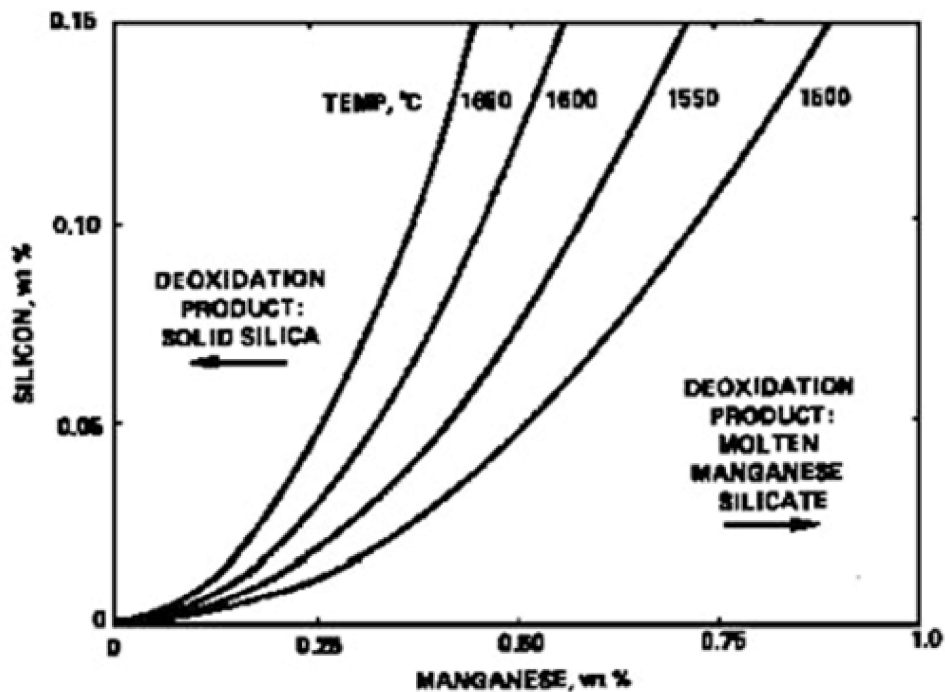**Figure 3a Activity MnO**
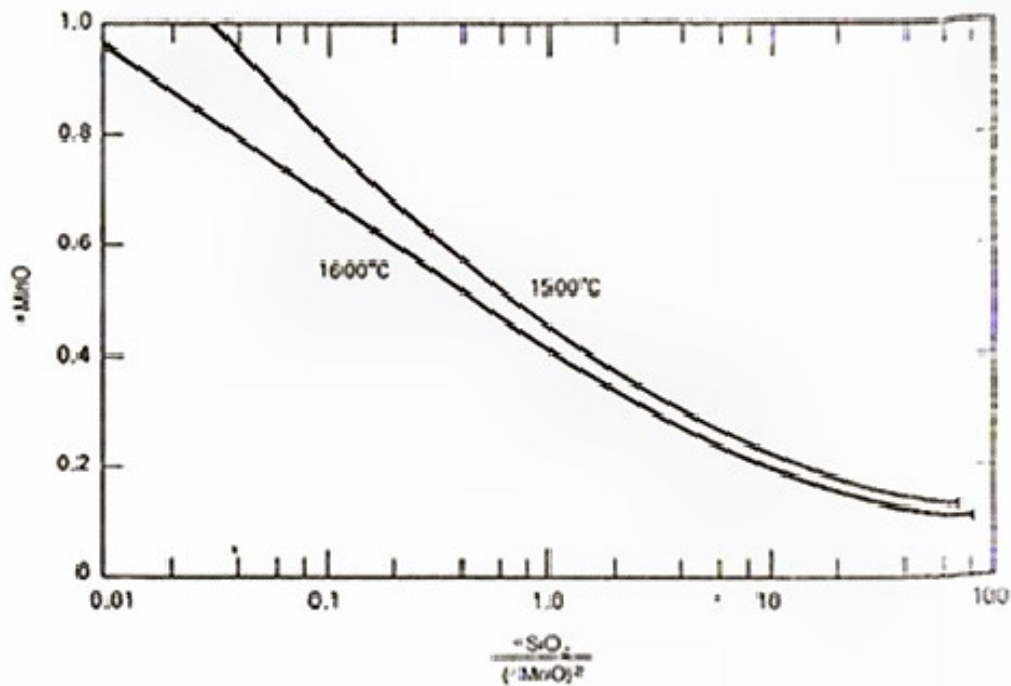
Figure 3b Activity MnO / SiO₂

General is that figure 3a and 3b give the activities in MnO-SiO₂ melts with respect to solid oxides, derived from the experimental data.

For liquid steel containing Mn > 0,4% the deoxidation product is a MnO-rich silicate with FeO < 8%.

Therefore the activity data in Figure 3 can be used together with equations (1) and (2) in computing the equilibrium state of the Si/Mn deoxidation as given in Figure 4a. The deoxidation product being either solid silica or molten manganese silicate depends on temperature, Si and Mn contents, as shown in Figure 4b.
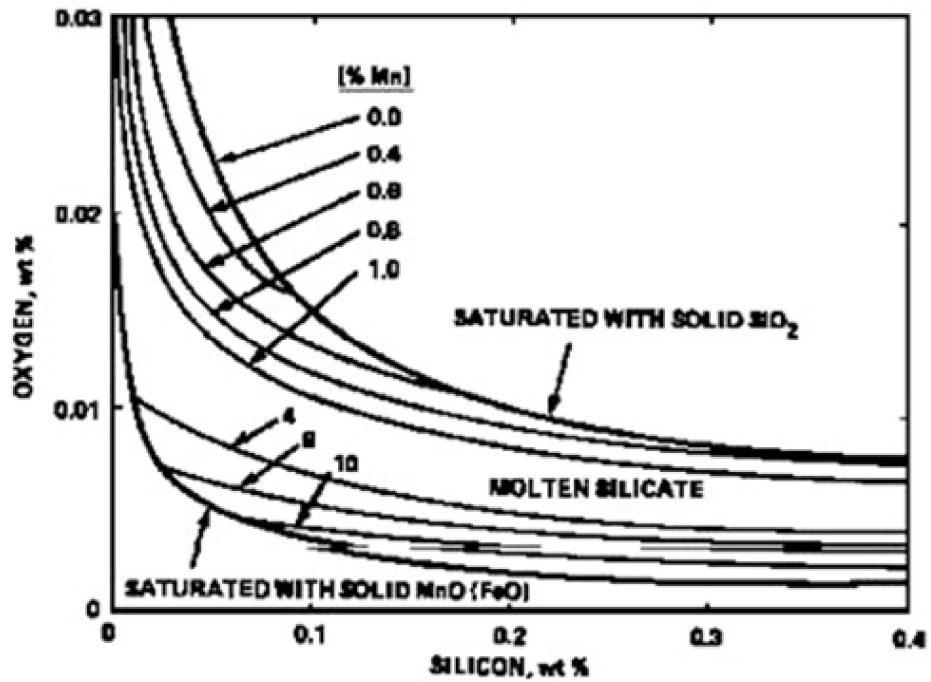
Figure 4a and 4b: Equilibrium relations for deoxidation of steel with silicon and manganese at 1600°C.

4.3 DEOXIDATION WITH Si / Mn / Al

Semi-killed steels with residual dissolved oxygen in the range 40 to 23 ppm are made by deoxidizing steel in the tap ladle with the addition of a small amount of aluminium together with silico-manganese or a combination of ferrosilicon and ferromanganese.

In this case, the deoxidation product is molten manganese alumino-silicate having a composition similar to $3MnO\ Al_2O_3\ 3SiO_2$.

With small addition of aluminum, e.g. about 35 kg for 220 to 240 t heat together with Si/Mn almost all the aluminum is consumed in this combined deoxidation with **Si** and **Mn**. The residual dissolved aluminum in the steel will be less than 10 ppm.
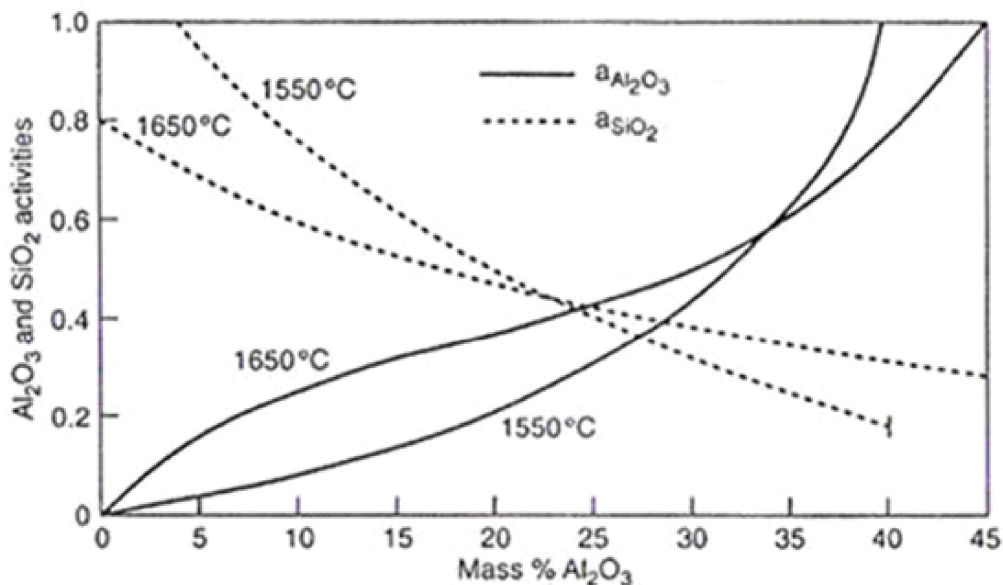

Figure 5: Al_2O_3 and SiO_2 activities in MnO-Al_2O_3-SiO_2 system for mass ratio of $MnO/SiO_2=1$.

As is seen from Figure 5, for the deoxidation product MnO-Al_2O_3-SiO_2 saturated with Al_2O_3, the silica activities are:

    0,27 at 1650°C;
    0,17 at 1550°C and decreasing probably to about
    0,12 at 1500°C.

Using these activity data and equation (1) the deoxidation equilibriums are calculated for Al/Si/Mn; these are compared in Figure 6 (see next page) with the residual oxygen [O] derived in ppm for the Si/Mn deoxidation at the same concentration of **Mn** and **Si**.
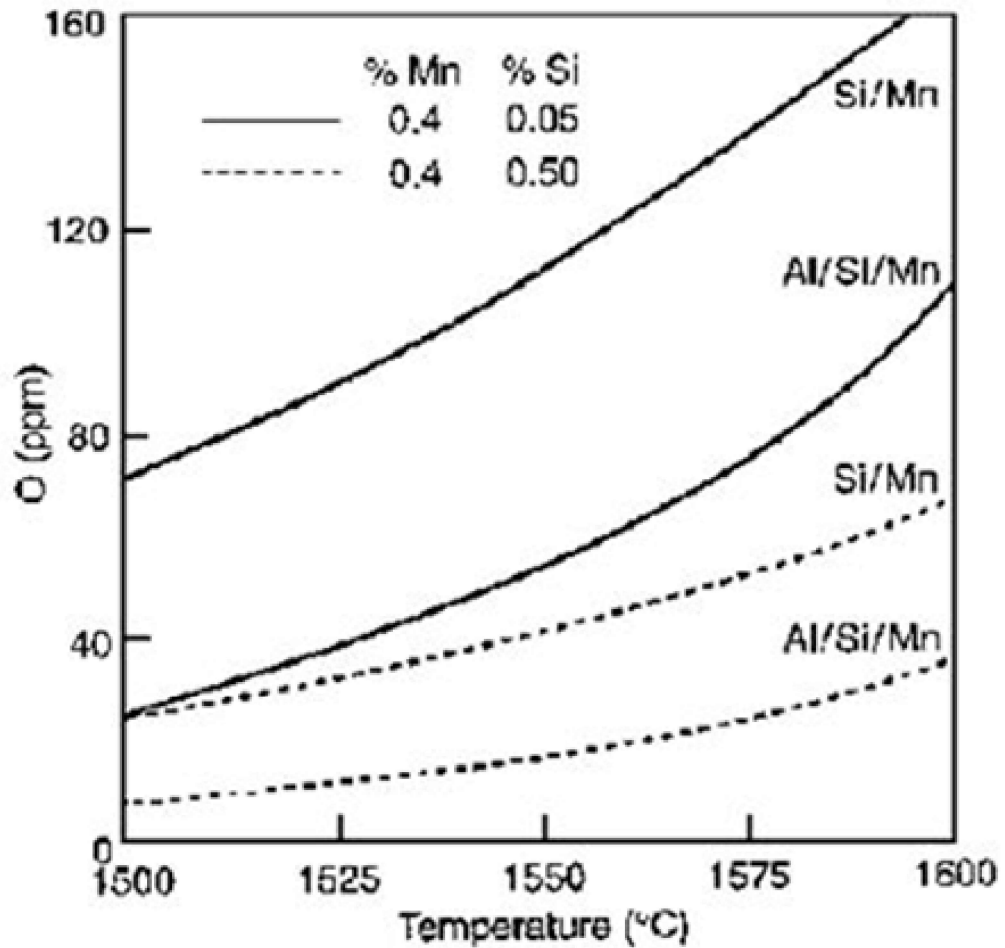
Figure 6: Deoxidation equilibriums with Si/Mn compared with Al/Si/Mn for the deoxidation product saturated with Al_2O_3.

4.4 DEOXIDATION WITH Al

Aluminum is a very effective deoxidizer which is used in most steelmaking operations.

Usually the aluminum-deoxidation is carried out in ladle; in special cases the aluminum additions are also made in the mold during ingot or continuous casting.

The equilibrium constants obtained from independent experimental studies agree with about a factor of two. An average values for the equilibrium constant is given below,
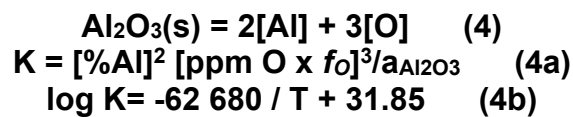
$$Al_2O_3(s) = 2[Al] + 3[O] \qquad (4)$$
$$K = [\%Al]^2 \, [ppm \; O \times f_O]^3 / a_{Al2O3} \qquad (4a)$$
$$\log K = -62\,680 / T + 31.85 \qquad (4b)$$

The alumina activity is with respect to pure solid Al_2O_3.

The effect of aluminium on the activity coefficient of oxygen dissolved in liquid steel is given by $\log f_O = -3,9 \times [\%Al]$.

At low concentration of aluminum, $f_{Al} = 1,0$.

Apparent equilibrium relations for the deoxidation products: pure Al_2O_3 and molten calcium aluminate with $\%CaO/Al_2O_3 = 1:1$ are shown in Figure 7 (next page).

When the Al-killed steel is treated with Ca-Si the alumina inclusions are converted to molten calcium aluminate.

For the ratio $\%CaO/Al_2O_3 = 1:1$ the activity of Al_2O_3 is 0,064 with respect to pure Al_2O_3 at temperatures in the range 1500-1700°C.
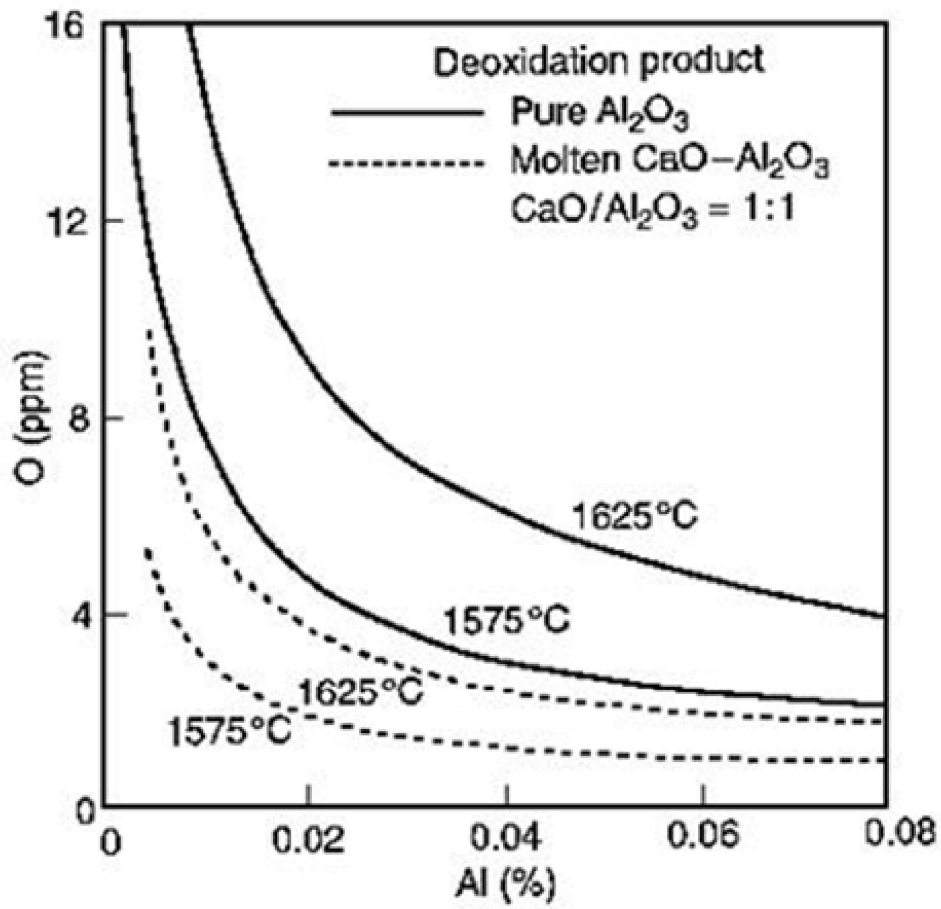
Figure 7: Deoxidation with aluminum in equilibrium with Al_2O_3 or molten calcium aluminate with CaO/Al_2O_3 = 1:1