

ASPECTS OF THERMODYNAMICS OF DEOXIDATION OF MOLTEN
STEEL WITH Mn AND Al

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Employing data from different sources, variations in the relationship between dissolved oxygen and dissolved element for deoxidation by Al, Si and Mn have been assessed. Thermodynamic calculations have been performed for simultaneous deoxidation by Al+Si+Mn and equilibrium compositions of the metal have been determined for various compositions of slag consisting of MnO, SiO₂ and Al₂O₃. Some calculated values have been compared with those reported in literature.

INTRODUCTION

Production of clean steel is intimately connected with control of oxygen dissolved in molten steel all the way from the finishing stage of the heat in the furnace to the mould and adoption of a correct deoxidation practice. Ghosh and his co-workers have been pursuing some studies in the area of "gas-metal interaction during ingot casting" for the last few years, currently under the sponsorship of the Department of Science and Technology, Govt. of India.

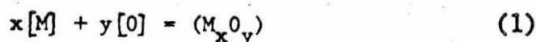
This is a very broad area. The studies have so far been primarily focussed on interaction of oxygen in connection with ingot casting of steel, specifically, oxygen absorption during teeming, study of rimming steel and blow-hole formation. However, some preliminary calculations have been performed on thermodynamics of deoxidation. In this article an attempt shall be made to briefly present a few relevant findings.

Systematic research and development work in the area of deoxidation of steel has not yet taken off the ground in India. In order to exploit the available scientific knowledge, the following steps are to be taken amongst others.

1. Thermodynamics and kinetics are to be exploited to the best possible extent. Thermodynamics of course comes first.
2. Immersion oxygen sensors based on solid electrolyte are to be employed extensively for measurement of dissolved oxygen content in molten steel.
3. Reliability of sampling and analysis for determination of total oxygen in steel (i.e. dissolved oxygen plus oxygen in oxide inclusions) by vacuum fusion/inert gas fusion apparatus is to be assessed.
4. Both the above measurements should be carried out in investigations.

THERMODYNAMIC ANALYSIS OF DEOXIDATION OF STEEL (1)

Precision of thermodynamic analysis would depend on precision of the thermodynamic data pertaining to the system. A deoxidation reaction may be represented as follows.



where the square bracket designates species dissolved in molten steel and the round bracket designates that dissolved

Table I: First-order interaction coefficients (top-most value from ref.2, next from ref.3 and 4 in order as shown. (e_{ij}))

$i \downarrow$ $j \rightarrow$	Al	C	Mn	O	Si
Al	0.043(2)	0.091	-	-1.98	0.056
	0.045(3)	0.091	-	-6.6	0.0056
	0.048(4)	0.11	-	-1.60	0.06
C	0.042	0.14	-0.012	-0.33	0.08
	0.028	0.14	-0.012	-0.34	0.08
	0.048	0.22	-	-0.10	0.10
Mn	-	-	-0.003	-0.10	0.060
	-	-0.07	0.0	-0.083	0.0
	-	-	-	-	-
O	-1.17	-0.44	-0.03	0.0	-0.14
	-	-0.45	0.021	-0.20	-0.131
	-0.94	-0.13	0.0	-0.20	-0.14
Si	0.058	0.18	0.033	-0.25	0.32
	-	0.18	0.002	-0.23	0.11
	0.063	0.24	0.0	-0.25	0.32

in the oxide phase. M denotes the de-oxidizer and O denotes oxygen.

$$K_M = \frac{(a_{M_x} a_{O_y})}{[h_M]^x [h_O]^y} \quad (2)$$

where K_M = equilibrium constant with 1 wt% standard state in metal as reference.

$a_{M_x} a_{O_y}$ = Raoultian activity of the de-oxidation product in the oxide phase.

h_M, h_O = activity of (M) and (O) respectively with 1 wt% standard state as reference.

$$\text{Again, } h_M = f_M \cdot [\text{wt\%M}] \quad (3)$$

$$\text{and } h_O = f_O \cdot [\text{wt\%O}] \quad (4)$$

$$\text{and } \log f_M = \sum e_M^j \cdot [\text{wt\% j}] \quad (5)$$

$$\text{and } \log f_O = \sum e_O^j \cdot [\text{wt\% j}] \quad (6)$$

where f denotes activity co-efficient with 1 wt % standard state as reference, e_{ij} denotes interaction co-efficient describing influence of solute j on f_i .

Since M_xO_y is pure in many cases and is at best in a binary solution, therefore basic thermodynamic data for

the deoxidation systems mean primarily values of K_h and e_{ij} . However, activity values in relevant slag systems are required when the deoxidation product is not a pure compound. K_h and e_{ij} values have been determined by many investigators over a period of 4 decades. Some are reliable and some unreliable. These have been assessed and compiled in several sources (2-4). Table 1 compares a few important values.

One may ask the question as to how much difference does it make to the predictions by employing these different data sources. It is important to possess this information for realistic appraisal of the reliability of thermodynamic analysis. Figure 1 presents the results of such calculations for simple deoxidation systems:

$[Al] - [O], [Si] - [O]$ and $[Mn] - [O]$. The products of deoxidation by Al is Al_2O_3 , by Si is SiO_2 and that by Mn is $FeO-MnO$ slag of variable composition. The difference amongst the different sets is within 15 pct. of one another except for deoxidation by aluminium at higher residual aluminium and by manganese at high manganese concentration.

Amongst the various computations carried out, results obtained for simultaneous deoxidation by manganese, silicon and aluminium would be briefly

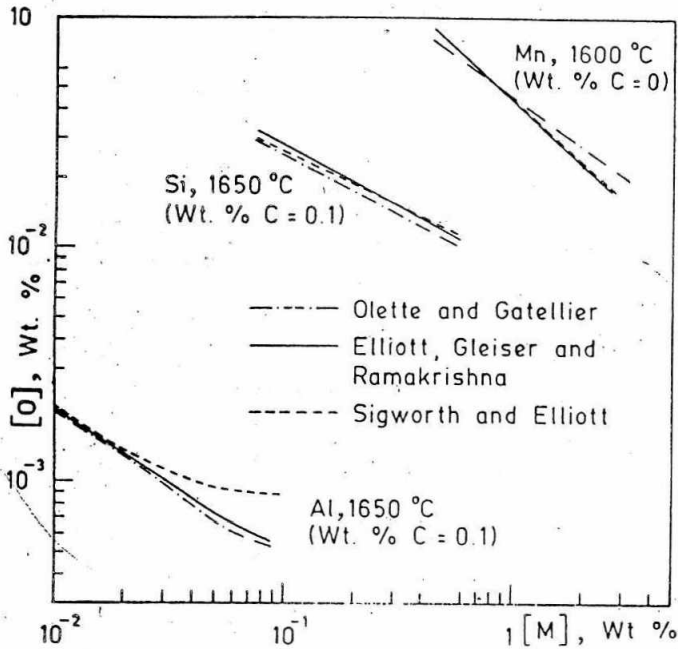
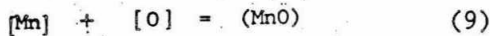
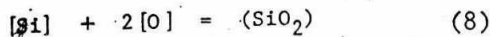
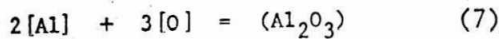


Fig. 1. $[M] - [O]$ equilibria in molten steel for aluminium, silicon and manganese showing variations for different data sources.

reported here. The deoxidation product at equilibrium would consist of a slag consisting of $MnO-SiO_2-Al_2O_3$ of variable composition.

Very briefly speaking, the procedure was as follows.

The three simultaneous reactions are:



Equilibrium relations for reactions (7), (8) and (9) are respectively:

$$\log K_{Al} = \log \frac{(a_{Al_2O_3})}{[h_{Al}]^2 \cdot [h_O]^3} = - \frac{62,780}{T} + 20.54 \quad (10)$$

$$\log K_{Si} = \log \frac{(a_{SiO_2})}{[h_{Si}] \cdot [h_O]^2} = - \frac{31,040}{T} + 12.0 \quad (11)$$

$$\log K_{Mn} = \log \frac{(a_{MnO})}{[h_{Mn}] [h_O]} = \frac{15,050}{T} - 6.70 \quad (12)$$

The activities of Al_2O_3 , SiO_2 and MnO in liquid ternary $MnO-SiO_2-Al_2O_3$ system have been reported by Fujisawa and Sakao(5). The diagram at $1650^\circ C$ is reproduced in Figure 2. A slag composition was chosen first. $a_{Al_2O_3}$, a_{SiO_2} and a_{MnO} for the composition were noted. Values of K_{Al} , K_{Si} and K_{Mn} (eqns. 10-12) are from Olette and Gatellier(2), and were employed. Next (h_O) was arbitrarily fixed. These allowed calculation of (h_{Al}) , (h_{Si}) and (h_{Mn}) with the help of eqns. (10)-(12). From these values, $[wt\% Al]$, $[wt\% Si]$, $[wt\% Mn]$ and $(wt\% O)$ were computed by solving the four simultaneous equations (Eqns. (3) - (6)). Newton-Raphson and Matrix method were employed. A master computer program was developed for this purpose. The interaction coefficients have been taken from Sigworth and Elliott(3) (Table II).

Using the computer program calculations have been performed over a wide range of slag composition, carbon content and (h_O) values. They are available elsewhere (1). Figure 3 presents

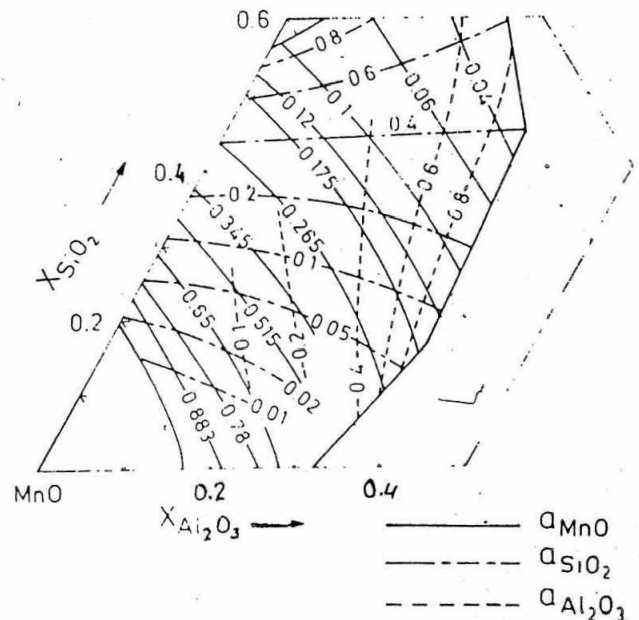


Fig. 2 Iso-activity curves for MnO , SiO_2 and Al_2O_3 in the molten ternary system at $1650^\circ C$; X denotes mole fraction.

Table II: Influence of carbon in the bath on equilibrium weight percentages of aluminium, silicon, manganese and oxygen.

Temperature: 1550°C

Slag composition: $(X_{Al_2O_3}) = 0.289, (X_{SiO_2}) = 0.287,$

$(X_{MnO}) = 0.424$

Corresponding activities: $(Q_{Al_2O_3}) = 0.8, (X_{SiO_2}) = 0.065,$

$(a_{MnO}) = 0.15$

Calculated h values	Weight percentages in steel					Case
	C	O	Al	Si	Mn	
$h_o = 1 \times 10^{-2}$	0.00	0.0015	0.0032	0.53	4.17	I
$h_{Al} = 3.18 \times 10^{-4}$	0.10	0.00164	0.0032	0.51	4.24	
$h_{Si} = 0.61$	0.25	0.0019	0.0031	0.48	4.35	
$h_{Mn} = 4.17$	0.40	0.0022	0.0030	0.45	4.45	
$h_o = 1 \times 10^{-1}$	0.00	0.0103	0.00012	0.0061	4.18	II
$h_{Al} = 1.01 \times 10^{-4}$	0.10	0.0114	0.00012	0.0059	4.25	
$h_{Si} = 0.61$	0.25	0.0134	0.00012	0.0055	4.36	
$h_{Mn} = 4.17$	0.40	0.0156	0.00012	0.0052	4.46	

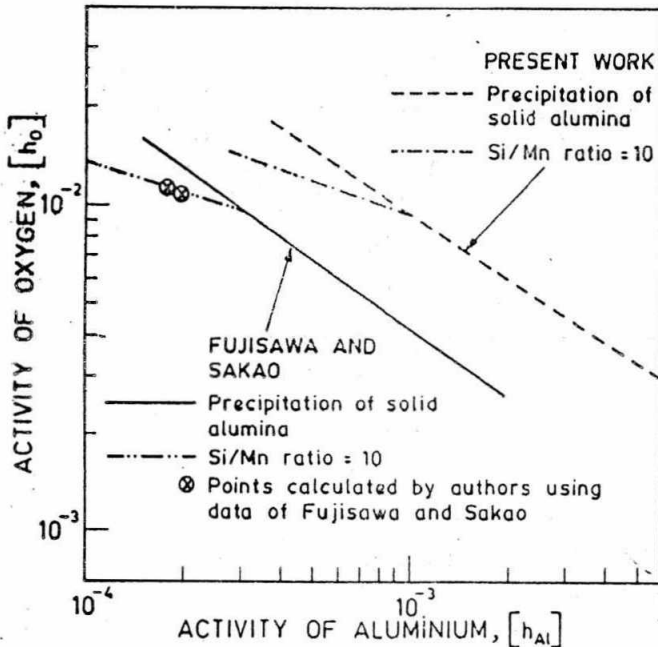


Fig.3 Complex deoxidation with silicon, aluminium and manganese; variation of activity of dissolved oxygen with activity of dissolved aluminium in steel containing Si+Mn=1wt.pct. and wt.pct. Si/wt. pct. Mn=10 at 1650°C.

calculation results for steel containing Si+Mn=1 wt%, Si/Mn = 10 at 1650°C. It may be seen that calculations by the present authors are at variance considerably with those of Fujisawa and Sakao(6). At a given value of $[h_o]$ the corresponding $[h_{Al}]$ value differs by a factor of 3. This difference is attributed to different thermodynamic data employed by Fujisawa and Sakao. They also took f_{Al} and f_{Mn} as equal to 1 and e_{Si}^{Si} as 0.318. The calculations by the present authors do not suffer from such limitations.

Carbon dissolved in molten steel modify the activity coefficients (f) of elements dissolved in steel through mutual interactions. Therefore, the equilibrium weight percentages of elements dissolved in steel would get altered. The significance of this effect is demonstrated in Table II by presenting two sample results at 1550°C. In each case the activity values both in the slag and the metal were constant. Case I differs from case II with respect to only metal composition. It is expected on the basis of equations (3) to (6) that log wt.% element would vary with wt% carbon dissolved in steel. Fig.4 shows the

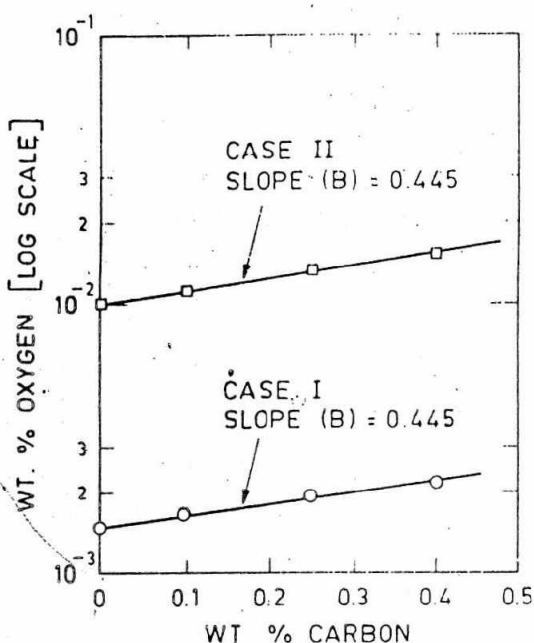


Fig.4 Influence of carbon on wt.pct.oxygen dissolved in liquid steel for de-oxidation by Mn+Si+Al at 1550°C.

relationship between $\log(\text{wt}\% \text{ oxygen})$ dissolved in steel and $(\text{wt}\% \text{ carbon})$ dissolved in steel for the two cases presented in Table II. Straight lines have been obtained. The slopes (B) as defined by:

$$B = \frac{\partial(\log(\text{wt}\% \text{ O}))}{\partial(\text{wt}\% \text{ C})} \dots \quad (13)$$

have been found to be 0.445 for both the cases.

The implication of this is demonstrated with the arguments noted below.

from eqn. (4)

$$\log(\text{wt}\% \text{ O}) = \log(h_{\text{O}}) - \log(f_{\text{O}}) \quad (14)$$

Presence of carbon is expected to alter f and $\text{wt}\%$ of all elements dissolved in steel through its interaction.

$$\log[f_{\text{O}}] = \sum(e_{\text{O}}^{\text{m}} [\text{wt}\% \text{ m}] - e_{\text{O}}^{\text{c}} [\text{wt}\% \text{ c}]) \quad (15)$$

where in eqn. (15), m denotes only Al, Mn and Si.

$$\text{Again, } \log[\text{wt}\% \text{ M}] = \log[\text{wt}\% \text{ M}]_{\text{O}} - e_{\text{M}}^{\text{c}} [\text{wt}\% \text{ c}] \quad (16)$$

where $\log(\text{wt}\% \text{ M})_{\text{O}}$ denotes the value when $\text{wt}\% \text{ c} = 0$ at constant (h_{M}) or

$$[\text{wt}\% \text{ M}] = [\text{wt}\% \text{ M}]_{\text{O}} \exp(-e_{\text{M}}^{\text{c}} [\text{wt}\% \text{ c}]) \quad (17)$$

combining eqns. (14), (15) and (17), noting that $[h_{\text{O}}]$ is a constant and then differentiating we obtain,

$$\delta \log \frac{[\text{wt}\% \text{ O}]}{[\text{wt}\% \text{ C}]} = -e_{\text{O}}^{\text{c}} + \sum e_{\text{O}}^{\text{M}} e_{\text{M}}^{\text{c}} \phi [\text{wt}\% \text{ c}] \quad (18)$$

where $\phi(\text{wt}\% \text{ c})$ is a slowly varying function of $(\text{wt}\% \text{ c})$. Noting that $e_{\text{O}}^{\text{c}} = 0.45$ (Table I), and the experimental slope (B) = 0.445, it may be concluded that $B \approx -e_{\text{O}}^{\text{c}}$ and the second term in eqn. (18) is negligible.

CONCLUSIONS

Results of some preliminary thermodynamic analysis for deoxidation by Mn, Si and Al have been presented. Further analysis is in progress. Simultaneously emphasis is being laid on measurement of dissolved oxygen as well as total oxygen in molten steel and further studies on these basis.

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