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 focused 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

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

\[ x[M] + y[O] = (M_xO_y) \]  (1)

where the square bracket designates species dissolved in molten steel and the round bracket designates that dissolved
in the oxide phase. M denotes the deoxidizer and O denotes oxygen.

\[ K_M = \frac{(a_{Mx}^{Oy})}{(\beta_{M})^{x} (\beta_{O})^{y}} \]  \hspace{1cm} (2)

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

\( a_{Mx}^{Oy} \) = Raoultian activity of the deoxidation product in the oxide phase.

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

Again, \( h_M = f_M \cdot [\text{wt}\% M] \) \hspace{1cm} (3) and \( h_O = f_O \cdot [\text{wt}\% O] \) \hspace{1cm} (4)

and \( \log f_M = \sum e_{ij} \cdot [\text{wt}\% j] \) \hspace{1cm} (5) and \( \log f_O = \sum e_{ij} \cdot [\text{wt}\% j] \) \hspace{1cm} (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 \( M_2O_y \) is pure in many cases and at best in a binary solution, therefore basic thermodynamic data for the deoxidation systems mean primarily values of \( K_M \) and \( e_{ij} \). However, activity values in relevant slag systems are required when the deoxidation product is not a pure compound. \( K_M \) 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\textsubscript{2}O\textsubscript{3}, by Si is SiO\textsubscript{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
The activities of Al₂O₃, SiO₂ and MnO in liquid ternary MnO-SiO₂-Al₂O₃ system have been reported by Fujisawa and Sakao (5). The diagram at 1650°C is reproduced in Figure 2. A slag composition was chosen first, as Al₂O₃, aSiO₂ and aMnO 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 $[Ho]$ 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 (ho) values. They are available elsewhere (1). Figure 3 presents

![Diagram](image-url)
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: $(a_{Al_2O_3}) = 0.8, (a_{SiO_2}) = 0.065, (a_{MnO}) = 0.15$

<table>
<thead>
<tr>
<th>Calculated h values</th>
<th>Weight percentages in steel</th>
<th>Case</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>$h_0 = 1 \times 10^{-2}$</td>
<td>0.00</td>
<td>0.0015</td>
</tr>
<tr>
<td>$h_{Al} = 3.18 \times 10^{-1}$</td>
<td>0.10</td>
<td>0.00164</td>
</tr>
<tr>
<td>$h_{Si} = 0.61$</td>
<td>0.25</td>
<td>0.0019</td>
</tr>
<tr>
<td>$h_{Mn} = 4.17$</td>
<td>0.40</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

|                     | C   | O   | Al  | Si  | Mn  |      |
| $h_0 = 1 \times 10^{-1}$ | 0.00 | 0.0103 | 0.00012 | 0.0061 | 4.18 |      |
| $h_{Al} = 1.01 \times 10^{-4}$ | 0.10 | 0.0114 | 0.00012 | 0.0059 | 4.25 |      |
| $h_{Si} = 0.61$ | 0.25 | 0.0134 | 0.00012 | 0.0055 | 4.36 | II   |
| $h_{Mn} = 4.17$ | 0.40 | 0.0156 | 0.00012 | 0.0052 | 4.46 |      |

calculation results for steel containing Si+Mn=1 wt%, Si/Mn = 10 at 1550°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 $[hO]$, the corresponding $[hAl]$ 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 $a_{Si}$ 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
relationship between $\log$ (wt% oxygen) dissolved in steel and (wt% carbon) dissolved in steel for the two cases presented in Table II. Straight lines have been obtained. The slopes (B) as defined by:

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

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)

$$\log \text{(wt\% O)} = \log (h_0) - \log (f_0) \ldots (14)$$

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

$$\log [f_0] = \sum [e_0^m \text{ [wt\% M]} - e_0^c \text{ [wt\% C]}] \ldots (15)$$

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

Again, $\log [\text{wt\% M}] = \log [\text{wt\% M}_0] - e_0^c \text{ [wt\% C]} \ldots (16)$

where $\log (\text{wt \% M}_0)$ denotes the value when wt% C = 0 at constant ($h_0$) or

$$[\text{wt\% M}] = [\text{wt\% M}_0] \exp (-e_0^c \text{ [wt\% C]}) \ldots (17)$$

combining eqns. (14), (15) and (17), noting that $[h_0]$ = a constant and then differentiating we obtain,

$$\delta \frac{\log [\text{wt\% O}]}{\delta \text{[wt\% C]}} = - e_0^c + \sum_{\text{M}} e_M^c \phi [\text{wt\% C}] \ldots (18)$$

where $\phi (\text{wt\% C})$ is a slowly varying function of (wt% C). Noting that $e_0^c = 0.45$ (Table I), and the experimental slope (B) = 0.445, it may be concluded that B = $e_0^c$ 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.

ACKNOWLEDGEMENT

Financial sponsorship by the Department of Science and Technology, Government of India, is being gratefully acknowledged.

REFERENCES