

Deoxidation of Molten Steel by Aluminum

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Abstract: The deoxidation equilibrium of liquid steel was investigated from a new perspective. Dissolved associate M_mO_n was used to describe the interaction between dissolved M and dissolved oxygen instead of the interaction parameter of Wagner. The concentration of unassociated oxygen could be considered as the activity of oxygen. Or, the percentage of unassociated oxygen in the total dissolved oxygen was the activity coefficient of oxygen. When the content of deoxidizer was low, the dissolved oxygen was mainly composed of the unassociated oxygen, while more and more M_xO formed with gradually increasing M content. The present model gave a good description to the aluminum deoxidation equilibrium after considering AlO and Al_2O . Furthermore, the higher the content of Al was, the higher the content of Al_2O relative to the content of AlO would be.

Key words: deoxidation equilibrium; activity coefficient; associated oxygen; unassociated oxygen; interaction coefficient

In the secondary refining process, deoxidizers M (e.g. Al) are always used to decrease the dissolved oxygen in liquid steel^[1]. Dissolved M reacts with the dissolved oxygen according to the precipitation reaction to generate M_xO_y , part of which floats upward and is absorbed by slag, while the other parts cannot complete the floatation and are trapped in steel, forming inclusions. For example, during smelting high aluminum steels (high aluminum TRIP steel, TWIP steel, 38CrMoAl, 10Ni3MnCoAl, etc.), which have high acid-soluble aluminum contents up to 0.5% or higher, Al is the main deoxidation agent as well as the key element. The deoxidation product Al_2O_3 not only can affect the cleanliness of steel, but also is the main cause for nozzle clogging during continuous casting^[2]. Therefore, a deep investigation on the deoxidation mechanism and the related thermodynamic equilibrium is beneficial to control of oxygen content and the clogging problem of nozzle. However, the related work on high aluminum steels is very limited.

Dissolved oxygen exhibits various behaviors when increasing the added amount of different deoxidizers^[3,4]. For example, when deoxidizing with Al, the concentration of dissolved oxygen decreases initially and then increases^[3,5-8], whereas in the case of Ca^[9,10] and Mg^[11,12] addition, the concentration of dissolved oxygen decreases rapidly to a very low value and then remains nearly constant. There must be some underlying reasons that cause the different variations of dissolved oxygen. Thermodynamic deoxidation equilibrium of liquid steel is usually described by the well-known interaction parameter of

Wagner^[13]. The negative interaction coefficient is always used to describe the strong interaction between M and O. Sometimes, the second-order interaction parameters are needed as well. However, the Wagner formalism has some limitations in that it cannot give the basic interpretation about what happens to the microscopic structure of Fe-M-O melt when increasing the addition of M, and in the case of very strong deoxidizers such as Ca, it proves to be incapable of satisfactorily describing the deoxidation equilibria. The present study aims to describe the deoxidation equilibria from a new perspective without considering the interaction coefficient.

1 Deoxidation Equilibrium of Liquid Steel by M

The deoxidation reaction between dissolved M and dissolved oxygen to generate precipitate M_xO_y is described as



According to precipitation reaction of Eq. (1), the increase of dissolved M concentration in liquid steel can only lead to the decrease of dissolved O content. However, there is always a minimum value of dissolved oxygen with increasing the addition of M (Al^[3], Cr^[14], V^[15], Ti^[16], etc.). Therefore, instinctively, other mechanisms must exist to increase dissolved oxygen when increasing M content.

Even in the pure M melt, there is a solubility of oxygen. From the Al-O phase diagram^[17], it can be seen that the saturation dissolved oxygen in liquid aluminum

is in equilibrium with $\alpha\text{-Al}_2\text{O}_3$. Thus, another kind of dissolved oxygen may be present in liquid steel by coordinating with M when the content of M is high. This kind of associate is marked as M_mO_n . It does not precipitate in steel, but dissolves in steel. Therefore,

$$(my-nx)[M]+nM_xO_y=y[M_mO_n] \quad (2)$$

If the concentrations of unassociated M, unassociated oxygen, and M_mO_n are $X_{[M]}$, $X_{[O]}$ and $X_{[M_mO_n]}$, respectively, the concentrations of the total dissolved M and O can be described as follows

$$X_{[M],T}=X_{[M]}+mX_{[M_mO_n]} \quad (3)$$

$$X_{[O],T}=X_{[O]}+nX_{[M_mO_n]} \quad (4)$$

When the concentration of dissolved M in steel is low, mechanism (1) is dominant, and M_mO_n contributes little to the concentrations of both dissolved M and dissolved oxygen, while most dissolved oxygen is bonded with M, and mechanism (2) becomes dominant when the concentration of M is high. Thereby, in this condition, the dissolved oxygen may be composed mainly of dissolved M_mO_n . However, M_mO_n still contributes little to the total dissolved M. It can be easily understood from the limiting case of pure M melt, in which the soluble oxygen is small and only a small part of M is bonded with dissolved oxygen as M_mO_n . Therefore, the total dissolved M can be approximately considered to be equal to the unassociated M.

$$X_{[M],T}=X_{[M]}+mX_{[M_mO_n]}\approx X_{[M]} \quad (5)$$

The equilibrium constants of chemical reactions (1) and (2) can be described as follows

$$K_1=X_{[M]}^x\cdot X_{[O]}^y=X_{[M],T}^x\cdot X_{[O]}^y \quad (6)$$

$$K_2=\frac{X_{[M_mO_n]}^y}{X_{[M]}^{my-nx}}=\frac{X_{[M_mO_n]}^y}{X_{[M],T}^{my-nx}} \quad (7)$$

According to Eq. (6), the content of unassociated oxygen is

$$X_{[O]}=K_1^{1/y}X_{[M],T}^{-x/y} \quad (8)$$

According to Eq. (7),

$$X_{[M_mO_n]}=K_2^{1/y}X_{[M],T}^{m-nx/y} \quad (9)$$

Thereby, the total dissolved oxygen can be described as follows

$$X_{[O],T}=K_1^{1/y}X_{[M],T}^{-x/y}+\frac{nM_O}{mM_M+nM_O}K_2^{1/y}X_{[M],T}^{m-nx/y} \quad (10)$$

where, M_O and M_M represent the atomic mass of element O and M, respectively.

Because the first term of the right hand of Eq. (10) is a monotonically decreasing function of total dissolved M, the second term should be a monotonically increasing function or a constant if Eq. (10) is utilized to describe the existence of minimum dissolved oxygen content (for Al as deoxidizer) or constant dissolved oxygen content (for Ca as deoxidizer). In the former case, a minimum value of dissolved oxygen can be estimated by Eq. (10), while in the latter case, a dissolved oxygen platform can be estimated because the first term of Eq. (10) gradually decreases to very low values relative to the second term with increasing the total M content. Consequently, $m-nx/$

$y\geq 0$, thus $m/n\geq x/y$. Because of the mass action law, in dilute solution, small associates as MO are much more thermodynamically favorable than larger ones. When the concentration of dissolved M is high, larger associate M_2O maybe also form. Since the content of dissolved oxygen is always very low, the associates MO_z ($z>1$) can be neglected.

2 Application to Aluminum Deoxidation Equilibrium

The Al deoxidation equilibrium has been experimentally and thermodynamically studied since the middle of the 1950s, as summarized in the work of Morita et al.^[3]. Large discrepancies exist between different results, even as large as an order of magnitude. In this study, the latest measured aluminum-oxygen equilibrium data and equilibrium constant of K_1 ($K_1=3.020\times 10^{-12}$) by Morita et al.^[3] are used. The precipitated oxide is Al_2O_3 ; thus, $x=2$ and $y=3$.

2.1 Case of forming AlO: $m=1, n=1$

In this case, Eq. (10) becomes

$$X_{\text{O, total}}=K_1^{1/3}X^{-2/3}+16/43K_1^{1/3}X^{1/3} \quad (11)$$

The value of equilibrium constant K_2 for reaction (2) is optimized to be 1.116×10^{-10} by best fitting the experimental data. The comparison of measured and calculated dissolved oxygen by Eq. (11) is shown in Fig. 1, in which the calculated dissolved oxygen only considering the precipitation reaction (1) is also included. It can be seen that when considering AlO, good consistencies can be obtained when the Al content is low but there are large deviations in the region of high aluminum content.

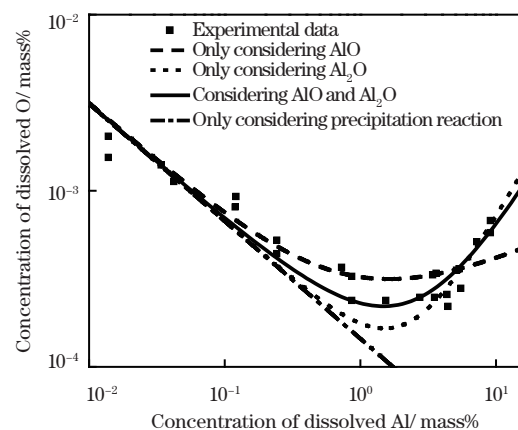


Fig. 1 Comparison of measured and calculated aluminum-oxygen equilibrium curves

2.2 Case of forming Al_2O : $m=2, n=1$

In this case, Eq. (10) becomes

$$X_{\text{O, total}}=K_1^{1/3}X^{-2/3}+16/70K_1^{1/3}X^{4/3} \quad (12)$$

The value of parameter K_2 is optimized to be 2.761×10^{-12} . From the comparison of measured and cal-

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