INNOVATIVE TECHNOLOGICA
METHODICAL RESEARCH JOURNAL
ISSN: 2776-0987 Volume 3, Issue 6, June, 2022

THERMODYNAMIC CALCULATIONS FOR SLAG OXIDATION HIGH MANGANESE STEEL 110G13L

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Abstract

The paper considers the possibility of rapid assessment of $\sum$ (FeO + MnO) by measuring the oxygen activity in liquid steel. Manganese monoxide MnO, found in steel, according to a large number of studies, significantly worsens its crack resistance, wear resistance, ductility, cold resistance and other properties.

Keywords: 110G13L **;** complex deoxidation **;** oxygen **;** non-metallic inclusions; modifier; silicon; aluminum.

1. Introduction

Oxide MnO is introduced into the metal together with an alloying dose of ferromanganese, and is also formed during the oxidation of manganese during the oxidation period of the steel production process, its tapping from the furnace and casting; MnO is a stable oxide with a melting point of 1750 ^{0}C . Based on a large amount of data on the content of MnO in castings, it has been established that its concentration in high-manganese steel varies within a fairly wide range and amounts to 0.01-0.15%. Research and practice have established a qualitative relationship between the contents in slag (MnO) and (FeO): the higher the concentration (MnO) in the slag, the more (FeO) in it . :one. However, the higher the content of oxide FeO in the slag , the higher its concentration in the metal, the more intensive the process of manganese oxidation will proceed inside the liquid metal with the formation of MnO. The resulting MnO dissolves FeO , resulting in non-metallic inclusions mFeO · n MnO, enriched in MnO. The ferromanganese non-metallic inclusions formed inside the liquid metal have a relatively low melting point, have sufficient solubility in steel and satisfactory wettability with respect to the solidifying metal [1]. During the crystallization of steel, these inclusions are located along the boundaries of its grains, violating the strength of intergranular bonds, therefore, the degree of steel deoxidation should be characterized by the total content in the pre-finishing slag (FeO) and (MnO). The more (FeO) + (MnO), the worse the deoxidized metal and the lower its mechanical and service properties.

When the content in the pre-finishing slag is 20-40% (MnO), the rejection of complex castings can reach 30-40%. The tendency of steel to form cracks in castings with an increase in slag (M n O) is indicated in the book (Fig. 1) [1].

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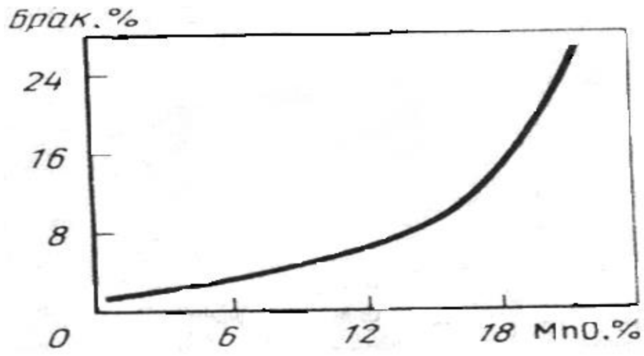

Figure 1 - Influence of the content in the slag (M n O) on the level of rejection of high-manganese castings along cracks

2. Methods

The paper considers the possibility of rapid assessment of ∑(FeO + MnO) by measuring the oxygen activity in liquid steel. This possibility follows from consideration of the following two reactions.

[F e] + [O] = (FeO) (1)

(FeO) + [Mn] = (MnO) + [Fe] (2)

The equilibrium constant of reaction (1) is equal to.

$$K_{FeO} = \frac{a_{FeO}}{a_{\text{Fe}} \cdot a_{[O]}} = \frac{a_{FeO}}{a_{[O]}} = \frac{(FeO) \cdot \gamma_{FeO}}{a_{[O]}} \quad (3)$$

where a_{FeO}, γ_{FeO} and (F eO) are activity, activity coefficient and content of iron oxide (II) in the slag, respectively;

$a_{[Fe]}$ and $a_{[O]}$ are the activities of iron and oxygen in liquid steel ($a_{[Fe]} = 1$).

From equality (3) we have

$$(FeO) = \frac{K_{FeO} \cdot a_{[O]}}{\gamma_{FeO}} \quad (4)$$

The equilibrium constant of reaction (2) is determined by the expression

$$K_{MnO} = \frac{a_{MnO}}{a_{\text{FeO}} \cdot a_{[Mn]}} = \frac{(MnO) \cdot \gamma_{MnO}}{(FeO) \cdot \gamma_{\text{FeO}} \cdot [Mn] \cdot f_{[Mn]}} \quad (5)$$

where a_{MnO}, γ_{MnO} and (Mn O) are, respectively, the activity, activity coefficient and retention of manganese (II) oxide in the slag;

[M n] and $f_{[Mn]}$ respectively, the content of manganese in liquid steel and its activity coefficient.

From expression (5) it follows

$$(MnO) = \frac{(FeO) \cdot K_{MnO} \cdot [Mn] \cdot f_{[Mn]} \cdot \gamma_{\text{FeO}}}{\gamma_{MnO}} \quad (6)$$

From equation (4) we substitute into (6)

$$(MnO) = \frac{K_{FeO} \cdot a_{[O]} \cdot K_{MnO} \cdot [Mn] \cdot f_{[Mn]}}{\gamma_{MnO}} \quad (7)$$

Summing up equations (4) and (7), we obtain

$$(FeO) + (MnO) = \frac{K_{FeO} \cdot a_{[O]}}{\gamma_{FeO}} + \frac{K_{FeO} \cdot a_{[O]} \cdot K_{MnO} \cdot [Mn] \cdot f_{[Mn]}}{\gamma_{MnO}} \quad (8)$$

After a series of transformations from (8) we obtain

(M nO) + (FeO) = $a_{[O]} \cdot \{ a + b \cdot [Mn]\}$, (9)

where coefficients a and b are equal

$a = K_{FeO} / \gamma_{FeO}$; (10)

$b = (K_{MnO} \cdot K_{FeO} \cdot f_{Mn} / \gamma_{MnO})$ (11)

The coefficients a and b contain as parameters the equilibrium constants of reactions (1) and (2), which depend only on temperature, as well as the coefficients γ_{MnO}, γ_{FeO}и $f_{[Mn]}$.

The values of the equilibrium constants were calculated from the equations of their temperature dependence [2]

$$lgK_{FeO} = \frac{6320}{T} - 0{,}734 \quad (12)$$

$$lgK_{MnO} = \frac{6440}{T} - 2{,}95 \quad (13)$$

For the conditions of steel melting (temperature of liquid steel in the furnace T = 1550 °C) we obtain

$$lgK_{FeO} = 2{,}733 \text{ и} K_{FeO} = 540{,}8 \quad (14)$$

$$lgK_{MnO} = 0{,}58 \text{ и} K_{MnO} = 3{,}802 \quad (15)$$

The activity coefficients γ_{MnO} and γ_{FeO} were found from the following assumptions [1]

1) With the basicity of the slag (Ca0) / (SiO_2) = 2.0, the ratio $\gamma_{MnO} / \gamma_{FeO}$ = 1.5, while $\gamma_{MnO} = 3$u $\gamma_{FeO} = 2$

2) With slag basicity (Ca0)/(SiO_2) >3.0 ratio $\gamma_{MnO} / \gamma_{FeO} \approx 1.0$

3) With an increase in the basicity of the slag γ_{FeO}, , increases, but γ_{MnO} would increase c tre .

From positions 1) and 2) it was assumed that during the melting of steel 110G13L, the basicity (Ca0) / (SiO_2) is close to the average value for the two options (Ca0) / (SiO_2)≈2.5, therefore, the ratios $\gamma_{MnO} / \gamma_{FeO} = (1,5 + 1)/2 = 1.25$. And from the position we get that γ_{FeO} = 3, and γ_{MnO} = 3 / 1.25 = 2.4.

The activity coefficient of manganese $f_{[Mn]}$ was found from the known pair of first-order interactions (table 1), taking into account the fact that $e_{Mn}^{Mn} = 0$.

$$lgf_{[Mn]} = \sum(e_{Mn}^{j} \cdot [\%j]) = (e_{Mn}^{Mn} \cdot [Mn] + e_{Mn}^{Si} \cdot [Si] + e_{Mn}^{C} \cdot [C] + e_{Mn}^{P} \cdot [P] + e_{Mn}^{S} \cdot [S])$$

$$e_{i,T}^{(j)} = e_{i,1873}^{(j)} \frac{1873}{T} \quad (16)$$

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As a result, for steel 110G13L with a content of 1.3% C, 0.7% Si , 13.2% Mn , 0.02% S , 0.06% P , we obtained $lg f_{[Mn]}= -0.0966$ and $f_{[Mn]}= 0.801$.

Table 1 − Values of interaction parameters e^{j}_{Mn}

Interaction options	e^{C}_{Mn}	e^{Mn}_{Mn}	e^{Si}_{Mn}	e^{P}_{Mn}	e^{S}_{Mn}
Parameter values e^{j}_{Mn}, at 1873 K	−0.0 538	–	−0.0327	−0.0035	−0.048
Parameter values e^{j}_{Mn}, at 1823 K	−0.0553		−0.0336	−0.0036	−0.049

Using the obtained values of the parameters, we determined the values of the coefficients a and b

$$a = K_{FeO} / \gamma_{FeO} = 540.8 / 3 = 180{,}3$$

$$b = (K_{MnO} \cdot K_{FeO} \cdot f_{Mn}/\gamma_{MnO}) = (3.802/2.4) \cdot 540.8 \cdot 0.801 = 686.2$$

Thus, instead of (17), we got

$$(MnO) + (FeO) = a_{[O]} \cdot (180.3 + 657.1 \cdot [Mn]) \quad (17)$$

According to formula (17), the expected values of ∑(FeO + MnO) were estimated at different oxygen activity in liquid steel. The results obtained are presented in Table 2 and Figure 10.

3. Results and Discussion

From table 2 it follows that with the oxygen activity in liquid steel $a_{[o]} = 0.0003\%$, the total content of iron and manganese oxides ∑(FeO + MnO) is 2.42 - 3.14% with a change in the manganese content in the range of 11.5 - 15.0% . With an increase in oxygen activity to $a_{[0]} = 0.0005$, 0.0007 and 0.001% under the same conditions, it ∑(FeO + MnO) increases to 4.04 - 5.24, 5.65 - 7.33 and 8.07 - 10.47% .

Table 2 - The effect of manganese on the change ∑(FeO + MnO) at different oxygen activity in liquid steel 110G13L

Oxygen activity $a_{[O]}$, %	Estimated values ∑(FeO + MnO) %, at manganese content [M n], %				
	11.5	12	13	14	15
0.0003	2.42	2.52	2.73	2.94	3.14
0.0004	3.23	3.37	3.64	3.91	4.19
0.0005	4.04	4.21	4.55	4.89	5.24
0.0006	4.84	5.05	5.46	5.87	6.28
0.0007	5.65	5.89	6.37	6.85	7.33
0.0008	6.46	6.73	7.28	7.83	8.38
0.0009	7.26	7.57	8.19	8.81	9.43
0.001	8.07	8.41	9.10	9.79	10.47

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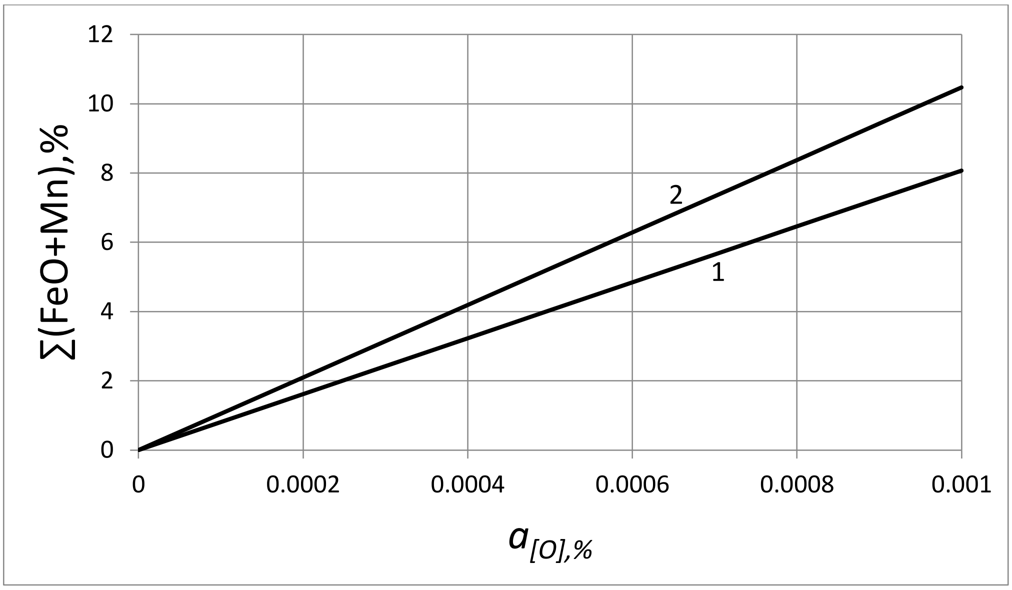

Figure 2 - Influence of oxygen activity in steel on ∑(FeO + MnO) in slag at different manganese content in it: 1 and 2 - content [M n] in steel 11.5 and 15.0%, respectively.

Figure 2 shows the dependence of the value ∑(FeO + MnO) in the slag on the oxygen activity $a_{[o]}$ in liquid steel. As can be seen, over the entire range of changes in the manganese content in steel (from 11.5 to 15.0%) ∑(FeO + MnO) , both the manganese content and the oxygen activity influence the value, but the role of the latter is predominant. Therefore, the determination ∑(FeO + MnO) of the measured values of oxygen activity $a_{[0]}$ using relation (17) ensures high reliability of the results obtained - the correlation coefficient K = 0.98.

At the same time, when steel is smelted by the oxidation method, the condition ∑(FeO + MnO) ≤ 4.5% is achieved at oxygen activity $a_{[0]} \leq (4.3 - 5.6) \cdot 10^{-4}$ %, where the lower and upper values are obtained with manganese content in steel, respectively, lower (11.5%) and upper (15.0%) limits. When steel is smelted by the method of remelting and fusion, the condition ∑(FeO + MnO) ≤6% under the same conditions is achieved at $a_{[0]} \leq (5.7 - 7.4) \cdot 10^{-4}$ %.

Conclusions

Technological recommendations have been developed for obtaining high-quality castings from high -manganese steel 110G13L. By measuring the oxygen activity $a_{[O]}$ in the melt using UKOS devices, we can predict Σ(FeO + MnO) in the slag; on the basis of this, we can accurately determine the amount of deoxidizer .

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