Calculation of sulfur removal in ladle furnace unit by means of ionic theory of slags

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Abstract. This article describes issues of sulfur removal in ladle furnace unit. First of all, metal desulfurization in ladle steel treatment units is achieved due to transition of sulfur to the slag phase. Coefficient of partition of sulfur between metal and slag is affected by sulfide capacity of slag, coefficient of activity of sulfur in the metal, oxidation potential of medium and reaction equilibrium constant of partition of sulfur between metal and slag. Temperature of liquid state in the ladle has significant impact on sulfide capacity of slag. Proposed calculation procedure based on provisions of ionic structure of slags allows evaluating a concentration of sulfur in steel on the basis of determination of coefficient of its partition between metal and slag. Optical basicity is suggested as criterion of refining property of slag, it has been shown that the amphoteric oxide Al₂O₃ is essential to calculation of this indicator. Its impact on sulfide capacity of slag is detected.

1. Introduction
After tapping of metal from the steelmaking vessel all further actions aimed at finishing of steel in terms of chemical composition and temperature are performed in the ladle. Ladle metallurgy is intended to solve three main tasks: refining of steel on nonmetallic inclusions and detrimental impurities; correction of chemical composition by means of addition of corresponding master alloys; homogenization of metal by temperature and chemical composition [1, 2]. The current level of the industry development requires the manufacture of steel with high purity in relation to nonmetallic inclusions and detrimental impurities [3–6]. Sulfur is one of the impurities that significantly reduces the service properties of steel and the content of which is strictly regulated in the finished product. A great number of theoretical and practical researches have been devoted to processes of desulfurization, but this topic is still relevant at present.

It is known that metal desulfurization can be achieved due to transition of sulfur to the slag [1]. This process can be implemented using ladle furnace unit at the metal surface of which fresh slag is
built up. Slag is a multi-component oxide melt that interacts with metal and performs important technological functions [1, 11, 12]. At present, it is considered that slag has an ionic structure and consists of positively charged cations and negatively charged anions. Evidence of the ionic structure of slags are numerous X-ray diffraction studies of solidified slags, electrical conductivity of molten slags, presence of electrical charges in the boundary layers of metal and slag, high values of surface tension of slags, etc.

2. Theoretical data

In molten metallurgical slags, there are ions of the following groups [1, 13–15].

1. Cations Са\(^{2+}\), Mg\(^{2+}\), Mn\(^{2+}\), Fe\(^{2+}\).
2. Anions O\(^{-2}\), S\(^{-2}\), SiO\(^{4\times}\), PO\(^{3\times}\), AlO\(^{3\times}\), FeO\(^{2\times}\).
3. More complex silica acid anions (SiO\(^{3\times}\))\(_n\), Si\(_3\)O\(_9\)\(^{6\times}\), Si\(_4\)O\(_{12}\)\(^{8\times}\), Si\(_6\)O\(_{18}\)\(^{12\times}\) etc. can form in acid slags [16–19].

Taking into account the presented data it is important to study metal desulfurization from the position of ionic theory of slag structure.

It is known that the sulfur partition coefficient between metal and slag is determined by the following formula [20]:

\[
L_S = \frac{(S)}{[S]} = C_S \times \gamma[S] \times \frac{1}{P_{(O_2)^{0.5}}} \times \frac{1}{K[S]}
\]

(1)

where \(C_S\) – sulfide capacity of slag, \(\gamma[S]\) – coefficient of activity of sulfur in the metal, \(P_{(O_2)^{0.5}}\) – oxidation potential of medium, \(K[S]\) – reaction equilibrium constant of partition of sulfur between metal and slag.

Let us review each multiplier in the right part of the equation 1.

Reaction equilibrium constant of partition of sulfur between metal and slag according to data [1] is determined by the formula

\[
\lg K_S = -\frac{6500}{T} + 2.625 \quad \text{where } T \text{– temperature, } K.
\]

In order to calculate values of coefficient of activity of sulfur dissolved in liquid steel, according to data, it is allowed to use values of interaction parameters:

\[
\lg \gamma[S] = \sum_{i=1}^{n} e^i_S \times [X_i] = e^1_S \times [X_1] + e^2_S \times [X_2] + \cdots + e^n_S \times [X_n]
\]

(2)

where \(e^i_S\) – parameter of interaction of corresponding metal element with sulfur, \(X\) – content of element in liquid iron, %.

According to data of [1, 21, 22] the content of FeO in metal and slag is one of the main factors determining the value of \(L_S\):

\[
L_S \approx \frac{1}{P_{(O_2)^{0.5}}}
\]

The higher oxidation potential of medium, the smaller \(L_S\), but this potential corresponds to the content of oxygen in the metal \([O]\), i.e. \(L_S\) depends on oxidation of the metal. Thus, oxygen in form of oxide (FeO) in slag, and oxygen in metal \([O]\) significantly reduce degree of desulfurization.

Sulfide capacity of slag \(C_S\) is one of the most important characteristics of refining property of the slags applied during extra-furnace steel processing. This value is determined as function of slag temperature and composition, i.e. this value is experimentally determined and thermodynamically evaluated.

One of the factors influencing on sulfide capacity is temperature of the process. Influence of the temperature on dependence of the sulfide capacity on the optical basicity was covered in the paper [21]. The data are provided in Figure 1.
Mathematical charts may be described using equation (3), with temperature intervals 1400–1650 °C and at optical basicity Λ not more than 0.75, error of provided formula is not more than 6 %.

\[
\log C_S = 14.3 \times \Lambda - 7.01 - \frac{9900.1}{T}
\] (3)

Optical basicity, which is characterized as the ability of oxygen anions which present in slag to give their electrons to ion acceptors (ions collected by probes [16–19]), is most often used as a criterion of basicity of oxide melts. For pure oxides, optical basicity (Λ) is connected with electronegativity of elements according to Poling (\(X_i\)) by the following ratio:

\[
\Lambda = \frac{1}{1.36 \times (X_i - 0.26)}
\] (4)

Earlier papers identified that optical basicity of oxide Λ is connected with electronegativity of cation according to Poling (\(X_i\)) by the following expression:

\[
\Lambda = \frac{0.75}{(X_i - 0.26)}
\] (5)

Use of equations 4 and 5 allows obtaining optical basicity for any multi-component systems consisting of nontransition (nonamphoteric) metals according to the following ratio:

\[
\Lambda = \sum_{i=1}^{n} (X_i \times \Lambda_i) = X_{MO_1} \times \Lambda_1 + X_{MO_2} \times \Lambda_2 + \cdots + X_{MO_n} \times \Lambda_n
\] (6)

where \(X_i\) – equivalent fraction of anions introduced by this component; \(\Lambda_i\) – optical basicity of system component.

Optical basicity of main, acid and amphoteric oxides is determined. However, we found that Al\(_2\)O\(_3\) may show both main and acid properties, i.e. optical basicity of this oxide will change depending on the slag composition, respectively.

The metallurgical slags built up in the steel-pouring ladle of the ladle-furnace unit contain oxides that absorb ‘free’ oxygen anions, such as SiO\(_2\), to form a complex anion SiO\(_4^{2-}\), and also contain amphoteric oxides, which can act both as donors and absorbers of free oxygen ‘anions’. These parameters in classical formula 5 are not taken into account.

To determine optical basicity on the basis of the calculation formula (7) proposed by us, it is necessary to add together main oxides (m.o.) and subtract acid oxides (a.o.), influence of amphoteric oxide Al\(_2\)O\(_3\) is taken into account additionally.

\[
\Lambda = (\sum_{i=1}^{n} (X_i \times \Lambda_i))_{\text{m.o.}} - (\sum_{i=1}^{n} (X_i \times \Lambda_i))_{\text{a.o.}} + X_{Al_2O_3} \times \Lambda_{Al_2O_3}
\] (7)
3. Research results

In the steel-pouring ladle of the ladle–furnace unit (LFU) free-running highly basic slags with the following chemical composition are built up (Table 1):

Table 1. Composition of liquid state of slag of the ladle-furnace unit.

| Values   | CaO  | SiO₂ | Al₂O₃ | MgO  | FeO  | MnO  |
|----------|------|------|-------|------|------|------|
| Range    | 45.0–61.9 | 10.0–30.2 | 1.8–29.6 | 2.1–9.8 | < 1.0 | < 1.0 |
| Medium   | 54.0 | 22.1 | 13.5  | 7.3  | –    | –    |

To determine the influence of amphoteric oxide Al₂O₃ on the final value of optical basicity ($\Lambda$), calculated by the formula (7), the melting parameters fixed on the ladle furnace unit were analyzed. The array of data was calculated for each melting: sulfur partition coefficient between metal and slag ($L_{SPRACT.}$); coefficient of activity of sulfur in the metal ($\gamma_{[S]}$); oxidation potential of medium $p^{0.5}_{O_2}$; reaction equilibrium constant of partition of sulfur between metal and slag ($K_S$); sulfide capacity of slag ($C_S$). Moreover, calculation of sulfide capacity was performed in compliance with the conditions of $L_{SPRACT.}=L_{STHEORET.}$, through variation of the optical basicity of oxide Al₂O₃ ($\Lambda_{Al_2O_3}$). Array of input data and results of calculation are provided in Table 2, influence of content of Al₂O₃ in the homogeneous constituent of slag on the optical basicity is shown in Figure 2.

Table 2. Indicators of analyzed processes of melting performed by the ladle-furnace unit and results of the calculation.

| $T$, °C | $L_S$ | $C_s$ ×10³ | $\gamma_{[S]}$ | $K_s$ | $P_{O_2}$×$10^8$ | $\Lambda_{Al_2O_3}$ | Composition, % wt. |
|---------|-------|-------------|----------------|-------|------------------|-------------------|------------------|
|         | actual| calculated  |                |       |                  |                   |                  |
| 1557    | 11.11 | 11.88       | 0.10           | 1.05  | 390.73           | 2.27              | 0.50             |
| 1553    | 16.33 | 18.80       | 0.13           | 1.06  | 394.80           | 1.80              | 0.47             |
| 1589    | 28.04 | 28.72       | 0.37           | 1.06  | 360.20           | 3.75              | 0.44             |
| 1574    | 26.32 | 34.89       | 0.36           | 1.06  | 374.07           | 2.89              | 0.38             |
| 1576    | 27.53 | 32.82       | 0.32           | 1.06  | 370.73           | 2.66              | 0.34             |
| 1557    | 25.23 | 29.49       | 0.21           | 1.06  | 390.73           | 1.96              | 0.34             |
| 1583    | 40.39 | 40.52       | 0.43           | 1.03  | 365.65           | 3.01              | 0.33             |
| 1591    | 12.00 | 13.15       | 0.28           | 1.01  | 358.40           | 5.91              | 0.33             |
| 1557    | 23.31 | 27.34       | 0.23           | 1.05  | 390.73           | 2.27              | 0.31             |
| 1582    | 30.78 | 31.65       | 0.52           | 1.17  | 366.58           | 5.28              | 0.20             |
| 1558    | 20.05 | 20.18       | 0.16           | 1.06  | 389.72           | 2.11              | 0.20             |
| 1581    | 19.07 | 20.20       | 0.44           | 1.17  | 367.50           | 6.94              | 0.16             |

Figure 2. Dependence of optical basicity on the content of Al₂O₃ in the homogeneous constituent of slag.

Presented data show that with an increase in the content of Al₂O₃ in slag, the optical basicity of this oxide decreases. It can be determined by the following expression:
\[ \Lambda_{\text{Al}_2\text{O}_3} = 1.65 \times e^{-0.090B \times X} \]  (8)

where \( \Lambda_{\text{Al}_2\text{O}_3} \) – optical basicity of oxide \( \text{Al}_2\text{O}_3 \); \( X \) – content of oxide in homogeneous constituent of metallurgical slag; \( e \) – base of the natural logarithm.

Therefore, optical basicity for heterogeneous slags built up using steel-pouring ladle of the ladle–furnace unit may be determined by the following expression:

\[ \Lambda = \left( \sum_{i=1}^{n} (X_i \times \Lambda_i) \right)_{\text{m,a}} - \left( \sum_{i=1}^{n} (X_i \times \Lambda_i) \right)_{\text{a,o}} + 1.65 \times e^{-0.090B \times X} \]  (9)

where \( X_i \) – equivalent fraction of anions introduced by this component; \( \Lambda_i \) – optical basicity of system component; \( X \) – content of oxide in homogeneous constituent of metallurgical slag.

The optical basicity level determines sulfide capacity of slag, sulfur partition coefficient between metal and slag and, as a result, content of sulfur in metal.

4. Conclusion

Thus, metal desulphurization in ladle steel treatment units is achieved, first of all, due to the transition of sulfur to the slag phase. Coefficient of partition of sulfur between metal and slag is affected by sulfide capacity of slag, coefficient of activity of sulfur in the metal, oxidation potential of medium and reaction equilibrium constant of partition of sulfur between metal and slag. Temperature of liquid state in the ladle has significant impact on sulfide capacity of slag. Proposed calculation procedure based on provisions of ionic structure of slag allows to evaluate concentration of sulfur in steel on the basis of determination of coefficient of its partition between metal and slag. Optical basicity is suggested as criterion of refining property of the slag, it has been shown that the amphoteric oxide \( \text{Al}_2\text{O}_3 \) is essential to calculation of this indicator.

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