METAL DESULPHURIZATION DURING STEELMAKING PROCESSES

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Abstract

The world trend of steelmaking forwards to economical steel production with continuously increasing demands on the quality of produced steel. This fact causes increasing production of micro alloyed steel at the expense of production of conventional steel. At the same time outgoing in forefronts ecological aspects related with steelmaking. These serious demands can be possible meet only using of properly functioning slag system in the metallurgical reactors. In all of these reactors, desulphurization depends on temperature, amount of oxygen and sulphur in the metal, but mainly on chemical composition and physical properties of slag. Metallurgical slag parameters must be defined using the complex of physical and chemical characteristics as an oxidation potential, optical basicity, sulphide capacity and sulphur distribution coefficient. A requirement for effective desulphurization is also the minimum amount of easy reducible oxides in the slag. There are many correlations that can describe the slag desulphurization capability, where their functional dependency on each other we can formulate.

Keywords: Steel, desulphurization, sulphur distribution coefficient, sulphide capacity

1. INTRODUCTION

Nowadays is steelmaking aimed mainly on improving the quality, effectiveness and competitiveness of its production. The analysis of thermodynamic possibilities of steel desulphurization by the distribution of steel between liquid steel and slag is often based on mathematical apparatus using slag optical basicity. The optical basicity in combination with the level of metal oxidation and activity of sulphur and temperature makes possible this process to be well managed. To have effective metallurgical technologies based on the interaction between metal-slag under control, it also means increasing of slag contribution on these aspects. Both slag and synthetic powders must be up to standard with required physical and chemical properties as mainly melting temperatures, viscosities and surface tensions. But also with chemical properties as oxidation or reduction ability, basicity, ability to absorb impurities, sulphide and phosphate capacity and so on. These properties depend mainly on the chemical composition of slag phase, but also on other conditions of given technology.

2. MATERIALS AND METHODS

The practical examples of application are interactions in system metal-slag during pig iron desulphurization, during refining in melting reactor and during secondary steelmaking processes. Some of them can we can evaluate in form of following equations:

$$[Me] + [S] = (MeS) \tag{1}$$

$$(CaO) + [S] = (CaS) + [O] \tag{2}$$

where:

(CaO), (CaS) a (MeS) are components dissolved in slag,

[S] and [O] are components of metal.

It is possible to formulate the thermodynamic sulphur distribution coefficient using equilibrium constant of the considered reactions. In the case of steelmaking slag, the value of sulphur distribution coefficient usually increases with CaO content in slag which, represents the exact measure of slag basicity and with the decreasing oxygen activity.

The optical basicity still remains not frequently used as a parameter in steelmaking practice, however using this characteristic of the complex nature; it is possible to describe various metallurgical properties of slag with high accuracy. The problem is that slag is not often in balance with the liquid metal. Therefore, the relationship among individual parameters may be traced with complications only. Moreover, the general relationship between this parameter and other metallurgical parameters are not so well known.

The slag sulphidical capacity dependency on the gaseous or metal phase we may formulate as:

$$(O^{2-}) + \tfrac{1}{2}\{S_2\} = (S^{2-}) + \tfrac{1}{2}\{O_2\} \tag{3}$$

$$C_s = (\%S^{2-})\sqrt{\left\{\frac{P_{O2}}{P_{S2}}\right\}} = K_O \frac{a_O^{2-}}{f_S^{2-}} \tag{4}$$

System slag - metal:

$$[S] + (O^{2-}) = (S^{2-}) + [O] \tag{5}$$

$$C_S^{'} = (\%S^{2-})\frac{a_{[O]}}{a_{[S]}} = K_O \frac{a_O^{2-}}{f_S^{2-}} \tag{6}$$

The sulphur distribution between slag and metal may be formulated using sulphur distribution coefficient L_S:

$$L_S = \frac{(\%S)}{[\%S]} = \frac{K_O a_{O^{2-}} f_{[S]}}{a_{[O]} f_{S^{2-}}} \tag{7}$$

where:

$a_{[O]}, a_{[S]}$ - oxygen and sulphur activity in liquid metal,

a_O^{2-}, a_S^{2-} - oxygen and sulphur ions activity in slag,

$(\%S^{2-})$ - weight % of sulphur in slag,

P_{O2}, P_{S2} - partial pressure of oxygen and sulphur in gaseous phase in balance with slag,

K_O - reactions equilibrium constants,

$f_{[S]}, f_S^{2-}$ - Henry´s activity coefficient of sulphur in metal and slag.

It is possible to determine L_s from known thermodynamical data of oxygen and sulphur dissolution in liquid metal using C_s. The sulphur distribution coefficient L_s is not the only function of slag composition but also depends on the oxygen activity in metal and also on the chemical composition of the metal. Experimental estimation of C_s is rather difficult and therefore new possible solutions of using optical basicity are tested. In literature [1] is given this equation:

$$\log L_S = \log C_S + \sum \%_j \, e_{[S]}^{j} - \log a_{[O]} - \frac{770}{T} + 1.303 \tag{8}$$

where:

$e_{[S]}^{j}$ - interaction coefficient of sulphur,

$\%_j$ - weight % of the third element.

From numerous models in literature [2,3,4], two models were selected. These models use the criteria of versatility in comparison to chemical compositions and close to the values of L_s, with real values of the investigated slag. According to [2]:

$$logC_S = \frac{22690-54640\Lambda}{T} + 43.6\Lambda - 25.2 \qquad (9)$$

and [3]:

$$logC_S = 14{,}2\Lambda - \frac{9894}{T} - 7.55$$

where:

Λ - optical basicity of the slag (10)

The values of the optical basicity can be calculated using data from [1].

In practice, they use a combination of the pig iron desulphurization with desulphurization in melting reactor, during tapping and finally in secondary steelmaking. The success of pig iron desulphurization is rather high which results from high sulphur activity and low oxygen content in the reaction system, however, is it influenced by slag removal after the desulphurization [5]. Various slag coagulators are used to improve possibilities of slag removal. The balance ratios during pig iron desulphurization we may express by this equation:

$$logK_{Mg} = \log\left(\frac{a_{MgS}}{p_{Mg}}.\frac{[S]}{f_S}\right) = \frac{22750}{T} - 9.63 \qquad (11)$$

The boiling temperature of metallic magnesia is 1105 °C [6].

3. RESULTS

Holds that for a decrease of the negative impact of sulphur on steel properties in necessary to ensure its lowest possible contents in the final product. It is also important to ensure formation of sulphuric and oxy-sulphuric inclusions, as best in the globular form [7,8,9].

On **Figure 1** is shown progress in sulphur content in full refining cycle: blast furnace, pig iron desulphurization using metal magnesia, oxygen converter and secondary metallurgy using Scandinavian lancers system.

Nowadays exists numerous information in the area of the effectiveness of the pig iron desulphurization in the ladle. Desulphurization is realised using soda, calcium carbonate, lime and metallic magnesia [10]. The effect of the pig iron desulphurization with the mixture of highly sintered lime and metallic magnesia [11], in proportion 7:3 performed in the ladle, which show dependency of desulphurization level on desulphurization mixture consumption per tonne of pig iron in the **Figure 2**.

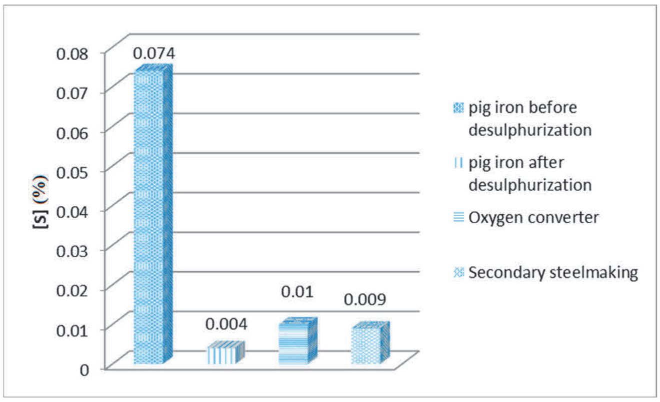

Figure 1 The progress in sulphur content

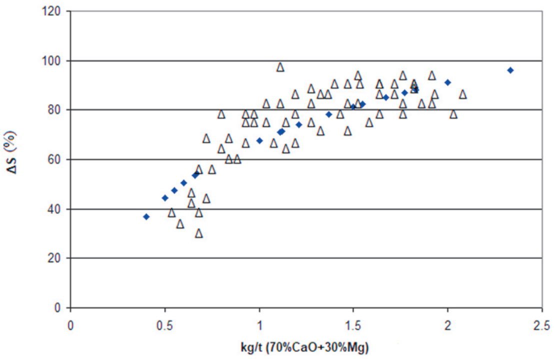

Figure 2 Dependency of desulphurization level

The high effectiveness and reproducibility of the desulphurization is conditioned by high sulphur activity in pig iron and low oxygen activity. It is important to remove the slag completely prior charging the metal to a converter with the objective to achieve the low sulphur content in the final product. The example of Fe-Mn-S sulphide inclusion in the final product after hot rolling is in the **Figure 3** and its EDX microanalysis is in the **Figure 4**.

Figure 3 Detail of sulphide inclusion

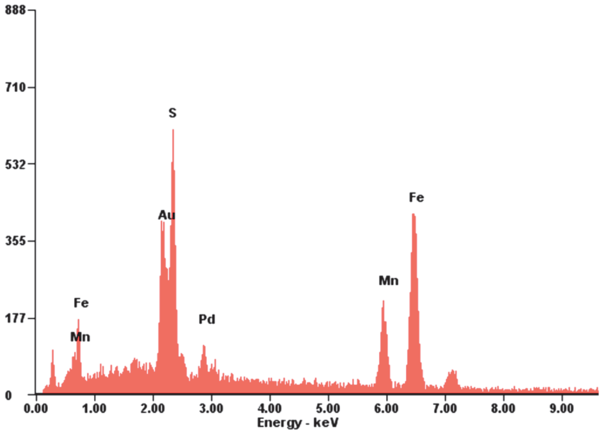

Figure 4 EDX microanalysis of the sulphide inclusion

A Very important factor that affect the process of metal desulphurization is the content of easily reducible oxides in slag [12,13]. An example of the influence of easily reducible oxides on sulphur distribution coefficient in ladle furnace is in the **Figure 5**.

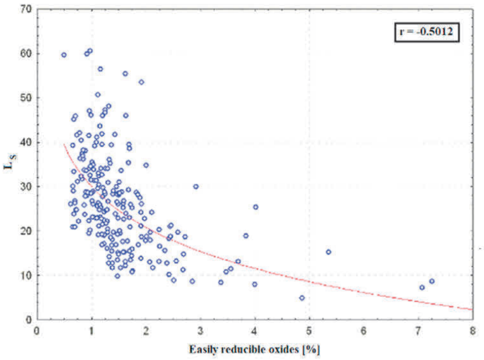

Figure 5 Relation of sulphur distribution coefficient on summary of easily reducible oxides SO

The analysis consists of 732 heats from oxygen converter and 594 heats from ladle furnace. Some parameters, as sulphur and oxygen activity in metal and slag sulphidical capacity, were assigned for individual stages [14].

Figure 6 shows values of sulphur activity in pig iron (BF), in crude steel from oxygen converter (L) and steel from ladle furnace (LF). High values of $a_{[s]}$ in pig iron are about its chemical composition, mainly on high content of carbon, silicium, which has an expressive positive level of interaction coefficients on sulphur. **Figure 7** shows values of sulphidical capacities of slag from blast furnace (BF), from oxygen converter (L) and ladle furnace (LF).

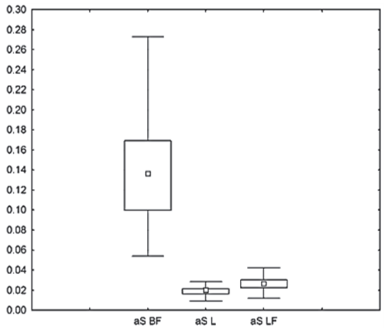

Figure 6 Values of sulphur activity

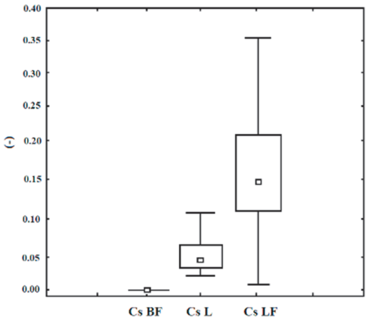

Figure 7 The values of sulphide capacities of examined slag

In **Figure 8** is the comparison of sulphur distribution between slag and metal in a ladle ($L_S´$) with theoretical sulphur distribution coefficient (L_S).

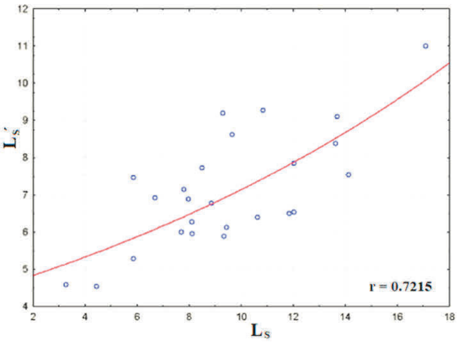

Figure 8 The comparison of sulphur distribution coefficient

To increase the value of sulphur distribution coefficient, it is necessary to increase the ion fraction of oxygen in slag and to reduce the oxygen content in the metal. Though this is more complex system defining the oxygen activity in the multi-component melt.

According to the equation (8), the sulphur distribution coefficient is a function of the slag sulphidical capacity, sulphur activity, the chemical composition of slag and metal, the activity of oxygen and temperature. As it is practically impossible to increase the metal desulphurisation simultaneously in the course of the metal oxidation refining applying the chemical composition of the metal. The main possibility of the desulphurization process control we can locate, though in rather limited range, in controlling of the slag chemical composition. Basic oxidising slag is having common composition always contain free oxygen anions. Therefore, the sulphur distribution coefficient between basic oxidising slag and metal in the course of converter process depend in particular on the calcium and silica oxides content, or on the slag basicity. It means that among the most profound tools enabling to assume the higher value of sulphur distribution coefficient at this stage of steel production is the reduction of SiO_2 content on the lowest possible value [15,16].

The role of FeO in the desulphurization process in basic oxidative slag may be of dual nature, with positive and negative effect on the steel desulphurization [17,18,19]. Ferrous oxide, as part of RO phase, affects the level of free oxygen ions in slag. Therefore also the value of sulphur distribution coefficient facilitates the lime dissolution and also positively affects the physical properties of slag. With increasing of the FeO content in slag, it rises oxygen content in metal, which is a negative effect.

4. CONCLUSIONS

In this paper were investigated the possibilities of application of parameter of optical basicity with other parameters related with metal desulphurization.

The analysis of the obtained relationship indicates certain difference following out from the design of model alone about the calculated parameters. There are the compositions of the metal and slag, temperature, but, in particular, the technology of individual stage of steelmaking. We obtained functions, based on chemical analysis of operational conditions, as well as the effect of the other significant factors. It enables their exploitations in the course of implemented operational technologies to affect the slag optimum composition from the point of the maximum steel desulphurization.

The process modelling, utilising the parameter of optical basicity, enables within the certain proximity, to balance the desulphurization possibilities under the change of chemical composition during steelmaking. This modelling is also useful in a combination of technology using three stages of desulphurization using the pig iron desulphurization. Desulphurization of crude steel in the course of tapping and desulphurization during secondary steelmaking process contributes to the low level of sulphur content in final steel.

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