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ISSN 0543-5846
METABK 47(4) 347-350 (2008)
UDC – UDK 669.14-418:539.37:620.17=111

DESULPHURIZATION OF STEEL AND PIG IRON

Received – Prispjelo: 2007-12-04
Accepted – Prihvaćeno: 2008-06-14
Preliminary Note – Prethodno priopćenje

Metallurgical slag qualities must be defined by the whole complex of physico - chemical characteristics, such as an oxidative ability, optical basicity, sulphide capacity up to slag fluidity, its surface tension etc. The understanding of regulation of basic physico - chemical qualities of molten metals and slag depending on a chemical structure and a temperature has its importance at the level of the metallurgical process control. Presented paper deals with the possibilities how to exploit the sulphidic capacity for the desulphurisation evaluation in course of the metal reafining in the oxygen converter based on the set of the operational data. The integral part of the work is the process of the pig iron desulphurisation.

Key words: slag phase, optical basicity, sulphide capacity,

Odsumporavanje čelika i sirovog željeza. Kakvoća metalurške troske je definirana kompleksom fizikalno-kemijskih karakteristika, kao što su oksidacijska sposobnost, optimalna bazičnost, sulfidni kapacitet, ali i tečljivost troske, površinska napetost itd. Poznavanje mogućnosti regulacije temeljnih fizikalno-kemijskih kakvoća tekućeg metala i troske ovisno o kemijskom sastavu i temperaturi osiguravaju vođenje metalurških procesa. U članku se daju mogućnosti kako rabiti sulfidni kapacitet za vrednovanje odsumporavanja tijekom rafinacije u kiskovom konvertoru pri danim pokazateljima. Članak je dopunjen i odsumporavanjem sirovog željeza.

Ključne riječi: troskova faza, optimalna bazičnost, sulfidni kapacitet, čelik, sirovo željezo

INTRODUCTION

The modern metallurgy of iron and steel is first of all oriented in quality improvement, effectiveness and competitiveness of its production. The implementation of new metallurgical technologies means, besides the expected effect in the production quality and price, also the rise in proportion of the slag phase on these aspects. Refining slag, protective and mould powders attract still more and more the interest of researchers and producers as well.

Slag and synthetic powders are to correspond to the requested physical and chemical properties, first of all by their melting temperatures, their viscosity and surface tension, but also by their chemical properties as the oxidative or reducing ability, basicity, ability to attract impurities, sulphide and phosphate capacity and so on. These properties depend first of all on the chemical composition of the slag phase, and also on further conditions defining the given technology.

The typical example represent the processes of interaction in the system metal – slag in course the pig iron desulphurisation, in course of refining in the refining reactor, in course of the ladle metallurgy. Some of them can be recorded in form of the following equations:

$$/Me/ + /S/ = (MeS) \quad (1)$$

$$(CaO) + /S/ = (CaS) + /O/, \quad (2)$$

where (CaO), (CaS) and (MeS) are the components dissolved in slag, and / S/ and /O/ are components of metal. It is possible to express the thermodynamic sulphur partition coefficient applying the equilibrium constant of the considered reactions. In case of the steel slag the value of the sulphur partition coefficient usually rises with the increased activity of CaO, which represents the exact measure of the slag basicity, and with the decreasing oxygen activity.

The slag optical basicity still remains not frequently used parameter in the steelmaking practice. However, using this characteristic of the complex nature, it is possible to describe various metallurgical properties of the metallurgical slag with high accuracy. The problem remains the fact that slag is frequently not in equilibrium with the metal melt. Therefore, the relationship among the individual parameters may be traced with complications only. Moreover, the general relationships among these parameters and other metallurgical indexes are not so well known.

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Slag desulphurisation capacity against the gaseous or metallic phase may be expressed as the slag sulphide capacity :

system slag – gas:

$$(O^{2-}) + ½\{S_2\} = (S^{2-}) + ½ \{O\}_2 \quad (3)$$

$$C_S = (\%S^{2-})*\{p_{O2}/ \ p_{S2}\}^{1/2} = K_{()}*a_O^{2-}/ \ f_S^{2-} \quad (4)$$

system slag – metal:

$$/S/ + (O^{2-}) = (S^{2-}) + /O/ \quad (5)$$

$$C'_S = (\%S^{2-})*a_{/O/}/ \ a_{/S/} = K_{()}*a_O^{2-}/ f_S^{2-} \quad (6)$$

Sulphur partition between slag and metal may be expressed using the sulphur partition coefficient L_S

$$L_S = (\%S) / /\%S/ = K_{()}*a_O^{2-}*f_{/S/} / a_{/O/}*f_S^{2-} \quad (7)$$

Where:

$a_{/O/}$, $a_{/S/}$ - oxygen and sulphur activity in molten metal,

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

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

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

$K_{()}$, $K_{()}$ - 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 thermodynamic data of oxygen and sulphur dissolution in molten iron using C_S. Sulphur partition coefficient L_S is not only the function of slag composition, but depends also on the oxygen activity in metal, i.e. also on the metallic phase composition. Experimental estimation of C_S values is rather toilsome and therefore they look for possible solutions when applied is the optical / theoretical/ basicity. In literature [1] there is given the relationship:

$$\log L_S = \log C_S + \Sigma\%_j*e^j_{/S/} - \log a_{/O/} - 770/T + 1{,}303 \quad (8)$$

where:

$e^j_{/S}$ - sulphur interaction coefficient

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

Two models were selected out of the numerous models provided in literature, based on the optical basicity, [2,3] applying the criteria of versatility in comparison to chemical compositions and close to the values of L_S, with the real values of the investigated slag. According to / 2 / :

$$\log C_S = (22690 - 54640\ \Lambda) / T + 43{,}6\ \Lambda - 25{,}2, \quad (9)$$

and /3 /:

$$\log C_S = 14{,}2\ \Lambda - 9894/ T - 7{,}55. \quad (10)$$

The values of the optical basicity may be calculated with the help of the data from reference /1/.

They use in many production units the combination of pig iron desulphurisation and subsequent desulphurisation in melting reactor, in course of steel discharging and sometimes even at the workshops of the ladle metallurgy.

The success of the pig iron desulphurisation is rather high. This fact follows out from the sulphur high activity and low oxidisation of the reaction system, however it is actually conditioned by the effectiveness of the slag removal after the desulphurisation. Various slag coagulators are applied with the objective to improve it.

The equilibrium conditions for the pig iron desulphurisation by magnesia may be expressed according to equation:

$$\log K_{Mg} = \log (a_{MgS/} / p_{Mg}*/S/*f_S) = 22\ 750/T - 9{,}63 \quad (11)$$

Metallic magnesia boils at the temperature of 1105 ^oC, [4].

RESULTS AND ANALYSIS

Generally holds that with the objective to eliminate the sulphur negative effect on the steel properties, it is necessary to assume systematically its possible least content in final product and to assume the formation of sulphuric and oxi–sulphuric inclusions – as the best in globular form. The limitation of the possibility to assume the metal "deep" desulphurisation within the individual units of the technology cycle under the conditions of the mass steel production, causes that the solution of the desulphurisation aspects ranks among the most complex problems of the practical metallurgy and frequently calls for the multiplied degrees of metal desulphurisation.

Recently, we have at our disposal numerous informations on the effectiveness of the pig iron ladle metallurgy desulphurisation. This is realised using soda, calcium carbonate, lime and metallic magnesia.

The effect of the pig iron desulphurisation with the mixture of highly sintered lime and metallic magnesia, in proportion 7:3 performed in the ladle is shown in Figure 1.

The melting temperature of magnesia is 651^{o}C, and its boiling point is 1105 ^{o}C, assume proper contact of the desulphurising media with the metal. Among the advantages rated can be not large volume of the formed slag and proper conditions of separate from iron. The high effectiveness and reproducibility of the desulphurisation is conditioned by high sulphur activity in pig iron

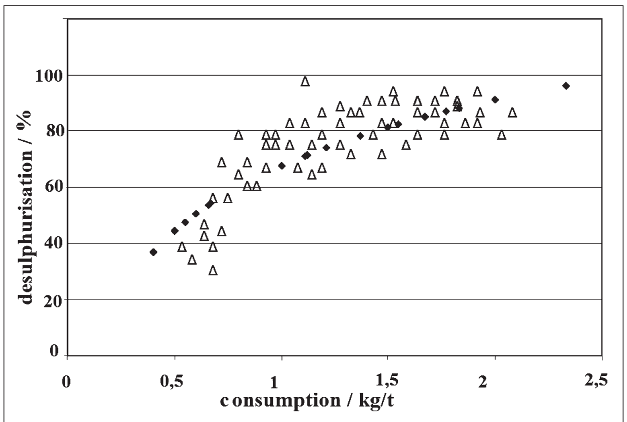

Figure 1. Course of degree of desulphurisation as depending on the desulphurisation mixture consumption per ton of pig iron.

and low melt oxidation. It is important to remove completely the slag prior charging the metal to converter with the objective to achieve the low sulphur content in the final product.

Essentially more complicated problem represents the primary desulphurisation in oxygen converter. The sulphur partition coefficient between slag and metal reaches rather law values – order in units, and besides the temperature, it is the function of the metal oxidation and ions proportion of oxygen in slag.

Figure 2. shows the course of the dependence of achieved sulphur partition between metal and slag taken from warranty set of heats.

Figure 3. shows the relationship of sulphur partition between metal and slag after heat blowing and reached

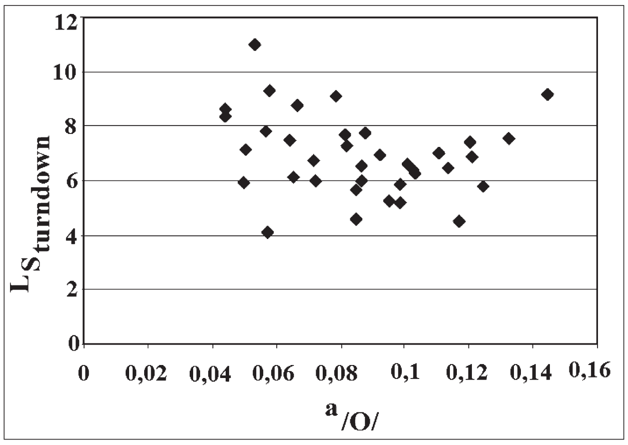

Figure 2. Course of sulphur partition between metal and slag after blowing period.

level of sulphur content in turndown analysis turndown analysis. The values scattering rises with the obtained desulphurisation level.

In general it is valid that in order to increase the value of the sulphur partition coefficient it is necessary to increase first of all the ion fraction of oxygen in slag and to reduce the oxygen content in metal, though this is a more complex system defining the oxygen activity in multi-component melt.

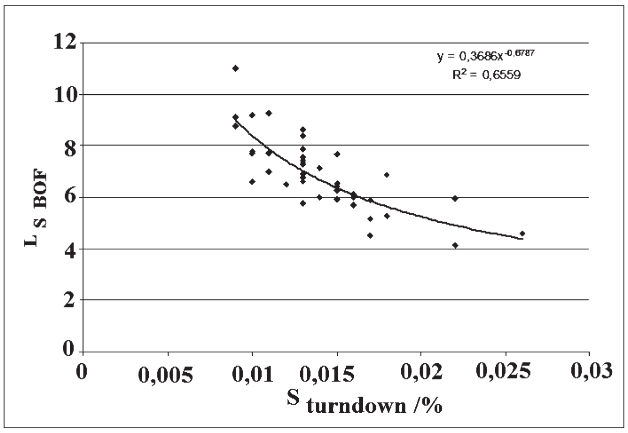

Figure 3. Relationship of the sulphur partition between metal and slag and sulphur content in sample.

According to the equation (8), the sulphur partition coefficient is a function of the slag sulphide capacity, sulphur, i.e. metal and slag composition, oxygen activity and temperature. Figure 4. presents the dependence of the slag sulphide capacity on the basicity of the investigated heats.

As, it is practically impossible to simultaneously increase the metal desulphurisation in course of the metal oxidising refining applying the chemical composition of metal, the principal possibility of the desulphurisation

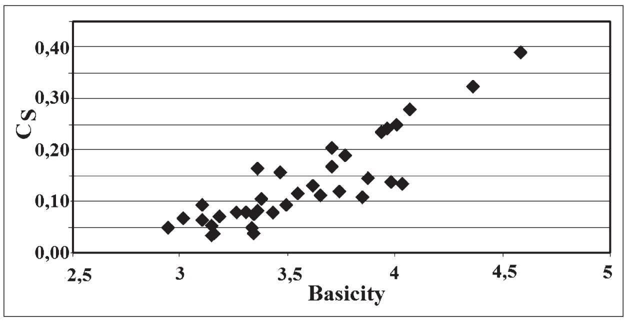

Figure 4. Relationship between slag sulphide capacity and basicity

process control lays, though in rather limited extend, in the control of the slag chemical composition. Basic oxidising slag having common composition contain always free oxygen anions, therefore the sulphur partition coefficient between basic oxidising slag and metal in 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 the sulphur partition coefficient in this stage of steel production is the reduction of SiO_2 content to the lowest possible value. Figure 5. presents the relationship between the sulphur partition coefficient and sulphide capacity for the investigated set of heats.

The role of FeO in the desulphurisation process in basic oxidative slags may be of dual nature, with positive and negative effect on the steel desulphurisation. Ferrous oxide, as part of RO phase, affects the level of free oxygen ions in slag, and therefore also the value of sulphur partition coefficient, facilitates the lime dissolution and also positively affects the slag physical properties. At the same time it holds, that as the FeO

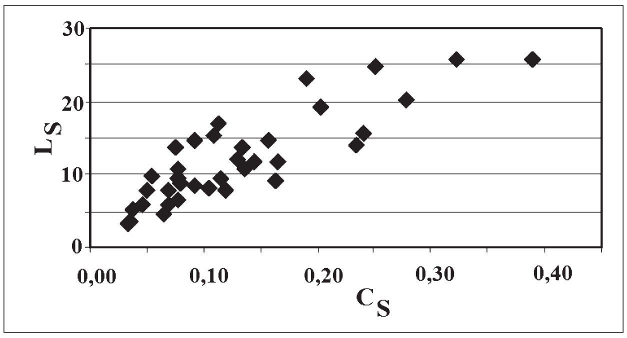

Figure 5. Relationship of the sulphur partition coefficient and the slag sulphide capacity.

content rises, so rises the oxygen content in metal. This fact will negatively influence the partition coefficient.

Comparison of sulphur partition between slag and metal in the oxygen converter with the sulphur partition coefficient calculated from equation (8) is presented in Figure 6.

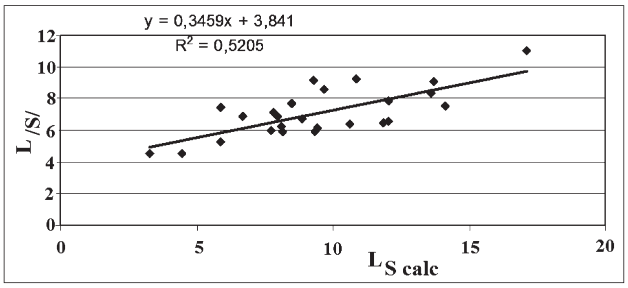

Figure 6. Comparison of sulphur partition between slag and metal in oxygen converter and values of sulphur partition coefficient

The analysis of the obtained relationship indicates certain differences following out from the design of model alone in relation to the calculated parameters. These are the composition of the metal and slag, temperature level, but in particular, the technology of the steel refining in oxygen converter alone. The obtained functions, based on the sampling and slag chemical composition analysis under operational conditions, as well as effect of other significant factors, enable their exploitation in course of implemented operational technologies in order to affect the slag optimum composition from the point of maximum metal desulphurisation.

CONCLUSIONS

Investigated was the possibility of the exploitation of the optic basicity parameter and subsequently the slag sulphide capacity for the slag regime optimisation when applied were the operational results from the steel production process in oxygen converters. Process modelling, applying the slag optical basicity, enables within the certain proximity, to balance the desulphurisation possibilities under the change of the slag chemical composition in oxygen converter, and also in the combination of the metal multistage desulphurisation technology using the means of the pig iron desulphurisation, desulphurisation carried out in the reactor with possible subsequent desulphurisation in course of steel discharging, or possibly in course of the ladle metallurgy and contribute in such a manner to the low level of sulphur content in final steel.

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Acknowledgement: This work has been supported by Scientific Grant Agency of Ministry of Education of Slovak republic and Slovak Academy of Sciences, grant. N^{o} VEGA. *1/3147/06*.

Note: The responsible translator for English language is Magdalena Repašová, Slovakia.