

UTILIZATION OF THE SECONDARY SUBSTANCES IN THE TECHNOLOGICAL ROUTES OF PRETREATMENT OF PIG IRON

Dobrovský L., Kopečný M., Kostiuková G., Dobrovská J.

Department of Physical Chemistry and Theory of Technological Processes, FMFI,

VŠB - Technical University Ostrava, Czech Republic

VYUŽITÍ DRUHOTNÝCH SUROVIN V TECHNOLOGIÍCH PŘEDÚPRAVY SUROVÉHO ŽELEZA

Dobrovský L., Kopečný M., Kostiuková G., Dobrovská J.

Katedra fyzikální chemie a teorie technologických pochodů, FMFI,

VŠB - Technická univerzita Ostrava, Česká republika

Abstrakt

V práci je věnována pozornost předúpravě surového železa s využitím odpadních surovin z metalurgických výrob. Je provedena teoretická analýza reakcí odsíření a odsfosfoření tavenin železa. Pro experimentální sledování byly připraveny modelové strusky s využitím podsítných podílů aglomerátu a ocelářských strusek. Provedené experimentální tavby potvrdily, že surové železo lze odsířit i zásaditou oxidační struskou, protože vysoký obsah uhlíku a křemíku udržuje nízkou aktivitu kyslíku v kovu. Dále bylo zjištěno, že jedině při nízkém obsahu křemíku lze účinně odsfosfořit taveniny železa.

Abstract

This work deals with preliminary treatment of pig iron by utilization of waste substances from metallurgical production. Theoretical analysis of the reactions of desulphurization and dephosphorization of iron melts is carried out here. Model slags with implementation of undersizes of sinter and of steelmaking slags were prepared. The experimental heats showed that pig iron could be desulphurized even by a basic oxidic slag because the high content of carbon and silicon keeps low activity of oxygen in the melt. In addition the efficient dephosphorization of the iron melt was found to be reached with low Si-content only.

Key words: preliminary treatment of pig iron, desulphurization, dephosphorization, slags

Introduction

The economical and environmental impacts are the reason for investigation into routes of outside-furnace pretreatment of iron melts even in the advanced countries having available well-

developed metallurgy. For example there is to mention the Kawasaki Steel [1] that makes intensive use of waste substances for modification of pig iron.

The heterogeneous reactions of desulphurization and dephosphorization of iron melts with the help of slag refining are influenced by numerous thermodynamical and kinetical factors. Moreover, under real conditions the attained degree of desulphurization and dephosphorization depends also on the full-scale possibilities.

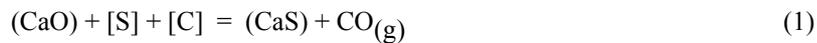
The outside-furnace refining of iron melts cuts especially down the content of phosphorus and sulphur. The pre-treatment of pig iron is a well-demanding task from the viewpoint of economy due to application of a selective slag for each of the mentioned elements.

In the framework of investigation into the GA ĀR project called The physico-chemical phenomena at refining of iron melts by slag there has been found out that dephosphorization of pig iron by a basic and strongly oxidic slag (some 38 wt-% of iron oxides) provided considerable drop in S-content [2].

This work is aimed at reasoning the experimental results of desulphurization and dephosphorization of iron melts by a basic oxidic slag in relation with the chemical composition of the metal melt. The chemical composition of the applied slags was modelled so that there is possible to use the waste substances from the steelmaking processes and/or the undersizes of sinter.

Theoretical

The reaction of desulphurization for pig iron, unlike to steel, can be expressed by the following equations [3-5]:



The equilibrium constants of the reactions (1) and (2) with indication of the S-content are written as follows:

In analogous way for Eq (2) there can be written

As can be seen the S-content varies with the content of carbon and silicon in the iron melt.

From the thermodynamics of equilibrium under conditions of permanent phase contact of metal-slag is obvious that the partition coefficient of sulphur is the function of sulphidic capacity of slag C_S and the activity of oxygen $a_{O/}$ in metal as follows:

(3)

Providing that the volume and basicity of slag are the same with all the heats then the C_S is constant and the desulphurization is governed by the activity of oxygen in liquid metal.

On the basis of such consideration the experimental heats were melted in which, with the help of chemical composition (content of C and Si) various activity of oxygen in iron melt has been modelled, namely, from approx. 1000 ppm down to almost 5 ppm.

The reaction of dephosphorization can be written as follows:



and for the equilibrium constant of Eq (4) with indication of P-content there is valid:

It is obvious that the P-content of the iron melt varies with the activity of oxygen and the calcium oxide in slag.

Experimental

Investigation into desulphurization of iron melts has been carried out in a medium-frequency induction furnace of the ISTOL-type. The principal data on the experimental heats and the achieved degree of desulphurization are listed in Table I. From the viewpoint of modelling the activity of oxygen in liquid metal the heats can be split into two groups. The first three series of heats (heat nos. 1-9) are characterized by a high activity of oxygen, the residual two series are featured by a low activity of oxygen.

Table I The principal data of the experimental heats of desulphurisation

The heats were melted in the following technological route: The metal-bearing charge weighing some 6 kg was melted down and kept at the temperature of 1873 K. The chemical composition was modified to the required values by addition of iron sulphide, manganese and ferrosilicon. After sampling for the purpose of analysing the basic oxidic slag was added, having the

following composition (wt-%): 55 CaO, 25 CaF₂, 20 FeO. The amount of slag was 10 kg per ton of charge. In order to examine the kinetics of sulphur transfer from metal into slag samples were taken in the course of each melting process to determine the percentage of the individual elements.

To investigate the efficiency of dephosphorization of iron melts the melting route in crucible with induction heating was chosen. The target was to compare the dephosphorization power of various sorts of synthetic slags. On the basis of a literary recherche some synthetic slags were prepared; the chemical composition of the individual slags is given in Table II. The composition of pig iron was as follows (wt-%): 4.8 C; 0.64 Mn; 0.15 P+ 0.011 S and the Si-content varied from 0.75 down to 0.031. The melting routes were as follows: Melting down of charge and enhancement of melt temperature up to 1773 K; then slags was charged in amount of 5 % to the weight of metal-bearing charge. In the course of any melting process samples were taken-off both for the sake of examination of the kinetics of P-transfer from molten metal into slag and for quantitative determination of content of the individual elements.

Table II Composition of synthetic slags used for experimental examination of dephosphorization

Results

The chemical composition of the metal-bearing charge was subjected to modelling so as to provide stability in high or low activity of oxygen in the course of the entire melting process. As was obvious from the theoretical analysis the partition coefficient of sulphur at constant sulphidic capacity C_S depends on the activity of oxygen in the metal bath. The experimental heats have confirmed this precondition to be true. In case of heats with a high content of carbon and silicon (low activity of oxygen) a degree of desulphurization of almost 75 % was reached in spite of some 20 wt-% FeO in the slag. On the other hand in heats with a very low content of carbon and silicon the degree desulphurization reached 12 %.

In this respect very low activity of oxygen in liquid metal should be kept in the course of entire process to attain a high degree of desulphurization in the iron melts. Accordingly, a high degree of desulphurization can be achieved even with application of a basic oxidic slag. This condition is fulfilled by the iron melts containing more than 1.5wt-% C and approx. 1 wt-% Si.

Figures 1, 2 and 3 illustrate examples of kinetic curves of desulphurization of heat-nos. 5, 9 and 13. As the heats were melted in induction furnace (low temperature of slag), the reaction time of desulphurization was longer.

Fig.1 Kinetic curve of desulphurization by basic oxidic slag (heat-no.5)

Fig.2 Kinetic curve of desulphurization by basic oxidic slag (heat-no.9)

Fig.3 Kinetic curve of desulphurization by basic oxidic slag (heat-no.13)

Figures 4, and 5 show the dependences of desulphurization of iron melts on the content of carbon and silicon. Figure 6 (multiple regression) illustrates the dependence of desulphurization on the content of the two elements. These dependences were evaluated from the acquired experimental results and there is uniquely obvious that the iron melts can be efficiently desulphurized even by basic oxidic slag when fulfilling the conditions cited above.

Fig.4 Desulphurization in relation with C-content

Fig.5 Desulphurization in relation with Si-content

$$Y = 12.244 - 2.515[\%C] + 55.183[\%Si] \quad I = 0.941$$

Fig.6 Desulphurization in relation with the content of carbon and silicon

Experiments have confirmed that the efficiency of dephosphorization varies significantly with the Si-content in iron melt. This outcome is confirmed even by the kinetic curves of dephosphorization, see Figs.7-9. The most relevant decrease in P-content with Si-concentration of about 0.02 wt-% was reached by slag marked G. At Si-concentration of about 0.03 wt-% the slag A provided a degree of dephosphorization of 76 %. The last figure (Fig.10) shows the multiple regression providing the dependence of P-content on time and on the Si-content. It was found out that addition of SiO₂ into slag is slightly diminishing the oxidation of silicium in pig iron.

Fig.7 Kinetic curve of dephosphorization after addition of 5 % slag A ([Si]_O = 0.751 %)

Fig.8 Kinetic curve of dephosphorization after addition of 5 % slag A ([Si]_O = 0.245 %)

Fig.9 Kinetic curve of dephosphorization after addition of 5 % slag A ($[\text{Si}]_{\text{O}} = 0.031 \%$)

$$[\%P] = 0.0977 - 5.0011 \cdot 10^{-5} t + 0.0950[\%Si] \quad I = 0.726$$

Fig.10 Dephosphorization in relation with Si-content and with time

Conclusion

In this work attention is devoted to desulphurization and dephosphorization of iron melts by means of slags prepared from waste substances.

For experimental examination of desulphurization of iron melts heats with various percentages of carbon and silicon were melted, whereby this content of carbon and silicon has provided permanently high and very low activity of oxygen. The composition of the desulphurizing slags was as follows (in wt-%): 55 CaO, 25 CaF₂, 20 FeO. The acquired knowledge has uniquely confirmed the activity of oxygen in liquid metal to be utmost significance for desulphurization of iron melts by means of slags, namely in conformity with the equation .

From the experiments of dephosphorization is obvious that pig iron containing about 0.7 wt-% Si cannot be efficiently dephosphorized. The most significant drop in P-content (by 76 wt-%) with Si-concentration of some 0.03 wt-% was reached by the slag A.

The chemical composition of the applied slags has been modelled so that even the waste substances from BOF-routes and/or sinter undersized with addition of lime or fluor spar could be utilized.

ACKNOWLEDGEMENT

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