DESIGN AND MODELLING OF FINAL STEEL DECARBURATION PROCEDURE THROUGH SELF-BUBBLING EFFECT

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Within the context of the Basic Oxygen Furnace (BOF), the decrease of the carbon concentration is certainly the chemical process ruling the conversion of pig iron into steel and to produce steel featured by a significant attitude to the deep drawing. At the end of the oxygen blowing and after the fulfilling of the chemical analysis the steelmakers have often to blow again to achieve the targeted low values of carbon concentration. The further blowing process implies a productivity loss and it is not usually strictly needed because the self-bubbling of the metal bath due to the CO formation can allow setting the carbon concentration within the required chemical range without a further oxygen blowing. Actually, due to the high temperatures and the value of the oxygen activity at the end of the blowing process, the decarburization process keeps moving up to the equilibrium. The present study describes and validates a thermodynamic-kinetic model that allow the steelmakers to forecast when the working conditions can avoid blowing again, thus exploiting the self-bubbling phenomenon. This action can increase the productivity and the working life of the refractories.

KEYWORDS: BASIC OXYGEN FURNACE – DECARBURATION - SELF-BUBBLING - THERMODYNAMIC MODEL

LIST OF SYMBOLS

a_x Raoultian activity of the x chemical species
p_x partial pressure of the x chemical species
t time (s)
τ_x characteristic constant time for the variable x
T temperature (K)
C carbon concentration
$C(t)$ carbon concentration at the time t
C_0 initial carbon concentration
C_{eq} carbon concentration imposed by the equilibrium with the oxygen activity and the temperature
$T(t)$ temperature at the time t
T_0 initial temperature
T_{env} environmental temperature (K)

INTRODUCTION

The present study is focused on the decarburization procedure performed through the self-bubbling that occurs during the tapping phase. The control of this phenomenon can provide interesting improvement in terms of productivity and protection of the oxygen converter refractories. The lowering of the carbon concentration can be achieved not only during the oxygen blowing, but also after its stop by the exploitation of the temperature decrease and of the concentration excess of the oxygen and of the carbon contained in the steel bath. The exploitation of this phenomenon, after the stop of the oxygen blowing, allows increasing the steel shop productivity and decreasing the refractory wear that is detrimentally affected by a longer time exposition to the high temperature imposed by the oxidation phenomena associated to the oxygen blowing. The bubbling phenomenon promoted by the combination of oxygen and carbon after the stop of the oxygen blowing and the tapping of the steel into the ladle permits to set the aimed carbon concentration and simultaneously to shorten the conversion time and the thermal exposure of the refractory lining [1-4].

The achievement of the carbon concentration imposed by the technical specification is a mandatory requirement to obtain hot steel at the end of the refining process. The production process is fulfilled by the

oxidation of the pig iron conversion and the following steel decarburization is carried out by the oxygen according to such a sequence that is synthetically summarized (Fig. 1): [5-10]
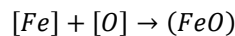
1. the direct oxidation of carbon at the metal surface in the hot spot:

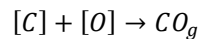$$[C] + \frac{1}{2}(O_2)_g \rightarrow CO_g$$
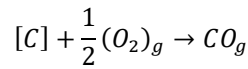
2. the indirect reaction between the iron oxide reacting with metal droplets formed within foaming mixed zone in the region surrounding the oxygen impinging zone, the metal surface and the slag:

$$[C] + (FeO) \rightarrow CO_g + [Fe]$$
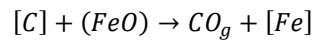
where FeO is a product of iron oxidation performed by a pure oxygen

$$[Fe] + [O] \rightarrow (FeO)$$

3. in the melt, a reaction between dissolved oxygen and carbon:

$$[C] + [O] \rightarrow CO_g$$

The thermodynamic equilibrium of these reactions indicates that they are favourable at high temperatures, because the high thermal level implies a maximization of the carbon removal and a minimization iron oxidation.
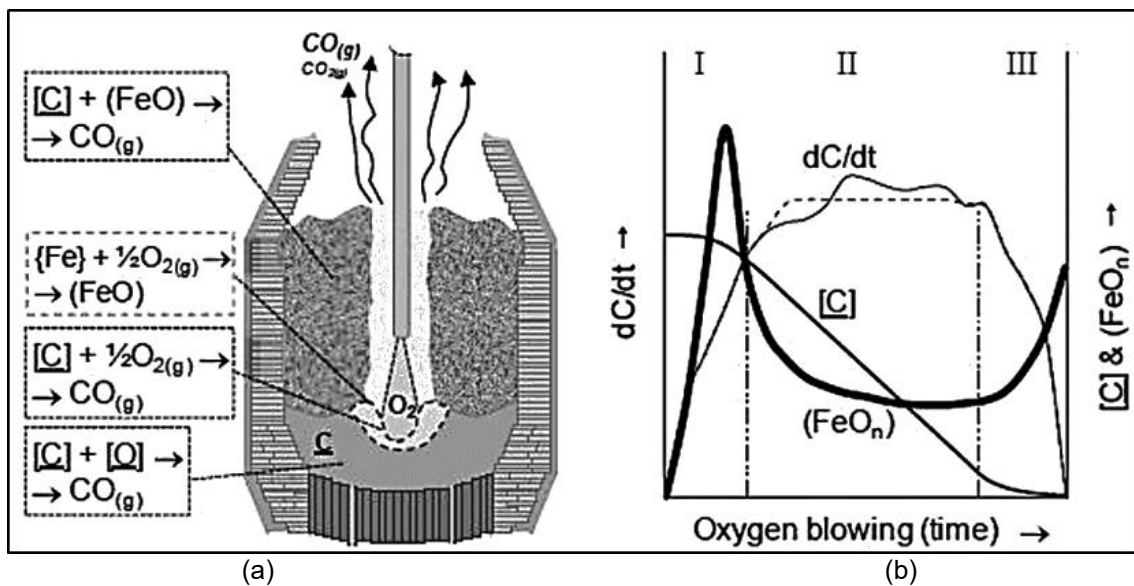

(a)   (b)

Fig. 1 - (a) Scheme of the decarburation process in a BOF, (b) the carbon and iron oxide concentration trend during the decarburation process (I) initial oxygen injection step (II) decarburation step (III) slowing down of the oxygen injection

As shown in Fig. 1, at the beginning of the process, the decarburization rate is low due to the oxidation of other elements (Si, Mn, Al) featured by a higher oxygen affinity. Moreover, in the opening minutes of the oxygen blowing procedure, the iron oxide droplets are projected into the slag and they do not participate to the reaction, so the decarburization rate is slowed.
After the first step, the maximum decarburization rate is reached and the described direct and undirect reactions take place. It is possible to note how the iron oxide influences the process: in fact, while the decarburization is at the maximum, the FeO_x decreases. The last stage of the blowing process occurs when the carbon concentration decreases below 0.1% and the rate of carbon removal is slowed by a tapering of the oxygen blowing, to avoid an excessive oxidation of the metal bath [11]. It has been demonstrated that for carbon concentration higher than 0.1% the decarburization process is governed by the oxygen flow, but below such a limit, the process is directly proportional to the bath stirring, assured also by the bottom introduction of argon or nitrogen [5,6,9,12,13].

Thus, the possibility to perform the decarburization by a self-bubbling phenomenon taking place after the end of the oxygen blowing and during the transfer of the ladle to the treatment plants represents a useful possibility.

The thermodynamic aspect of the self-bubbling process are well defined [12,14], because it lies mainly on the thermodynamic equilibrium between the activity of the dissolved oxygen and carbon present in the metal bath, but a good control of the process also by the automatic facilities of the plants needs a good comprehension of the kinetic aspects that have to be modelled and validated to design and build the control algorithm. The activities of this study have been focused on the construction of a thermodynamic and kinetic model to describe the self-bubbling (effervescence) of the metal bath after the tapping of the steel from the converter. The developed and described model has been validated and it is successfully applied in one of the largest European steel-shop using BOF.

DESIGN OF THE MODEL

Both the thermodynamic and kinetic aspects have been included in the model. The decarburization procedure by the self-bubbling phenomenon is fulfilled by the carbon oxidation developed by three fundamental stages: [5,15,16]

1. carbon and oxygen transfer to already present gas phases (usually formed on the porosity of the lining refractories). The presence of the already formed gas phases usually trapped within the porosity of the refractory lining is thermodynamically and kinetically favourable because it avoids the homogeneous nucleation step within the bulk of the liquid metal phase;
2. CO formation at the gas-metal interface;
3. CO transfer to the gaseous phase.

The reaction trend can be described through the variation of the chemical species as a function of the time according to the following differential equation:

$$\frac{d[X]}{dt} = -\beta \frac{A}{V}\left[[X] - [X_{eq}]\right] (1)$$

- where β is the transfer coefficient of the liquid bath;
- $\frac{A}{V}$ is a surface on volume ratio where V is the volume of the metal bath and A represents the overall area between the metal bath and the gaseous phases that are enriched by the formation of CO through the self-bubbling mechanism;
- X and X_{eq} are the current and the equilibrium concentration of the considered chemical species, i.e. carbon. It is possible to define the difference between these two concentration terms, $([X] - [X_{eq}])$ as the thermodynamic driving force of the chemical reaction.

The product $\beta \frac{A}{V}$ is the so-called characteristic time constant τ_C of the reaction, that represents the 62% of the time spent before arriving at the equilibrium concentration.

The integration of the equation (1) can be performed by the separation variable and under the hypothesis of an initial carbon concentration set at $\%C_0$ the relation can be defined as:

$$C(t) = \%C_{eq} + \left(\%C_0 - \%C_{eq}\right) * e^{\left(-\frac{t}{\tau_C}\right)} (2)$$

An analogous differential equation can be applied for studying the thermal evolution of the steel bath contained in the ladle:

$$\frac{d[T]}{dt} = -k\frac{A}{V}\left[[T] - [T_{env}]\right] (3)$$

- where k is the overall thermal conductivity of the system (ladle and molten steel);
- A is the overall exchanging area between the molten steel and the ladle;
- V is the overall volume of the molten steel;
- T_{env} represents the environmental temperature.

The relation (3) can be integrated by the separation variable method under the hypothesis of an initial temperature T_0 that is the measured temperature of the molten steel bath 5 s after the tapping:

$$T(t) = T_0 + (T_0 - T_{env}) * e^{\left(-\frac{t}{\tau_T}\right)} (4)$$

In this case τ_T is the characteristic time constant of the heat transfer, that represents the 62% of the time spent before cooling at the environmental temperature.

The environmental temperature, the initial temperature and carbon concentration of the steel bath at the tapping are known through the measurement after the end of tapping, but the carbon equilibrium concentration has to be estimated through the equilibrium relation,

$$K_{eq} = \frac{[a_C] \cdot [a_O]}{p_{CO}} \quad (5)$$

where p_{CO} is approximated at 1bar because during the described self-bubbling phenomenon nearly pure CO is formed and the equilibrium constant has been defined as: [5,17]

$$\log K_{eq} = -\frac{1160}{T} + 2.003 \quad (6)$$

The estimation of the temperature is a fundamental step to state the value of the equilibrium constant (6) used to compute the equilibrium value used for the reaction (5). For this reason, the temperatures were measured before the tapping. The model has been elaborated based on the historical data taken from several production trials of the low carbon steels (all the studied heats have been featured by a carbon concentration lower than 0.02%) and the model has been finally validated by a new experimental campaign. The experimental observations described in the following paragraph have allowed tuning the τ_T and τ_C characteristic parameters. The study has evaluated the carbon and temperature variation at finite time (from 0 to tapping time) for each heat and the aim has been to calculate the carbon reduction.

EXPERIMENTAL PROCEDURE
The current BOF converter is featured by a 320 t steel capacity and during the experimental campaign the average weight of each heat has been 318 t (±5.3 t). The ladle receiving the steel, where the temperature decreasing, and the effervescence promoted by CO bubbles takes place, is built by a 25 mm steel mantle for the lateral side and a 30 mm steel mantle for the bottom. The internal refractory lining is featured by a nominal internal thickness of 275 mm and the refractory is constituted by dolomite bricks used to allow the desulphurization treatment performed by the basic slag. The outer diameter at the bottom of the ladle is 3900 mm at the bottom and 4400 mm at the top and the ladle is 5600 mm high. The surface on volume ratio (S/V) of the steel contained in the ladle assumes an average value of 1.42 and this value is important for the definition of the thermal exchange and of the related characteristic time constant (τ_T) used in the equation to forecast the variation of the average temperature of the steel bath. The chemical composition of the scraps was sampled before to obtain the Al and other element content. The temperature and the carbon concentration have been measured 5 s just after the end of the steel tapping in the ladle and 10 s before the beginning of the desulphurization treatment (that is performed at the RH station). Neither deoxidiser (Al, Si), nor alloying elements such as ferromanganese or ferrosilicon have been added before the arrive at the desulphurization treatment otherwise the self-bubbling effect is not allowed. This procedure allows estimating the thermal and the carbon concentration evolution of the steel as a function of the different time of the transfer from the BOF converter to the secondary metallurgy treatments. All the observed heats have been featured by a final chemical composition characterized by a carbon concentration lower than 0.02% because these are the steel grades that can take a greater advantage from the self-bubbling phenomenon.
800 heats have been observed following the described experimental procedure to tune the model through the definition of τ_T and τ_C parameters; such values have been defined to minimize the difference between the measured and the forecast values of the temperature and of the carbon concentration to estimate the reliability of the built model. The actual value of $[C] \cdot [O]$ in % by weight was estimated at $5 \cdot 10^{-4} \pm 5 \cdot 10^{-5}$.

RESULTS
The tuning procedure has allowed defining the two characteristic time parameters for predicting the thermal and the carbon evolution of the molten bath:

$$\tau_C = 4 \cdot 10^3 \, s$$
$$\tau_T = 10^4 \, s$$

The variation of the temperature and of the carbon concentration assumed are ruled by a trend as a function of time that is imposed by the described equation (Fig. 2a and Fig. 2b).
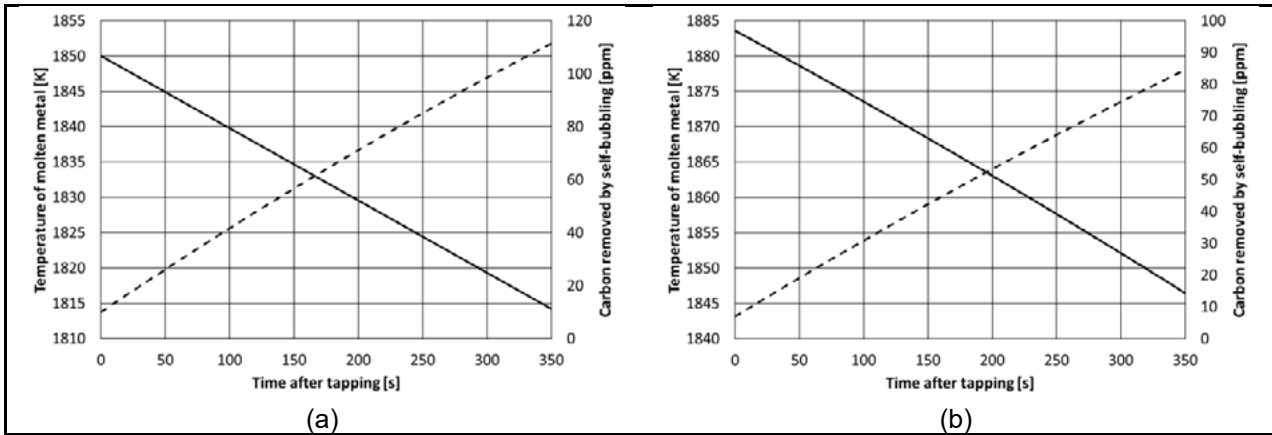
Fig. 2 - example of the trend pointed out by the temperature and by the removed carbon concentration as a function of time starting from an initial tapping temperature of 1853 K (a) and 1883 K (b)

The lower the starting temperature after the tapping, the higher the carbon removal by the self-bubbling phenomenon and this statement is due to the lowest equilibrium carbon concentration imposed by a lower temperature.

Apart from 18 heats, representing the 2.25% of the population sampled for the validation procedure, the predicting model as described appears robust and reliable as demonstrated by the comparison between the measured carbon concentration 10 s before the beginning of the desulphurization treatment and the estimated one (Fig. 3).
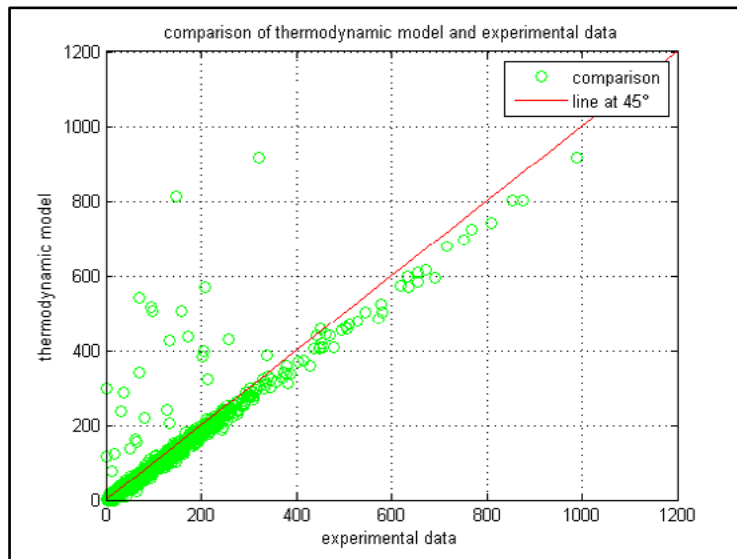

Fig. 3 - Comparison between the carbon removal forecast by the thermodynamic and kinetic model and the experimental data (ppm)

Thus, the self-bubbling effect (causing the effervescence in the ladle bath of the molten steel) can be exploited under a correct control supported by reliable algorithm in order to achieve the desired carbon concentration even for the heats that are featured by a carbon concentration higher than the maximum level at the end of the oxygen blowing.

CONCLUSIONS
In the performed study the thermodynamic and kinetic model has been developed in order to predict the carbon removal after the end of the oxygen blowing in the BOF converter. The thermodynamic component of the algorithm is based on the equilibrium constant between the carbon and the oxygen dissolved in the molten steel. The kinetic component has been obtained after the integration of two analogous differential equations describing the temperature and the carbon concentration variation as a function of time. The relations obtained by the integration of the differential equations depend on the values assumed by the two characteristic time constants for the temperature and for the carbon concentration that have been determined after a tuning trial that has involved 800 heats:

- the time constant for the temperature $\tau_T=10^4$ s;
- the time constant for the temperature $\tau_C=4\cdot10^3$ s.

This value can represent a first reliable estimation for the adaptation of the described algorithm to other industrial plant, but it is worth noting that they significantly depend on the shape of the ladle and on the volume of the charged molten steel, so a new tuning procedure could be used to obtain the reliable results shown in this study.

The exploitation of the self-bubbling (effervescence) phenomenon to remove the excess carbon concentration is a useful practice to increase the productivity and to decrease the refractory wear, because it can avoid to re-blow oxygen and to cause the consequent thermal increase.

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