Mechanisms and Modeling of Liquid Steel Decarburization below 10 ppm Carbon

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Steel grades for packaging or automotive industry applications require ultra low carbon levels and carbon contents below 10 ppm have to be obtained in the industrial decarburization reactor (tank degasser or vacuum circulation degasser, known as RH). In the ultra low carbon range (below 10 ppm in the vacuum vessel), the decarburization kinetics cannot be obtained from the analysis of metal samples but can be deduced from continuous exhaust gas analysis and flow rate measurements. This was done on an industrial RH-OB degasser and a reliable and precise measurement of reaction rates in the ultra low carbon range was obtained. The rate was evaluated by an overall volumetric coefficient of decarburization ak/S . A model of decarburization kinetics in vacuum vessel has been developed at IRSID based on a physical description of three different reaction sites: spontaneous CO boiling in metal layer just beneath bath surface where carbon and oxygen contents are in excess with respect to equilibrium CO partial pressure, decarburization by purging gas in zones where metal and injected gas bubbles are in contact and decarburization of metal drops projected in vacuum vessel by bubble bursting. The experimental results indicate that CO boiling is responsible for the largest part of decarburization, but, the decarburization of metal drops projected in vacuum vessel is dominating below 10 ppm. The dynamic modeling of the process describes simultaneously the evolution of vessel pressure, oxygen and carbon contents. It explains with very good accuracy the experimental results and is used to define optimal process parameters for industrial treatments.

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1. Introduction

Steel grades for packaging or automotive industry applications require ultra low carbon levels and carbon contents below 10 ppm have to be obtained in the industrial vacuum decarburization reactor.

Optimization of the industrial treatments requires a good knowledge of the decarburization mechanisms. The reaction kinetics has been modeled on the basis of a physical description of the reaction sites, for the two types of industrial reactor: tank degasser and vacuum circulation degasser, known as RH.

Specific trials were made in SOLLAC plants based on a reliable and precise measurements of reaction rates deduced from continuous exhaust gas analysis.

After a brief description of the basis of the model, this paper compares the calculated and experimental results obtained in the case of RH reactor, especially in the Ultra Low Carbon range (ULC).

2. Description of the RH-reactor

The schematic of the RH reactor is shown in Fig. 1. The RH has two legs or snorkels which go into the ladle.

The vacuum created by the pumping group provokes firstly the liquid metal rise in the vacuum vessel, then the pressure decrease required for the reaction and the suction of the produced gases.

Neutral gas (argon or nitrogen) is injected in the up-leg to create steel circulation between the ladle and the vacuum vessel. So, as steel is decarburized in the vacuum vessel, it is progressively replaced by metal with higher C and O contents coming from the ladle.

If required by the reaction, oxygen can be introduced into the vacuum vessel by tuyeres (RH-OB reactor).

Fig. 1 Schematic of RH-OB reactor.

3. Basis of the Model

The developed dynamic model simultaneously describes the evolution of the vessel pressure and the metal composition during the treatment. Three regions are considered (Fig. 2):

- (1) the volume of gas in the vacuum vessel and in the pumping group where pressure and composition are continuously varying throughout the treatment,
- (2) the volume of the vacuum vessel occupied by liquid metal which is the main site of decarburization reactions,
- (3) and the ladle which acts as a reserve of high C and O contents metal.

Fig. 2 Decomposition of the RH-reactor in three regions.

3.1 Steel circulation rate

Steel circulation rate between the vacuum vessel and the ladle essentially depends on the geometry (snorkels diameter, number and position of tuyeres) and on the gas flow rate injected in the up-leg.^{1,2)}

3.2 Mass balances

The numerical program solves the coupled equations system of mass balance in the three regions summarized in Table 1:

- (1) the vessel pressure evolution depends on the balance between entering gas namely injected neutral gas, CO gas emitted by the reaction and air leaks, and suction of them by the pumping group. The suction capacity of the pumping group, characteristic of the industrial installation, is given in the model as a function of the pressure;
- (2) the composition of metal in the vacuum vessel and in the ladle results from the mass balances between CO formation in the vacuum vessel due to pressure decrease, and the exchange of C and O between these two regions.

3.3 Reaction sites

Three mechanisms are responsible for carbon removal from the metal by CO production in the vacuum vessel: sponta-

neous boiling of CO inside the metal, forced decarburization by purging neutral gas injected in the up-leg and eventually in the tuyeres and degassing of metal droplets splashed by bubble bursting in the atmosphere under vacuum.

3.3.1 Spontaneous CO boiling

This mechanism concerns the metal layer in the vacuum vessel just beneath the free surface, in which the CO partial pressure in equilibrium with the metal exceeds the local ferromagnetic pressure (Fig. 3).

The general expressions of corresponding reaction rates are similar to those developed for decarburization in the vacuum tank degasser.³⁾

During the treatment, the depth of the metal layer concerned by this phenomenon varies with the vacuum level and the carbon and oxygen bath contents.

Note that they include an additive term of critical pressure necessary for bubble nucleation. With the taking into account of this term, a complete extinction of boiling can be observed at very low C content.

3.3.2 Forced decarburization produced by purging gas

The transfer of C and O elements between liquid metal and injected gas bubbles can be adequately represented using a mixed-control model.^{4,5)} It takes into account three steps (Fig. 4):

- (1) the liquid phase mass transfer of carbon,
- (2) the liquid phase mass transfer of oxygen,
- (3) the CO formation interfacial reaction itself.

The coupling between steps results in the determination of the equilibrium conditions at the bubble-metal interface (carbon and oxygen contents and CO partial pressure).

Table 2 resumes the used general expressions of reaction rates and the kinetics data (mass transfer coefficients and chemical reaction rate).

At a given bath composition, the amount of produced CO-gas mainly depends on the flow rate of injected gas, the injection depth and the pressure above the bath.

At given injection conditions, it decreases when the carbon content diminishes and it can be strongly affected by the presence of surface-active elements, such as oxygen and sulfur, in the bath (effect on the chemical reaction rate constant).

In simulated conditions, on the one hand, oxygen is found in large excess with respect of carbon and, on the other hand, the overall kinetics is essentially limited by liquid mass trans-

Table 1 Coupled equations system of mass balances in the three regions.

Reactor region	Mass balance	
Vacuum vessel	$\frac{dP}{dt} = \frac{101300}{V} (Q_{in} - Q_{out})$	(1)
Metal in vacuum vessel (Reactions zone)	$\frac{dC_{vacuum}}{dt} = \frac{Q_{metal}}{W_{vacuum}} (C_{ladle} - C_{vacuum}) - \frac{12/22.4}{W_{vacuum}} (Q_{boiling}^{CO} + Q_{purging}^{CO} + Q_{splashing}^{CO})$	(2)
Metal in ladle	$\frac{dC_{ladle}}{dt} = -\frac{Q_{metal}}{W_{ladle}} (C_{ladle} - C_{vacuum})$	(3)

P, V : Pressure and volume of vacuum vessel (Pa·m³).

Q_{in}, Q_{out} : Total entering gas (CO, argon, air) and exhaust gas flow rates (Nm³·s⁻¹).

C_{ladle}, C_{vacuum} : Metal C-contents respectively in vacuum vessel and in ladle (mass-ppm).

W_{ladle}, W_{vacuum} : Metal weights respectively in vacuum vessel and in ladle (kg).

Q_{metal} : Metal recirculation rate between ladle and vacuum vessel (kg·s⁻¹).

$Q_{boiling}^{CO}, Q_{purging}^{CO}, Q_{splashing}^{CO}$: CO gas flow rates respectively generated by CO boiling, gas purging and metal splashing (Nm³·s⁻¹).

port of carbon.

3.3.3 Splashing droplets decarburization

When a bubble injected or produced in the metal bath reaches the free surface, it bursts and projects small liquid

Fig. 3 Schematic of the CO boiling phenomenon.

Fig. 4 Schematic of the three elementary steps of the mixed-control model for gas purging phenomenon.

Table 2 General expressions of reactions rates in the mixed-controlled model of decarburization by gas purging phenomenon.

Liquid phase mass transfer

carbon atomic flow rate across the unit area of interface

$$\dot{n}_C = k_{mC} \cdot \frac{\rho_M}{121000} \cdot ([C] - [C]^m) \text{ in mol C} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \quad (1)$$

oxygen atomic flow rate across the unit area of interface

$$\dot{n}_O = k_{mO} \cdot \frac{\rho_M}{161000} \cdot ([O] - [O]^m) \text{ in mol O} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \quad (2)$$

driving force=difference of C and O contents between the interface and the metal bulk

$[C] - [C]^m$ in mass ppm and $[O]^i - [O]^m$ in mass ppm

Mass transfer coefficient

$$k_{mC} = 0.59 \cdot \left(D_C \cdot \frac{u_{\text{bubble}}}{d_B} \right)^{\frac{1}{2}} \text{ and } k_{mO} = 0.59 \cdot \left(D_O \cdot \frac{u_{\text{bubble}}}{d_B} \right)^{\frac{1}{2}} \quad (3)$$

Interfacial kinetics

CO molar flow rate across the unit area of interface

$$\dot{n}_{CO} = \frac{k_C}{101300} \cdot (P_{CO}^B - P_{CO}^i) \text{ in mol CO} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \quad (4)$$

driving force=difference of CO equilibrium partial pressure between the interface and the bubble

$P_{CO}^i - P_{CO}^B$ in Pa

Chemical reaction rate constant⁽⁶⁻⁸⁾

$$k_C = \frac{k_{CO}}{1 + 770 \cdot a_{[O]} + 620 \cdot a_{[S]}} \quad (5)$$

$k_{CO} = 1.48 \cdot 10^{-6} \text{ mol CO} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1}$ for pure iron at 1600°C⁽⁹⁾

Coupling of three steps: $\dot{n}_C = \dot{n}_O = \dot{n}_{CO}$

ρ_M : Density of metal (kg·m⁻³).

u_{bubble}, d_B : Bubble relative velocity in metal (m·s⁻¹), bubble diameter (m).

D_C, D_O : Diffusion coefficients of carbon and oxygen in the metal (m²·s⁻¹).

$a_{[O]}, a_{[S]}$: Activity of oxygen and sulfur in liquid metal (—).

metal droplets in the atmosphere. These droplets, exposed to a vacuum, are decarburized similarly to CO boiling mechanism.

After literature⁽¹⁰⁻¹²⁾ the amount of splashed liquid metal depends on injection conditions (total gas flow rate crossing the bath surface, bubble size) and on physical properties of the two phases, particularly liquid metal viscosity and interfacial tension.

From macroscopic point of view, a linear relation between splashed metal and gas flow rates can be used. The proportionality constant is considered as an adjustable parameter of the model.

4. Results-Discussion

4.1 Industrial trials

Using specific industrial trials in the SOLLAC-Dunkirk RH-OB⁽¹³⁾ led to obtaining the curves of variations of the vessel pressure and the flow rate and composition of the exhaust gases during decarburization treatment. The evolution of the metal carbon content deduced from these gas measurements was validated by chemical analysis on metal samples.

Figure 5 presents the good agreement between experimental evolution of pressure and C-content and those predicted by the model.

4.2 Model validation

Figure 6 shows the distribution of the calculated instantaneous CO flow rate emitted by the bath according to the three mechanisms of boiling, purging and splashing:

- (1) at the beginning of the treatment, a delay is observed in CO emission with respect to the pressure decrease and the metal rise in the vacuum vessel,

Fig. 5 Comparison between experimental evolution of pressure and C-content and those predicted by the model.

Fig. 6 Effect of the three mechanisms of decarburization (boiling, purging and splashing) on the emission of CO during the treatment. (a) distribution of the calculated instantaneous CO flow rate emitted by the bath in mol.s⁻¹. (b) distribution of the calculated instantaneous CO flow rate due to each mechanisms in percent of the total CO flow rate emitted by the bath.

- (2) during most of the treatment, the CO boiling mechanism is responsible for the largest part of decarburization,
- (3) at the end of the treatment, with the decrease of carbon content, boiling mechanism is progressively going out and decarburization of metal droplets splashed in the vacuum vessel becomes dominating.

During the industrial trials, particular attention was paid to obtain precise and reliable measurements of the overall reaction rate in the ultra low carbon range.

Decarburization kinetics in the vacuum vessel, $\dot{n}_{CO}$ (mol.s⁻¹), is usually expressed¹⁴ as the product of an overall volumetric coefficient, ak/S (m.s⁻¹), at the bath surface, S (m²), and the excess of carbon content in liquid metal relatively to equilibrium with the atmosphere under vacuum, $C_{vacuum} - C_{eq}$ (mol.m⁻³), according to:

$$\dot{n}_{CO} = ak(C_{vacuum} - C_{eq}). \quad (1)$$

Knowing the metal circulation rate between the ladle and the vacuum vessel, the instantaneous values of ak/S and carbon content in the vacuum vessel were deduced from gas analysis results. Figure 7 presents the resulting evolution of ak/S versus C_{vacuum} obtained for two different injected gas flow rates:

- (1) out of the ultra low carbon range, the more C-content diminishes during treatment, the smaller is the observed ak/S , corresponding to the progressive extinction of boiling phenomenon,
- (2) in the ultra low carbon range (below 10 ppm), ak/S becomes independent of carbon content and seems to be proportional to total gas flow rate crossing bath surface. This first order overall kinetics relatively to the carbon content is coherent with a decarburization regime domi-

Fig. 7 Evolution of ak/S versus C_{vacuum} . The symbols represent industrial measurements with two different injected gas flow rates. The curves are resulting from model calculations.

Fig. 8 Influence of total injected gas flow rate on decarburization kinetics in ultra low carbon range (below 10 ppm). The straight line represents the adjusted model law.

nated by the metal splashing phenomenon.

This assumption enabled to adjust, for all the heats of the campaign, only one value of the model parameter which links splashing metal rate and gas flow rate crossing the bath surface (Fig. 7).

4.3 Discussion

In spite of the scatter obtained for the whole industrial trials, Fig. 8 confirms the effect of the total gas injected on the ak/S -value final level (below 10 ppm). A similar effect was previously observed on other industrial plants^{15,16} as shown in Fig. 8. Note that the ak/S -value range corresponding to very high gas flow rate tested by NSC, was estimated from published data.¹⁵

So, the main process control lever for improving the decarburization kinetics in the ultra low carbon range appears to be an increase of the total injected gas flow rate. Obviously injection of very high gas flow rates has to be compatible with the suction capacity of the pumping group in order to avoid a detrimental effect on kinetics of a vacuum pressure level increase.

5. Conclusion

A model of decarburization kinetics in vacuum vessel has been developed at IRSID based on a physical description of three different reaction sites: spontaneous CO boiling in the metal layer just beneath the bath surface, decarburization by purging gas in zones where metal and injected gas bubbles are in contact and decarburization of metal drops projected in the vacuum vessel by bubble bursting. The dynamic modeling of the process describes simultaneously the evolution of vessel pressure, oxygen and carbon contents.

Specific trials were done on the SOLLAC-Dunkirk RH-OB degasser in order to reliably and precisely measure the reaction rates. That was made by continuous exhaust gas analysis and flowrate measurements.

The results indicate that CO boiling is responsible for the largest part of decarburization, but, below 10 ppm, the decarburization of metal drops projected in vacuum vessel is dominating.

Note that Ultra Low Carbon levels of about 6–8 ppm are currently achieved on this industrial reactor with normal process conditions.

The validate model is used to:

- (1) evaluate the effect of operating parameters (initial C and O contents, neutral gas flow rates injected in snorkel and vacuum vessel, grading during vacuum treatment, . . .),
- (2) define standard treatment conditions (treatment time, additions pattern, . . .) for obtaining the desired steel composition,

- (3) define required new equipment characteristics (vacuum system, . . .) or new operating conditions (oxygen-blowing, . . .).

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