A Mathematical Model for Reactions during Top-Blowing in the AOD Process: Validation and Results

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Abstract

In earlier work, a fundamental mathematical model was proposed for side-blowing operation in the argon-oxygen decarburization (AOD) process. In the preceding part "Derivation of the Model", a new mathematical model was proposed for reactions during top-blowing in the AOD process. In this model it was assumed that reactions occur simultaneously at the surface of the cavity caused by the gas jet and at the surface of the metal droplets ejected from the steel bath. This paper presents validation and preliminary results with twelve industrial heats. In the studied heats, the last combined-blowing stage was altered so that oxygen was introduced from the top lance only. Four heats were conducted using an oxygen-nitrogen mixture (1:1), while eight heats were conducted with pure oxygen. Simultaneously, nitrogen or argon gas was blown via tuyères in order to provide mixing that is comparable to regular practice. The measured carbon content varied from 0.4–0.5 wt-% before the studied stage to 0.1–0.2 wt-% after the studied stage. The results suggest that the model is capable of predicting changes in steel bath composition and temperature with a reasonably high degree of accuracy. The calculations indicate that the top slag may supply oxygen for decarburization during top-blowing. Furthermore, it is postulated that the metal droplets generated by the shear stress of top-blowing create a large mass exchange area, which plays an important role in enabling the high decarburization rates observed during top-blowing in the AOD process. The overall rate of decarburization attributable to top-blowing in the last combined-blowing stage was found to be limited by the mass transfer of dissolved carbon.

Keywords: stainless steelmaking, AOD process, top-blowing, mathematical modelling.

1   Introduction

The argon-oxygen decarburization (AOD) process is the most common process for refining stainless steel.[1] The gas blowing mixture is diluted with argon or nitrogen in order to decrease the partial pressure of the carbon monoxide, thus promoting the decarburization reaction and reducing the chromium losses to slag.[2] Due to the lesser oxidation of metallic species, the consumption of reducing agents is likewise reduced.[3] In the original concept, the blowing mixture was delivered through tuyères located on the sidewall of the vessel, but modern designs also feature a top lance.[1,4] **Figure 1** shows an example of a blowing practice, which consists of a combined-blowing decarburization stage, multiple side-blowing decarburization stages and a reduction stage with desulphurization and alloying.[5]

Figure 1   Ref. [5]

The primary interest of this work is the combined top- and size-blowing decarburization stage, which aims to maximize the decarburization rate by employing a high oxygen supply rate. Typical blowing rates at this stage are approximately 1.0–1.6 Nm^3/(t·min) through the top lance and 0.80–1.25 Nm^3/(t·min) through the tuyères.[6] Both subsonic and supersonic lances can be employed in the AOD process.[1,4] While supersonic lances are water-cooled and positioned one to four meters from the surface of the steel bath, subsonic lances are placed closer to the bath and are not necessarily water-cooled.[1] The supersonic gas jet is obtained with a de Laval nozzle, which can feature one or more exit ports. The main advantages of supersonic lances over subsonic lances are the increased oxygen delivery rate and improved penetrability of the gas jet.[1] On the other hand, subsonic lances enable more post-combustion, which in turn improves the energy efficiency of the process.[1] It has been suggested that approximately 30–100% of the blown oxygen reacts with the steel bath depending on the design and position of the lance.[1]

In comparison to decarburization during side-blowing, modelling of reactions during top-blowing in the AOD process has received relatively little attention. Watanabe and Tohge[7] conducted a study on mechanisms of decarburization under reduced pressure and proposed a simple reaction scheme for top-blowing with O_2, an Ar-O_2 mixture and CO_2. Later, Tohge et al.[8] proposed a model for combined blowing. In their model, the carbon removal rate was calculated based on a volumetric mass transfer coefficient that was extracted from experimental data.

Kikuchi et al.[9,10] proposed a mathematical model for the decarburization of stainless steel in a

combined-blowing converter in the low carbon range. In their study, the top lance was not employed for oxygen-blowing, but for stirring the bath with nitrogen. Three reaction zones were considered by the model: 1) the free surface created by the nitrogen gas jet, 2) the slag-metal interface, and 3) the bottom-blowing zone. The gas-metal interfacial area was determined based on the stirring energy provided by the gas jet.

Zhu *et al.*[11] proposed a model for combined top- and side-blowing in the AOD process and assumed a three-step reaction cycle during top-blowing in the AOD process: first, part of the top-blown oxygen reacts with escaping CO, then part of the oxygen reacts with emulsified droplets, and finally the remainder of the oxygen penetrates the steel bath, dissolves into the melt and oxidizes the elements in the metal phase. The volume of metal droplets was defined to be equal to the volume of the cavity, and the total reaction area between the oxygen jet and the steel bath was adjusted by changing the assumed average droplet size. However, neither the metal droplet size employed nor the contribution of top-blowing were presented explicitly in the related validation study[12]. Later, Wei *et al.*[13] modified the model with improved heat analysis.

The objective of this work is to derive and validate a new model for reactions during top-blowing in the AOD process. Making use of the scientific basis established by the previous models, this model aims to provide more insight into the dynamics of the AOD process during gas injection from the top lance. The description of the model was presented in the first part of this paper[14], while this second part focuses on the validation of the model and presents preliminary results.

2   Materials and methods

In contemporary practice, both tuyères and a top lance are employed for delivering the required oxygen into the melt in combined top- and side-blowing decarburization. In order to validate the model developed in this work, however, it is necessary to have experimental data on the contribution of top-blowing to the rate phenomena.

2.1   Validation material

Twelve validation heats were conducted with a 150 metric ton AOD vessel at Outokumpu Stainless Oy, Tornio Works. The vessel is fitted with seven tuyères along the side wall and a supersonic top lance (see **Table 1**). In their operating practice, the combined-blowing stage is divided into steps, which differ in terms of material additions and the employed blowing mixture. In the studied heats, the last combined-blowing stage was altered so that oxygen was introduced from the top lance only.

100   Four heats (Series A) were conducted using an oxygen-nitrogen mixture (1:1), while eight heats
101   (Series B) were conducted with pure oxygen; in both cases the total specific gas flow rate through the
102   top lance was approximately 1.3 Nm^3/(t·min). In order to provide mixing that is comparable to regular
103   practice, nitrogen or argon gas (heats 54870 and 54872) was blown via the tuyères at a specific flow
104   rate of approximately 0.8 Nm^3/(t·min). When the vessel was tilted from sampling position to operating
105   position or from operating position to sampling position, gas stirring was employed at a lower specific
106   flow rate of approximately 0.3 Nm^3/(t·min), while top-blowing was halted. No metal-slag reactions
107   were assumed to take place during tilting, although the melting of material additions as well as the
108   cooling effect of the gas-stirring were taken into account in the simulations. An initial temperature of
109   298.15 K (25 °C) was assumed for the injected gas.
110
111   **Table 1**
112
113   Steel and slag samples were taken before and after the blowing sequence. The samples were analyzed
114   with an optical emissions spectrometer (OES) and an X-ray fluorescence spectrometer (XRF). The
115   temperature of the steel bath was measured using a temperature probe on the same occasions. The
116   mass of the steel bath before the studied process stage was calculated based on the Ni balance and
117   charge weight. The initial mass of the top slag was calculated based on the gas balance assuming that
118   oxygen was bound in the slag according to the composition measured before the studied process stage.
119   Because the oxygen content could not be determined from the steel samples, it was estimated based
120   on literature data. Schürmann and Rosenbach[15] and Masuda *et al.*[16] studied the decarburization of
121   stainless steel using experimental vessels, in which argon was blown through tuyères while oxygen
122   was supplied through a top lance. Making use of their data, the oxygen content was determined as a
123   function of carbon content according to a power-law fitting curve (see **Figure 2**).
124
125   **Figure 2**   Refs. [15,16]
126
127   Based on light optical microscopy (LOM) it became apparent that some fine metal droplets were left
128   in the analyzed slag samples. As illustrated by Lindstrand *et al.*[17], the fine metal droplets can distort
129   the XRF analysis of the slag composition considerably; this stems from the fact that the XRF method
130   yields the elemental distribution of species. Therefore, the slag composition was re-calculated by
131   excluding the Fe, Cr, Mn, Si and Ni brought by the fine metal droplets. Similarly to Lindstrand *et*
132   *al.*[17], the mass fraction of the steel phase in the slag sample was calculated based on the Ni content
133   of the slag sample assuming that all the Ni originated from the fine metal droplets and that the
134   composition of the metal droplets corresponded to the composition of the steel bath. In addition to

135 metal droplets, some undissolved lime particles with diameters ranging from 20 mm to 50 mm were

136 also found. The lime particles were covered by a shell structure, which is known to have a retarding

137 effect on the dissolution rate[18].

138

139 The material additions during the studied process stage are shown **Table 2**. An initial temperature of

140 298.15 K (25 °C) and an average particle size of 50 mm was assumed for all the material additions.

141 The feeding time of additions was taken into account by employing a constant feed rate separately

142 for each batch of additions. The employed feed rates were determined based on the feeding times

143 measured during the studied heats.

144

145 **Table 2**

146 **2.2 Description of material additions**

147 Similarly to our earlier work,[19–21] the melting times of materials with a melting point lower than that

148 of the steel bath were determined based on the melting time of spherical particles. More specifically,

149 the melting times of additions were calculated according to

150

$$\tau_m = \frac{d_p^2 \rho_p l_m}{\lambda_e (T_{bath} - T_m)}, \tag{1}$$

151

152 where d_p is the diameter of the particle, ρ_p is the density of the particle, l_m is the latent heat of

153 melting, λ_e is the effective heat conductivity, T_{bath} is the temperature of the steel bath and T_m is the

154 melting temperature of the particle. In order to account for the effect of shell formation, the effective

155 heat conductivities were fitted to experimental data on melting times of nickel-bearing ferroalloys[22]

156 and carbon steel scrap[23]. The values of ρ_p, l_m and T_m and were obtained from the same references.

157 In the absence of suitable data, the effective heat conductivity of copper was assumed to be equal to

158 the heat conductivity of pure copper. A reasonably good agreement with experimental data was

159 achieved by assuming a linear dependency of the effective heat conductivity from the diameter of the

160 particle. In the absence of suitable measurement data, it was assumed that the effective heat

161 conductivity of stainless steel scrap is the same as that of carbon steel scrap. The effect of the material

162 additions on the temperature of the steel bath was calculated as follows:

163

$$\Delta T_{bath} = -\frac{m_a \left[\int_{T_a}^{T_{bath}} c_{p,a} \, dT + l_m + \Delta h_{dis} \right]}{m_a c_{p,a} + m_{bath} c_{p,L}}, \tag{2}$$

164

165 where m_a is the mass of the added material, m_{bath} is the mass of the steel bath, T_a is the temperature

166 of the added material, Δh_{dis} is the specific enthalpy of dissolution into liquid iron, $c_{p,a}$ is the specific

167 heat capacity of the alloying additions and $c_{p,L}$ is the specific heat capacity of the liquid steel phase.

2.3 Modelling parameters

169 All the simulations were conducted with a time step of five seconds. Considering the length of the

170 studied process stages, this provides a reasonable resolution for the predicted changes in bath

171 composition and temperature. In this work, it was assumed that the volume fraction of solids in the

172 slag is equal to their weight-fraction, *i.e.* $\phi_{(s)} = y_{(s)}$. The weight-fraction of solids was defined to be

173 a linear function of the weight-fraction of solid Cr_2O_3 in the slag:

174

$$y_{(s)} = A \times y_{Cr_2O_3(s)}, \tag{3}$$

175

176 where A is a fitting parameter and $y_{Cr_2O_3(s)}$ is the weight-fraction of solid Cr_2O_3 in the slag. The

177 weight-fraction of solid Cr_2O_3 was calculated as follows:

178

$$y_{Cr_2O_3(s)} = \max\left(y_{Cr_2O_3} - y_{Cr_2O_3(l)}, 0\right), \tag{4}$$

179 where $y_{Cr_2O_3}$ is the total weight-fraction of Cr_2O_3 in slag and $y_{Cr_2O_3(l)}$ is the maximum weight-

180 fraction of Cr_2O_3 soluble in liquid slag. The solid fractions of the slag samples taken in this work

181 were calculated with the FactSage 7.0 thermodynamic software[24] at the temperature measured from

182 metal bath at corresponding occasions. With the help of the results of these calculations, the values

183 of $y_{Cr_2O_3(l)}$ and A were determined based on method of least squares. The best agreement was

184 obtained with $y_{Cr_2O_3(l)} = 0.078$ (*i.e.* 7.8 wt-%) and $A = 1.55$ (see **Figure 3**). It should be noted that

185 the employed value of Cr_2O_3 solubility is quite close to the value of $y_{Cr_2O_3(l)} = 0.05$ (*i.e.* 5 wt-%)

186 employed by Wei and Zhu[25].

187

188 **Figure 3**

189

190 As explained in the preceding part of this work[14], the metal droplet generation rate ($\dot{m}_{md}$) in the

191 splashing cavity mode is calculated according to the correlation proposed by Rout *et al.*[26]

$$\frac{\dot{m}_{md}}{\dot{V}'_{G,lance}} = \frac{(N'_B)^{3.2}}{[2.6 \times 10^6 + 2.0 \times 10^{-4}(N'_B)^{12}]^{0.2}},$$ (5)

where N'_B is the modified blowing number and $\dot{V}'_{G,lance}$ is the modified volumetric gas flow rate through the lance (in Nm³/s). In order to account for the effect of different cavity modes, the effective metal droplet generation rate was calculated similarly to Sarkar *et al.*[27] by multiplying the metal droplet generation rate by the parameter J_{eff} as shown in Eq. 6.

$$\dot{m}_{md,eff} = J_{eff} \times \dot{m}_{md}.$$ (6)

On average, the best modelling results *vis-à-vis* the measured values were obtained with $J_{eff} = 1.75$ and hence this value was used in all the other simulations. An illustration of the effect of the parameter J_{eff} on the predicted carbon content in heat 57872 is shown in **Figure 4**.

Figure 4

The validity of the chosen value of the parameter J_{eff} can also be examined by comparing the resulting fraction of metal droplets residing in the emulsion. Lindstrand *et al.*[17] analyzed slag samples from a simple side-blowing operation and reported that the total amount of metal in AOD decarburization slags was approximately 20 wt-%, of which 2–7 wt-% originated from fine metal droplets. Koch *et al.*[28] reported that the total amount of metal droplets in the slag samples taken from combined-blowing operation was approximately 10–35 wt-%. In this work, the slag samples were taken from a tilted vessel and it is likely that part of the metal droplets had already returned back to the metal bath. Large metal splashes were removed from the slag samples before chemical analysis. Based on composition of the slag samples, fine metal droplets were estimated to account for 2–9 wt-% of the slag samples before the studied process stage and 2–15 wt-% after the studied process stage. With the employed value of J_{eff}, the predicted fraction of metal droplets in the slag was higher than that measured in this work, but varied typically within the experimental range reported by Koch *et al.*[28]. In view of these considerations the chosen value of J_{eff} appears to be of appropriate magnitude.

3   Results and discussion

3.1   Predicted final compositions and temperatures

Table 3 presents a comparison of the predicted steel compositions and the samples taken before and after the studied process stage. It can be seen that the measured steel bath compositions are in good accordance with the measured compositions. The predicted bath temperatures are scattered approximately evenly around the measured values.

Table 3

A comparison of the predicted top slag composition and slag samples taken before and after the studied process stage is shown in **Table 4**. Considering the great heterogeneity of decarburization slags and the challenges in sampling and analyzing such slags, the agreement is acceptable. However, the deviation of the predicted composition variables from the measured values is much larger in the case of the liquid metal phase. The predicted MnO and Cr_2O_3 contents are systematically higher than those found in the samples, while the opposite is true for FeO. As the initial mass of the top slag was determined based on the composition of the slag sample taken before the studied stage, it is reasonable to expect that undissolved lime constitutes a considerable source of inaccuracy in some heats. Another source of inaccuracy is the simplification that the model considers the slag as only one homogenous phase, although the effect of the solid fraction on the viscosity of the slag is taken into account. Recent calculations by Ternstedt *et al.*[29] show that the solid fraction can vary in a wide range depending on the studied case, and in some cases the top slag can be almost entirely solid. In addition, they found that the amount and type of solid phases depends greatly on the start temperature and the amount of EAF slag at the start.

Table 4

A statistical analysis of the results was conducted in order to compare the model to those proposed in the literature. The employed statistical indicators consist of a correlation coefficient (R^2), root-mean-square error (RMSE) and mean absolute error (MAE), which were calculated according to Eqs. 7, 8 and 9, respectively. It should be noted that the expression given in Eq. 7 defines R^2 as the square of the Pearson product-moment correlation coefficient.

$$R^2 = \left[\frac{\sum_{i=1}^{n}(f_i - \overline{f})(y_i - \overline{y})}{\sqrt{\sum_{i=1}^{n}(f_i - \overline{f})^2 (y_i - \overline{y})^2}} \right]^2 , \tag{7}$$

$$\text{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - f_i)^2} , \tag{8}$$

$$\text{MAE} = \frac{1}{n}\sum_{i=1}^{n}|y_i - f_i| , \tag{9}$$

where f_i is the predicted variable, $\overline{f}$ is the mean of the predicted variables, y_i is the measured variable and $\overline{y}$ is the mean of the measured variables.

The results of the statistical analysis are shown in **Table 5**. The mean absolute errors in final Mn, Si, C and Ni contents are less than or equal to 0.05 wt-%, while the MAE in temperature is below 10 K. The MAE for chromium is somewhat larger, being approximately 0.1 wt-%. With respect to the final carbon content, a better agreement was achieved with experiments using an oxygen-nitrogen mixture as the top-blowing gas (Series A) than those with pure oxygen (Series B). With the exception of carbon, the R^2 values of predicted variables are high. It is likely that the low R^2 of the predicted carbon content is explained to some extent by inaccuracies in the measurement data. For example, in the beginning of heats 54874, 54876, 54878 and 54934 a small amount of pressurized air was injected through the tuyères due to some latency in process control. Theoretically, the pressurized air could account for a maximum of 0.01 to 0.02 wt-% decrease in carbon content (CRE = 100%). Subtracting the removed carbon from the predicted final carbon contents would increase R^2 from 0.23 to 0.35.

Table 5   Refs. [30] [31] [32] [33] [34] [13]

The statistical indicators for other studies focusing on combined-blowing or simple side-blowing in comparable carbon ranges were employed as a benchmark. The MAE and RMSE in final carbon content were found to be lower than that presented by Kleimt *et al.*[33] and roughly on par with the models proposed by Deb Roy *et al.*[30], Semin *et al.*[31] and Sjöberg[32], but much higher than those reported by Wei and Zhu[34] and Wei *et al.*[13]. In the case of final chromium content, the MAE was lower than those reported by Deb Roy *et al.*[30] and Semin *et al.*[31] and on par with Wei *et al.*[13]. The MAE in final bath temperature was found to be much lower than those reported by Deb Roy *et al.*[30] and Semin *et al.*[31], and slightly lower than that reported by Wei and Zhu[34], but higher than that

reported by Wei et al.[13]. It should be stressed that due to different data, the R^2 is not an appropriate metric for quantitative comparison of the models.

3.2 Dynamic changes in bath composition and temperature

One of the main advantages of the model developed in this work is the ability to follow dynamic changes in bath composition and temperature. **Figures 5, 6** and **7** illustrate the simulated dynamic change in carbon, chromium, manganese and nickel contents in heats 37876, 38032 and 34878, respectively. At first, the predicted carbon content decreases rapidly as carbon reduces oxides from the slag, which is reflected in the rapidly increasing chromium content. Thereafter, oxidation of carbon and chromium proceed at virtually constant rates. In both heats, the predicted final manganese content is slightly above the measured value. Nevertheless, the absolute error in final Mn content is acceptable.

Figure 5

Figure 6

Figure 7

Figure 8 illustrates the simulated dynamic change in bath temperature in heat 38032. In this heat, feeding of copper, carbon steel scrap and FeNi20 started at 1.9 minutes and ended at approximately 7.3 minutes. The simulated bath temperature decreases until all of the additions and scrap have dissolved in the steel. After this, the predicted bath temperature rises at rapidly due to exothermic oxidation of carbon and other elements in the steel.

Figure 8

In general, the calculated temperature of the cavity interface was roughly the same as that of the metal bath, while the calculated temperature of the metal droplet interface was significantly elevated. As expected, the calculated excess temperature of the metal droplet interface was lower in the case of heats with an oxygen-nitrogen mixture as the top-blowing gas (Series A) than those with pure oxygen (Series B). In the case of Series B, the calculated temperatures of the metal droplet interface varied the range of 2000 K (1727 °C) to 2200 K to (1927 °C). These results compare well with the hot spot temperature suggested by Delhaes et al.[35]. They estimated based on vaporization of Mn that the average temperature of the hot spot should be approximately 2173 K (1900°C) during pure-oxygen combined-blowing in the initial period of the AOD process; the proposed value denotes an excess temperature of 300–400 K.[35]

3.3 Carbon removal efficiency

The efficiency of oxygen use is commonly assessed with the concept of carbon removal efficiency (CRE), which is the ratio of oxygen used for decarburization to the total amount of oxygen blown.[36] It is important to note that the definition of CRE does not account for the top slag as a possible source of oxygen. For this reason, some authors[36] have questioned its purposefulness in evaluating the efficiency of decarburization.

The predicted carbon removal efficiencies and the values calculated based on the steel samples are in good agreement, as seen in **Table 6**. In the case of O_2-N_2 mixtures (Series A), the dilution ratio of oxygen is higher in the studied process stage than in the preceding process stage, the top slag must settle into a new dynamic equilibrium with the steel phase. It follows that the predicted transient CRE value starts from above or close to 100%, because carbon reduces slag species with lower oxygen affinity (see **Figure 9**). This finding is in agreement with the calculations by Swinbourne et al.[37] and Wijk[38] for side-blowing operation in comparable carbon ranges. However, the calculated CRE decreases rapidly as the carbon content decreases. In the case of pure oxygen-blowing (Series B), virtually no reduction of slag species takes place. In heat 54870, for example, the predicted transient CRE value remains well below 100% throughout the studied stage (see **Figure 10**).

Table 6

Figure 9

Figure 10

Although only a few experimental estimates of the contribution of the top lance to the decarburization rate are available as such, the available measurement data permits the calculation of decarburization rates attributable to top-blowing. A compilation of this analysis is presented in **Table 7**. It can be seen that the CRE varies in a wide range depending on parameters such as lance type, lance height carbon content, or intensity of side-blowing.

Table 7   Refs. [7] [39] [40] [41] [16] [15] [42] [8] [43]

In this work, the average CRE calculated based on steel samples was approximately 51% in Series A and 44% in Series B. In terms of the employed specific top-blowing rates and the studied carbon range, the studies published by Koch et al.[39], Kuwano et al.[41], Masuda et al.[16] and Schürmann and Rosenbach[15] constitute a reasonable experimental benchmark. Koch et al.[39] studied top-blowing decarburization of Fe–C–Cr and Fe–C–Cr–Si melts under atmospheric and reduced pressure (100,

40, 6.7 and 0.4 kPa). Under atmospheric pressure, the average CRE was much higher in the case of Fe–C–10 Cr heats (78%) than in the case of Fe–C–18 Cr–Si heats (17%). The higher CRE of the Fe–C–10 Cr heats may be explained to a large extent by their higher initial and final carbon contents. Reduced pressure increased the decarburization rate markedly only in the case of the Fe–C–Cr–Si heats, which exhibited substantial splashing under reduced pressure. The data from Kuwano et al.[41] for low-silicon heats in the range of 0.02 wt-% to 0.6 wt-% carbon suggests an average CRE of 42%. Although Koch et al.[39] and Kuwano et al.[41] did not have any stirring at all, it is likely that efficient mixing was obtained due to low lance position and small crucible size. The average CRE values from Masuda et al.[16] and Schürmann and Rosenbach[15] were in the order of 20%. In comparison to this work, Masuda et al.[16] and Schürmann and Rosenbach[15] employed much lower specific stirring rates and pure oxygen as the top-blowing gas. According to the experimental results available in the literature,[40] the decarburization rate should increase and the chromium losses should decrease if the stirring flow rate is increased while employing the same top-blowing rate of oxygen. Moreover, in view of the physical and numerical modelling studies available in the literature, the use of a top lance should deteriorate the mixing characteristics in comparison to simple side-blowing.[44–47]

In the case of two lances with the same flowrates, there should be less splashing with a three-hole lance than with a one-hole lance.[48] The model presented in this work considers this effect indirectly through the nozzle throat diameter and the gas jet angle. However, the effect of the inclination angle is not clear-cut. Li et al.[43] studied the effect of inclination angle of the nozzle by comparing two 3-hole lances and found that a higher CRE was obtained with an angle of 11° than with an angle of 15° (see **Table 7**). Virtanen et al.[49] compared two three-hole lances with inclination angles of 11° and 13° for decarburization of ferrochrome melts in a 90 metric ton AOD converter. In comparison to the study by Li et al.[43], a much lower lance position was employed and it was found that a higher CRE was obtained using the higher 13° inclination angle. Therefore, in view of these studies it appears that the optimal inclination angle is not independent of the lance height.

3.4 Sensitivity analysis

After main validation with the measurement data, the model was employed for a sensitivity analysis in heat 38034. The analysis was conducted *ceteris paribus* by changing either the lance height or the oxygen content of the top-blowing mixture. **Figure 11** illustrates the predicted effect of the oxygen content in the top-blowing gas mixture with $O_2:N_2$ ratios of 1:3, 1:1 and 3:1, which correspond to volumetric oxygen contents of 25%, 50% and 75%. As expected, the $O_2:N_2$ ratio of 3:1 enables the lowest predicted final carbon content in the studied stage. The predicted average CRE values corresponding to the $O_2:N_2$ ratios of 1:3, 1:1 and 3:1 were 87%, 50% and 36%, respectively.

Therefore, it is apparent that an increased decarburization rate comes at the price of lower carbon removal efficiency.

Figure 11

The effect of lance height on the predicted carbon content is illustrated in **Figure 12**. The results suggest that decreasing the lance height by 10% decreases the predicted final carbon content by approximately 0.03 wt-%, while increasing the lance height by 10% increases the predicted final carbon content by 0.05 wt-% *vis-à-vis* the normal lance position. The predicted CRE values corresponding to the lower, normal and higher lance position were approximately 56%, 50% and 40%, respectively. The effect of the lance position employed may be explained to a large extent by changes in droplet generation rate and thus in the interfacial area available for mass exchange. However, the model does not account for post-combustion of CO to CO_2 in the converter atmosphere. It is likely that increased post-combustion would decrease the CRE even further in the case of the higher lance position.

Figure 12

3.5 Macrokinetics

The macrokinetics of reactions during top-blowing are characterized by the interaction of the gas jet and the steel bath. However, the impact area of the top-blowing gas jet alone is too small to be responsible for the high decarburization rates observed during top-blowing in the AOD process. For this reason, it is reasonable to expect that the small metal droplets generated by the shear stress of the gas jet play an important role. These postulations are in agreement with the findings of Scheller and Wahlers[50], who reported that with equal nitrogen blowing rates from the tuyères and the top lance, the reaction area of the metal droplets and the surface area of the bath should together account for 8–15% of the reaction area of the gas bubbles in the metal bath, depending on the method of calculation. Under the conditions of the present study, this should correspond to a mass exchange area in the order of hundreds of square meters. However, because small metal droplets have a high microkinetic efficiency even at short contact times, the surface area of the metal droplets is underestimated if the conservation of mass in the metal droplets is not accounted for. The findings of this work suggest that the surface area of the metal droplets should be in the order of thousands of square meters.

At their place of origin, the majority of the cumulative weight is constituted by relatively large droplets.[51–53] Thereafter, various mechanisms alter the droplet size distribution. Large droplets may

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disintegrate upon contact with the gas jet[54] or impact on the slag,[55] while the smallest droplets can be carried out of the vessel with the flue gas. In this work, it was assumed that all the generated droplets continue their trajectory into the slag undisturbed without any break-up or loss to flue gas. **Figure 13** shows that the predicted Sauter mean diameter of the metal droplets in heat 38034. The reason for the small Sauter mean diameter is that the small metal droplets tend to have a very low terminal velocity, which results in long residence times. Therefore, the droplet size distribution in the emulsion shifts towards smaller droplets than at their place of origin. These conclusions are in keeping with results of laboratory-scale experiments.[51,56] One factor affecting the calculations is the slag viscosity, which increases as the chromium oxide content of the slag increases. Studies concerning decarburization slags suggest that fine metal droplets are effectively trapped in the slag until the reduction stage.[18,28]

Figure 13

According to the blowing number theory, the metal droplet generation rate is a function of the blowing number.[57] On the basis of the blowing number, it can be deduced that the droplet generation rate is increased by the higher dynamic pressure of the gas jet and decreased by an increase in the density and surface tension of the steel.[57] As the blowing practice was virtually identical in the studied heats, both the calculated blowing number and the calculated droplet generation rate were virtually constant. The calculated blowing number was $N_B \approx 5.8$, which exceeds the criteria for the onset of splashing ($N_B > 1$) and for the swarming region of droplet formation ($N_B > 3$) proposed by Subagyo[58]. Some authors[59,60] have reported that the maximum metal droplet generation rate is obtained at a certain lance height. However, such behavior could not be identified using the blowing number theory employed in this work. The reason is that the blowing number theory does not properly account for the decreasing metal droplet generation rate when the cavity mode changes from the splashing to the penetrating region.[61] In practice, there are also other factors that affect the splashing phenomena. For instance, it has been reported that the interaction of top-blowing and bottom-blowing increases splashing.[60]. In addition, chamfering of the nozzles may have an effect on the splashing phenomenon, as it causes coalescence of gas jets and reduces their maximum velocities.[62]

3.6   Microkinetics and rate limiting mechanisms

The mass transfer coefficient of the gas jet decreases with increasing dimensionless lance height. In the studied heats, the calculated Sherwood number of the gas species at the cavity interface varied between 2,800 and 3,200. Kärnä *et al.*[63] employed a computational fluid dynamics model to study the same top lance at operating conditions corresponding to those of this work. Calculating an average

Sherwood number over the whole melt surface, Kärnä et al.[63] proposed a value of Sh = 3,120, which is in good agreement with the range of values obtained in this work using the Lohe[64] correlation. Nevertheless, because the model does not account for cavity oscillation, it is reasonable to expect that the model proposed in this work might still underestimate the contribution of the cavity interface to the overall decarburization rate. The calculated Sherwood numbers for liquid species at the cavity interface were Sh ≈ 200,000. The value for liquid species can be compared to the results of Wei and Zuo[44], who studied mass transfer in a 1:4 scale physical model of a 120 t AOD vessel. Under combined-blowing conditions, their mass transfer correlations for liquid species yield Sh ≈ 3,000 using the same values of Re and Sc as in this work. The aforementioned value, which corresponds to conditions inside the bath, is two decades smaller than the values obtained in this work for turbulent mass transfer at the cavity interface.

At the metal droplet interface, the calculated mass transfer coefficients of C, O_2 and Cr_2O_3 were in the order of $0.7–5\times10^{-4}$ m/s, 5–11 m/s and $0.4–4\times10^{-4}$ m/s, respectively. The mass transfer of the gas phase in contact with the metal droplets was defined according the Steinberger and Treybal[65] correlation, which accounts for both natural and forced convection. Experimental findings from decarburization of levitated Fe-C[66,67] and Fe-Cr-C[68] droplets suggest that this correlation can reproduce the experimental data with high accuracy except for cases where the temperature gradient between the gas phase and the reaction interface is very large. In this work, the predicted temperature of the gas film was very close to the temperature of the reaction interface and hence the error caused by the temperature gradient should be small. The mass transfer rate in the metal droplets was according to the Kronig and Brink [69] solution, while the mass transfer correlation for the slag phase surrounding the metal droplets was taken from Calderbank[70]. Both of the employed correlations assume a flow pattern according to the Hadamard stream function and were found to be in good accordance with experimental data[71].

Based on the aforementioned considerations, the chosen mass transfer correlations appear appropriate for analyzing the rate limiting factors. Here, the concept of *control factor* is employed for observing the controlling mass transfer mechanisms in the process. The control factor has a value of 1 when the concentration gradient approaches its maximum value and 0 when the concentration gradient approaches zero. In other words, all non-zero values for the control factor represent some degree of mass transfer resistance. In mathematical terms the control factor of species i is defined as follows:

$$C_i = \min\left(\left|1 - \frac{y_i^*}{y_i}\right|, \left|1 - \frac{y_i}{y_i^*}\right|\right), \tag{10}$$

where y_i^* is the mass fraction of species i at the reaction interface and y_i is the mass fraction of species i in the corresponding bulk volume. The bulk volume for metal species at the cavity interface is the metal bath, while at the metal droplet interface the bulk volume is constituted by the metal droplets. At both reaction interfaces gas jet and top slag constitute the bulk volumes for gas and slag species, respectively.

As expected, only a small residual amount of oxygen is not consumed in the reactions. Under the conditions employed in this work, the calculated partial pressures of oxygen at both reaction interfaces are between 10^{-7} to 10^{-10} atm, which means that there is an almost total absence of oxygen. Therefore, the control factors of gaseous oxygen are very close to unity at both interfaces. This does not, however, imply that mass transfer of oxygen would be the rate-limiting step, because virtually all the supplied oxygen is consumed. At the reaction interfaces, all the species are in equilibrium with each other according to the set of reversible reactions defined in the model. With respect to decarburization, it follows that not only carbon, but also other species are in equilibrium with CO and CO_2. In the following, the competing oxidation reactions of carbon and chromium as well as the overall reaction defined by Eq. 11[38] are studied.

$$(Cr_2O_3) + 3[C] \rightleftharpoons 2[Cr] + 3\{CO\}, \tag{11}$$

As can be seen in **Figure 14**, the control factor of C at the cavity interface is much higher than that of CO, and hence the mass transfer of C is the controlling step for direct decarburization. Considering the direct oxidation of chromium at the cavity interface, the mass transport of Cr_2O_3 forms a greater resistance than that of Cr. The overall rate defined by Eq. 11 is limited by mass transfer of carbon.

Figure 14

Similar to the cavity interface, the control factor of C at the metal droplet interface is much larger than that of CO (see **Figure 15**). The control factor of Cr is larger than that of Cr_2O_3. It needs to be kept in mind that the reaction rates are defined by both macrokinetic and microkinetic factors. A closer examination of the predicted composition of the metal droplets reveals that the concentration gradients between the metal droplet interior and the interface are small, indicating that the oxidation reactions of C and Cr are not limited to significant extent by the microkinetic mass transport rate. Consequently, the oxidation rates are defined primarily by the macrokinetic factors, most importantly

the generation rate of the metal droplets. The same conclusion applies also for the overall rate described by Eq. 11.

Figure 15

In conclusion, it can be stated that the predicted overall rate of decarburization attributable to top-blowing in the studied stage can be described by first-order kinetics and is limited by the supply of carbon to the reaction sites. At the cavity area, the constraint is of microkinetic nature, while the decarburization of metal droplets is limited mainly by macrokinetic factors. With these considerations in mind, the critical carbon content of top-blowing should be greater than the carbon contents measured before the studied process stage. Shi *et al.*[12] reported that the critical carbon content for top-blowing was 1.2 wt-%. Wei *et al.*[13] suggested a slightly lower range of values: 0.895 to 0.942 wt-%. Therefore, the predicted rate limiting step is in agreement with the aforementioned studies.

3.7   Experimental observations

It was found that the slag samples taken before and after the studied decarburization stage contained a considerable number of metal droplets. In order to study the slag samples in more detail, micro-sections were prepared and analyzed using light optical microscopy. The analyzed cross-sectional surfaces were found to be qualitatively similar to those reported earlier in the literature[18]. Most of the apparent surface area of the metal droplets was comprised of droplets in the range of 0.1 mm to 5 mm. An example of a spherical metal droplet in slag is shown in **Figure 16**. Droplets with an equivalent diameter up to 1 mm were found to be mostly oval or spherical in shape, while larger droplets were usually of irregular shape. It should be noted that because the slag samples were collected by tilting the vessel, the studied metal droplets represent the size distribution in the slag, which differs from the size distribution of at the immediate vicinity of the gas jet impact area.[51,56]

Figure 16

The chemical composition of a few metal droplets entrapped in slag (mm range) was determined with combustion analysis. Their carbon content was found to be approximately the same as in the bulk metal; the accuracy of the chemical analysis, however, did not permit further conclusions. Rubens and co-authors[28,72] analyzed metal droplets from combined-blowing in the AOD process. The carbon content of the metal droplets was found to be substantially lower than the carbon content of the metal bath, although the observed difference in carbon content decreased towards the end of the decarburization stage.[28,72] During combined-blowing, the chromium content of metal droplets in the

17

mm-range was slightly higher than that of the metal bath, while the chromium content of fine metal droplets (μm-range) was considerably below the chromium content of the metal bath. [28,72] This indicates that the decarburization of fine metal droplets takes place primarily in contact with gaseous oxygen, while larger metal droplets are decarburized mainly in contact with the top slag. Considering the low carbon content in the studied process stage, it is reasonable to expect that the decarburization of the metal droplets takes place primarily in direct contact with top-blown oxygen and that the reduction of the slag species by carbon is only of secondary importance. Nucleation of CO within the metal droplets and the resulting decrease in the apparent density of the metal droplets appears to have a significant effect on the residence time of metal droplets in the slag during BOF processing[73,74]. In the studied heats, in which the carbon content of the steel bath was below 0.5 wt-%, no such behavior was observed in the fine metal droplets found in the slag samples. However, it might be necessary to take the bloating effect into account with higher carbon content.

4   Conclusions

The objective of this work was to validate a new model for reactions during top-blowing in the AOD process. The model developed in this work focuses on the local physico-chemical phenomena that control the rate phenomena during top-blowing. The approach employed was based on the law of mass action and complies automatically with the controlling mass and heat transfer mechanisms, which may vary during the process. The employed blowing practice, converter geometry and additions are adjustable in the user interface of the model. The model can be employed to improve the existing blowing practice so that the use of a top lance is more techno-economically viable.

A set of twelve industrial heats were conducted in order to validate the model. A comparison with steel samples showed that the model is capable of predicting the composition of the steel phase with a reasonably high degree of accuracy. The results of statistical analysis suggest that with respect to final carbon content, chromium content and steel bath temperature, the accuracy of the predictions is on par with other models available in the literature. The calculations indicate that the top slag may supply oxygen for decarburization during top-blowing.

In view of the modelling results it appears that the surface area of the cavity alone is too small to account for the high decarburization rates associated with top-blowing. Excluding the effect of top slag, surface instability criteria as well as criteria for swarming mechanism of metal droplet generation were fulfilled in all the studied heats. The splashing of metal droplets was confirmed by slag samples, which were found to contain a large amount of small metal droplets. Consequently, it

587 is suggested that both the direct and indirect oxidation of metal droplets play an important role in

588 obtaining the high decarburization rates obtained in the AOD process.

589

590 A sensitivity analysis was conducted in order to study the effect of top lance height and the oxygen

591 content of the blowing mixture on the predicted final carbon content. It was found that the oxygen

592 content of the top-blown gas has a greater effect on the predicted decarburization rate than the lance

593 position. Finally, the model was employed for studying rate limiting factors during top-blowing. The

594 predicted overall rate of decarburization was found to be limited by the mass transfer of carbon in the

595 studied process stage. This finding is in agreement with previous studies available in the literature. In

596 future work, the developed model for top-blowing could be combined with a previously developed

597 model for side-blowing in order to predict changes in bath composition and temperature during

598 combined side- and top-blowing.

Acknowledgements

Nomenclature

610 $c_{p,L}$ Specific heat capacity of liquid metal [J/(kg·K)]

611 d_t Nozzle throat diameter [m]

612 d_p Diameter of the particle [m]

613 $C_{i,\omega}$ Control factor of species i at the reaction interface ω

614 J_{eff} Multiplication factor of the metal droplet generation rate

615 h_{lance} Distance of the top lance from the surface of the steel bath [m]

616 Δh_{dis} Specific enthalpy of dissolution into liquid iron [J/kg]

617 l_m Latent heat of melting [J/kg]

618 m_a Mass of the added material [kg]

619	m_{bath}	Mass of the metal bath [kg]
620	$\dot{m}_{md}$	Metal droplet generation rate [kg/s]
621	$\dot{m}_{md,eff}$	Effective metal droplet generation rate [kg/s]
622	MAE	Mean absolute error
623	n_{lance}	Number of exit ports in a nozzle
624	N'_B	Modified blowing number
625	p_0	Stagnation pressure at upstream part of the top lance [Pa]
626	Re	Reynolds number
627	RMSE	Root-mean-square error
628	R^2	Correlation coefficient (square of the Pearson product-moment correlation coefficient)
629	Sc	Schmidt number
630	Sh	Sherwood number
631	T_a	Temperature of the added material [K]
632	T_{bath}	Temperature of the steel bath [K]
633	T_{bath}^{new}	Updated temperature of the steel bath [K]
634	T_m	Melting temperature of the particle [K]
635	$\dot{V}'_{G,lance}$	Volumetric gas flow rate through top lance [Nm^3/s]
636	y_i	Mass fraction of species i in the bulk phase
637	y_i^*	Mass fraction of species i at the reaction interface
638	θ	Inclination angle of each nozzle relative to lance axis [°]
639	ρ_p	Density of the particle [kg/m^3]
640	λ_e	Effective heat conductivity [W/(m·K)]
641	τ_m	Melting time of additions [s]

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757

758

759 **List of tables**

760 **Table 1.** Geometry of the top lance.

761 **Table 2.** Additions during processing.

762 **Table 3.** Samples and predictions for steel composition and temperature.

763 **Table 4.** Samples and predictions for slag composition.

764 **Table 5.** Statistical indicators for predicted compositions and temperatures.

765 **Table 6.** Carbon removal efficiency in the studied process stage.

766 **Table 7.** Carbon removal efficiency attributable to top-blowing.