1. Introduction

In order to remove carbon and silicon from the melt in the production of stainless steel, oxygen is blown into steel melt in the AOD process. In addition to decarburization and desiliconization some chromium is also oxidized due to oxygen blowing and hence transferred to the slag. As the decarburization proceeds, oxygen blow is partly replaced by nitrogen and then by argon in order to decrease the oxidation of chromium. Nitrogen content of melt is increased to the level of 1 000–1 500 ppm during nitrogen injection due to the high equilibrium nitrogen content of stainless steel. Nitrogen debilitates the properties of the final steel product and therefore excess nitrogen has to be removed from melt. Nitrogen removal is executed by argon blowing. Due to financial reasons it is important that nitrogen-to-argon switch-point is determined accurately.

Many studies of nitrogen absorption and desorption in iron alloys1–16) and in stainless steels or chromium rich alloys17–22) have been published in literature. Effect of surface active elements such as oxygen and sulphur, composition of steel melt as well as partial nitrogen pressure and total pressure on nitrogen absorption and removal have been studied in these investigations.

It is known that surface active elements decrease nitrogen flow through the gas–melt interface by occupying reaction sites. Typically, in the industrial cases the rate of absorption and desorption of nitrogen is limited by high interfacial contents of sulphur and oxygen of melt. Many researchers9,10,13–23) have reported that absorption of nitrogen is first order or second order reaction depending on the amount of vacant sites and desorption is second order reaction. Reaction rate constants for first and second order reactions with different melt composition have been determined in many studies. Furthermore, the correlations between the melt composition and reaction rate constant have been investigated. However, there has not been studies in which the effective reaction area for nitrogen mass flow through the gas–melt interface depending on the melt and gas composition have been connected with thermodynamic equilibrium data.

Purpose of the present study was to create a model for nitrogen behavior in stainless steel during decarburization and slag reduction stages in industrial AOD process based on the thermodynamic equilibrium (temperature as well as stainless steel melt and gas compositions) and effective reaction area between the gas bubbles and steel. In the present study the numbers of free vacant sites for nitrogen transfer at the interface have been calculated by the Butler's equation for Fe–N–S–O system.

2. AOD Process

Process tests were made by a 150 ton AOD converter which is equipped with a top lance and seven sidewall nozzles at Outokumpu Stainless Tornio Works in Finland. Typical austenitic stainless steel melt and slag composition in the AOD are presented in Table 1.

Carbon and chromium contents of the steel melt as a function of blowing time in the AOD process are presented in Fig. 1. It is seen from Fig. 1 that decarburization takes place in four stages. In the first stage only oxygen is injected into the steel via sidewall nozzles and a top lance. As carbon content decreases, inert gas dilution rate is increased.
to minimize chromium oxidation (2nd Stage and 3rd Stage in Fig. 1). In the last steps of decarburization (3rd Stage and 4th Stage in Fig. 1), gas mixture is blown only through sidewall nozzles. The final stage of the AOD process is the combined desulphurization and reduction of the slag in which the oxidized chromium is reduced from the slag with ferrosilicon or ferromanganese by argon injection. Used oxygen inert gas ratios are presented in Table 2. Composition of steel melt in studied heats and duration of process stages are presented in Table 3.

3. Mechanism of Nitrogen Transfer

Many investigators\textsuperscript{9,10,13,14} have concluded that absorption and desorption of nitrogen between gas phase and steel melt occurs by either single-site or dual-sites mechanisms. The single-site mechanism is only possible mechanism when other surface active elements, such that oxygen and sulphur, are blocking the movement of adsorbed nitrogen atoms on the surface (Fig. 2). In the single-site mechanism the dissolved nitrogen atom is first transferred into the monomolecular layer at the surface. Transferred nitrogen atom meets another nitrogen atom and these two atoms react and form a nitrogen molecule (N\textsubscript{2}). The nitrogen molecule transfers into the gas phase by diffusion and convection. If there are low contents of other surface active elements, dual-site mechanism is more probable (Fig. 3). In absorption by dual-site mechanism nitrogen molecule is transferred from the gas phase on the surface of the melt and dissociates into two nitrogen atoms that have sites in the gas–melt interface. In next step dissociated nitrogen atoms are transferred into the bulk melt.\textsuperscript{13,14}

In the present work, we have assumed that nitrogen transfer follows dual site mechanism on the first stage of the AOD process and single site mechanism on the latter stages of the AOD process. This assumption is based on the changes of circumstances between different stages of the AOD process: composition of the blowing gas which is changed as function of the blowing time and the content of carbon and silicon of the stainless steel melt. During the first decarburization stage content of dissolved oxygen is very low because of the high silicon and carbon contents. The change of the sulphur content in the stainless steel melt is not remarkable during decarburisation period and it is assumed to be constant during decarburisation.

It is generally proved that nitrogen absorption and desorption in pure iron or iron alloy in high temperature follow mass transfer Eqs. (1) and (2)

\[ R = \frac{dC}{dt} = k_1 \frac{A_{\text{eff}}}{V} (C_e - C) \]  

\[ R = \frac{dC}{dt} = k_2 \frac{A_{\text{eff}}}{V} (C_e^2 - C^2) \]

where \( R \) is the reaction rate, \( k_1 \) is the first-order rate constant, \( k_2 \) is the second-order rate constant, \( A_{\text{eff}} \) is the effective surface area of reaction, \( V \) is the volume of melt, \( C \) is the concentration of melt at time \( t \) and \( C_e \) is the equilibrium concentration of melt at time \( t \). These equations based on the many experimental studies where absorption and des-
The absorption of nitrogen by pure liquid iron have been studied. The absorption of nitrogen is a dominating phenomenon during the stages 1–3 in the AOD process and its rate is calculated using the first-order equation, Eq. (1). Second-order equation, Eq. (2), is used to calculate desorption rate which is dominant during the 4th stage and the reduction stage. Nitrogen behavior is calculated stage by stage and either absorption or desorption can be possible during each stage depending on the circumstances. Integrating both equations with respect to time gives equations for nitrogen concentration of melt as a function of time during absorption and desorption alike

\[ C(t) = C_e - (C_e - C_0) e^{-kt} \]  
\[ C(t) = C_e e^{bt} - 1 \]  

where

\[ a = \frac{C_e + C_0}{C_e - C_0}, \quad b = 2C_e k_{eff} \frac{A_{eff}}{V} \]

and \( C_0 \) is the initial nitrogen concentration of stainless steel melt. The model has been created based on these two Eqs. (3) and (4) in this study.

4. Submodels

Industrial AOD process is complicated and therefore detailed on-line simulations of stainless steel’s nitrogen content based on the fundamental phenomena during process are time consuming. Simplified sub-models including relevant phenomena affecting on the nitrogen transfer are needed. The purpose of the sub-models was to rationalize calculations by taking into account only the most important factors and by simplifying relations between the parameters. The role of the sub-models as well as their relations are illustrated in Fig. 4. The areas of the AOD modeling that are considered in this paper are marked with the boxes with black background, whereas the boxes with white background indicate the areas of the modeling/research which
are excluded from this paper due to the fact that they are not in focus when the emphasis of the paper is on the average nitrogen content of the molten metal. Although the macroscale computational fluid dynamics has an essential role when considering the local nitrogen contents in the different areas of the AOD process, it is not the dominating factor when the average values are considered.

4.1. Equilibrium Nitrogen Content of Stainless Steel Melt

The equilibrium content of nitrogen has been calculated using computational thermodynamic software FactSage and its databases. Because thermodynamic calculations cannot be directly included in the final nitrogen model due to time-consuming calculation, it has been necessary created simplified descriptions for equilibrium content of nitrogen. The description of equilibrium content of nitrogen aims to define how much nitrogen can be in the stainless steel melt in equilibrium with Ar–N₂-gas as a function of steel and gas compositions.

The effects of different solute elements on the nitrogen content of melt in equilibrium with Ar–N₂-gas have been studied in our previous work. The result of this research indicates that the most significant elements affecting on the equilibrium content of nitrogen in the melt within the composition range of the melt in the AOD are chromium and nickel (Fig. 5). These elements exist in the melt in AOD process with high contents and quite wide range. Mn content was below 1.5 wt% in studied heats and therefore its effect on the nitrogen equilibrium content of steel can be considered as negligible in comparison with the effects of other elements. Additionally, the partial pressure of nitrogen in gas bubble has been found to affect remarkable on equilibrium content of nitrogen in steel melt.

In the present work, the equilibrium nitrogen content of stainless steel melt with Ar–N₂-gas mixture has been described as a function of nickel and chromium contents and partial pressure of nitrogen by Eq. (5)

\[
[N \text{ wt}%] = (-11.786m_{\text{Cr}} + 1.8136m_{\text{Cr}} - 0.2325)m_{\text{Ni}} + 9.6786m_{\text{Cr}} - 1.1532m_{\text{Cr}} + 0.1518)p_{\text{N}}^{0.2325}
\]

where \([N \text{ wt}%]\) is the equilibrium content of nitrogen in the steel melt in wt%, \(m_{\text{Cr}}\) is the mass fraction of chromium in the steel melt and \(m_{\text{Ni}}\) is the mass fraction of nickel in the steel melt and \(p_{\text{N}}\) is the partial pressure of nitrogen in the gas phase in contact with steel.

4.2. Effective Surface Area \(A_{\text{eff}}\)

Many investigators have noticed significant decreases in absorption and desorption of nitrogen with increases in contents of surface active elements such as oxygen and sulphur. The effect is remarkable even at very low solute contents. Surface active elements have been found cover the interface and block nitrogen transfer through the gas–melt interface. In the present model, nitrogen transfer during absorption has been assumed to happen on sites of other component of steel melt than oxygen, sulphur or nitrogen. During desorption, nitrogen transfer has been assumed happen on sites in which nitrogen atoms has transferred on the interface.

Composition of interface and effective surface area for nitrogen transfer has been calculated by model based on modified form of Butler’s equation. The model calculates composition of gas–iron alloy interface for Fe–N–S–O system by Newton–Raphson root-finding technique. This model has been presented in detail in our previous work. The average contents of the oxygen, sulphur and nitrogen in blowing stages have been defined from the experimental data with an exception concerning the oxygen content of the melt during the 2nd, 3rd and 4th stages, in which the oxygen content is assumed to be at maximum of 400 ppm due to the thermodynamic equilibrium content of oxygen with Cr₂O₃ in 17Cr8Ni steel melt. (Table 4) Surface area covered by sulphur, nitrogen and oxygen under that circumstances have been calculated by the model based on Butler’s equation (Table 5).

According to the calculations gas–melt surface is mainly covered by oxygen. Role of sulphur is insignificant except on the 1st stage. Nitrogen can also act as a surface active element according to the calculations. This is also found out in the previous studies. Effective surface area for nitrogen transfer \((A_{\text{eff}})\) during the absorption is defined as a difference between total surface area ant the area covered by oxygen, sulphur and nitrogen. During the desorption \(A_{\text{eff}}\) is the area that is covered only by nitrogen. Effective surface area for nitrogen transfer achieved its maximum during the 1st stage (absorption). During the desorption effective reaction surface area is only approximately 7–9%. In the present model effective surface area for nitrogen transfer has been
described by simplified relations in Eqs. (6) and (7). Equation (6) describes surface area during absorption and Eq. (7) during desorption. Effective reaction area \( A_{\text{eff}} \) decreases during absorption (as seen from Eq. (6)) due to the increase of contents of surface active elements during the 1st–3rd stages. When nitrogen removal takes place during the 4th stage and the slag reduction, the nitrogen content decreases as a function of process time which causes a decrease in the values of \( A_{\text{eff}} \) for the desorption (as seen from Eq. (7)).

\[
A_{\text{eff}} = (1 - 1.8 \cdot 10^{-4}t - 0.57)A \quad \text{(6)}
\]

and

\[
A_{\text{eff}} = (-4.8 \cdot 10^{-5}t + 0.19)A \quad \text{(7)}
\]

where \( t \) is process time (s) and \( A \) is total surface area between gas bubble and melt (m²). Total surface area between gas bubbles and melt in AOD is calculated by CFD. According to the CFD simulations total surface area is approximately 600 m² with usual process gas flow rates.

4.3. Rate Constant

In the present work rate constants for nitrogen absorption and desorption have been found from the literature. Rao and Lee\(^ {16} \) have studied nitrogen absorption in molten Fe–C alloys. In this model \( k_1 = 23 \cdot 10^{-5} \text{ cm/s} \) has used as a value for the first order rate constant and \( k_2 = 45 \cdot 10^{-6} \text{ cm/(s · ppm)} \) for the second order rate constant.\(^ {16} \) These values for \( (k_1 \text{ and } k_2) \) have been used although Rao and Lee have observed that reaction rate constants are influenced by sulphur content of melt and partial pressure of nitrogen. Rate constant values of pure Fe–C alloy were used because the effects of surface tension elements have been taken into account by effective surface area. It was also assumed that the partial pressure of nitrogen has no effect on the reaction rate constant but it effects on the nitrogen transfer is accommodated as a form of thermodynamic driving force.

4.4. Partial Pressure of Nitrogen in the Gas Bubble

The partial pressure of nitrogen in the gas bubble in each process stage depends on blowing gas composition and nitrogen content of steel melt. For the model, the nitrogen partial pressure in the gas bubble is calculated from the measured nitrogen content of melt and gas volumes in the AOD process (Table 6). These average nitrogen partial pressure values were used in Eq. (5) to calculate thermodynamic equilibrium content of nitrogen. According to the calculations there is very high thermodynamic driving force for absorption of nitrogen during the 1st stage.

5. Results and Discussion

Changes of nitrogen contents of steel melts corresponding typical austenitic stainless steels during the AOD process are presented in Fig. 6 and Fig. 7 as an examples. Experimental measurements are described by (diamond) markers. Due to the difficulty of the measurements, only one measurement per heat was taken before the slag reduction period in addition to the initial and final samples. Nitrogen content of melt increases during three first decarburization stages when nitrogen is used to decrease partial pressure of CO. Absorption is assumed to take place by dual site mechanism during the 1st stage due to the low contents of the surface active elements and by single site mechanism during the 2nd and the 3rd stage when the contents contents of sulphur, oxygen and nitrogen are higher. When argon is utilized, nitrogen content of melt decreases at the final period of decarburization and during slag reduction. Typical initial nitrogen contents were about 400 ppm whereas the maximum values of 1000–1500 ppm were achieved before nitrogen argon switch-point. Calculations show that desorption rate of nitrogen is low and final nitrogen contents below 400 ppm’s are very difficult to achieve economically.

Figure 8 shows differences between calculated and measured nitrogen contents of the steel melt. The nitrogen model seems to predict the nitrogen content of the steel melt during different stages of AOD process relatively well. The biggest differences are in top contents and the smallest in final contents. Other samples are contents of nitrogen before slag reduction period. Mean deviation between calculated and measured final contents is about 50 ppm, Table 7. There are difficulties to predict nitrogen content when process time is short (Heats 3 and 9). On the other hand there are also examples of good predictions (Heat 1 and 6) for heats of short processing time.
The effective reaction surface area is only approximately 7–9%.

During the 1st stage (absorption) during the desorption effective surface area for nitrogen transfer achieved its maximum. According to the study effective surface area for nitrogen transfer are treated separately. Advantages of the model. These effects are emphasized in heats, which have a short processing time.

In the presented model thermodynamic driving force, chemical reaction itself and kinetic barriers for nitrogen transfer in gas–melt interface are treated separately. Advantage of model is that it can be used to define the nitrogen-argon switch-point for production of different stainless steel grades. Furthermore, model can be utilised as a tool to study effects of individual factors like oxygen content on the nitrogen removal in industrial AOD.

In our future work nitrogen model will be implemented in to the CFD and developed with a more detailed description of average partial nitrogen pressure in gas plume inside the melt. Furthermore, the total surface area between the steel melt and gas bubbles has to be defined as a function of injected gas.

### 6. Conclusions

A computational model based on mass transfer and thermodynamic data as well as kinetic information from the industrial AOD process has been created in order to simulate the nitrogen content of the stainless steel melt as a function of blowing time. The model uses the Butler’s equation to calculate the reaction area available for nitrogen transfer between the steel and gas bubbles. According to the study effective surface area for nitrogen transfer achieved its maximum as well as thermodynamic driving force is also high during the 1st stage (absorption). During the desorption effective reaction surface area is only approximately 7–9%.

Typical initial nitrogen contents were about 400 ppm whereas the maximum values of 1000–1500 ppm were achieved before nitrogen argon switch-point. Simulations showed that desorption rate of nitrogen is low and final nitrogen contents below 400 ppm’s are very difficult to achieve economically. According to the simulations model predicts final nitrogen content of stainless steel melt after AOD process with 50 ppm accuracy.

### Acknowledgements

This research was financially supported by Finnish Funding Agency for Technology and Innovation, Academy of Finland and Outokumpu Stainless, which are kindly acknowledged by the authors. The authors would also like to thank Paavo Hooli and Veikko Juntunen from Outokumpu Stainless, Mika Järvinen from Helsinki University of Technology and Olli Mattila from University of Oulu for many discussions and comments concerning the topic.

### REFERENCES