A Fundamental Investigation of Decarburization Reactions in the Argon–Oxygen Decarburization Converter Using Coupled Computational Fluid Dynamics and Thermodynamics Databases

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Metallurgical converters such as the argon–oxygen decarburization (AOD) converter generally utilize gas blowing for the mixing and refinement of liquid steel. Due to the harsh environment of the complex and opaque system, it is common practice to study the stirring of the process through physical and numerical models. Effective mixing in the bath has an important role in refinement such as decarburization and has been vividly studied before. However, high-temperature chemical reactions that also play a major role are sparsely investigated. With the help of modeling, a computational fluid dynamics model coupled with chemical reactions is developed, allowing the study of both dynamic fluid transport and chemical reactions. Herein, the chemical reactions for a single gas bubble in the AOD are investigated. The study shows that a 60 mm oxygen gas bubble rapidly reacts with the melt and is saturated with carbon in 0.2–0.25 s at low-pressure levels. The saturation time is affected by the pressure and the composition of the injected gas bubble. The impact of ferrostatic pressure on the reactions is more significant at larger depth differences.

1. Introduction

Decarburization is a common step for carbon reduction in the steel-making practice. Decarburization involves oxygen injection to reduce the carbon content in the steel melt and is crucial for secondary steelmaking processes such as the argon–oxygen decarburization (AOD) process. In general, decarburization is similar to other secondary steelmaking processes such as the basic oxygen furnace (BOF). However, in the AOD process, it is also a requirement to maintain the stainless properties acquired by elements such as chromium. Hence, the difficulty is to oxidize the excess carbon without oxidation of chromium described by the main reactions in the AOD.\(^\text{(1)}\)

\[
2[\text{C}] + 2[\text{O}_2] = 2[\text{CO}]
\]

\[
4[\text{Cr}] + 3[\text{O}_2] = 2(\text{Cr}_2\text{O}_3)
\]

Combined to

\[
3[\text{C}] + (\text{Cr}_2\text{O}_3) = 2[\text{Cr}] + 3[\text{CO}]
\]

where \([\text{C}]\) is the gaseous form, \([\text{C}]\) is dissolved in liquid, and \([\text{C}]\) is in the slag.

A lot of work has been dedicated to understanding the complexity of the AOD and BOF systems and gas stirring is involved, numerical modeling has been a popular choice.\(^\text{(2)}\) With numerical modeling, it is possible to lower the design cost and add transparency to the highly complex metallurgical systems, which otherwise cannot be observed or easily measured. Although there exists an extensive amount of work, this work mostly covers the fluid dynamics of the process ranging from sonic jet top lance to more abstract areas such as mixing and homogenization. Therefore, further understanding and development of the complex processes require investigations into different aspects of the thermodynamic parts such as the high-temperature decarburization reactions. One of which is the decarburization zone.

Fruehan\(^\text{(3)}\) studied the reaction sequence and mechanisms for oxidation of chromium and carbon and found that chromium oxidation is considerably faster than carbon oxidation. The study states the possibility that the main reaction at the nozzle region is the oxidation of chromium at the bubble interface. Further, as the bubble rises in the bath, Cr\(_2\)O\(_3\) is reduced by carbon. In this way, there are local reactions taking place at one part of the process which further up in the bath reacts with other products due to species transport and implies that total equilibrium exists in the AOD converter. The combined reaction above states that a lower partial pressure of CO benefits decarburization. The partial pressure of CO is partly governed by the ferrostatic pressure,\(^\text{(4)}\) which implies that decarburization is more effective at the surface due to the lower ferrostatic pressure. On the contrary, another hypothesis is that local equilibrium exists in the AOD instead of total equilibrium. For this hypothesis, most of the
Decarburization occurs at the nozzle region which is affected by the ferrostatic pressure imposed by the bath height above the nozzle. Thus, decreasing the height between the nozzle and the bath surface could introduce more efficient decarburization.

Asai and Szekely\cite{5,6} presented an early mathematical model to describe temperature and composition trajectories for decarburization. The model is based on component balances using driving force expressions, equilibrium relationships, and heat balance. A new mathematical model for the AOD process was developed by Wei and Zhu et al.\cite{17–14} However, this model treats all possible oxidation and reduction reactions simultaneously and reaches a combined equilibrium in competition at the liquid/bubble interfaces. With the help of Gibbs free energies of oxidation reactions, the model characterizes the competitive oxidation among the elements and determines the corresponding oxygen distribution. The model also considers the difference in the existing regimes of rate control for decarburization at high and low carbon levels by the assumption that the oxidation rate of elements at high carbon levels is mostly related to the supply of oxygen, while at high carbon levels the supply of oxygen is mostly related to the transfer of liquid bulk to the reaction interface determines the decarburization rate for lower carbon levels. In addition, the model assumes that the nonreacting oxygen blown into the bath escapes at the liquid interface rather than accumulating as a dissolved phase in the steel bath.

Järvinen et al.\cite{12} developed a reaction submodel for a computational fluid dynamics (CFD) solver describing chemical reactions as well as heat and mass transfer taking place on the surface of a gas bubble. The method assumed a fast/infinite kinetic rate, with the mass transfer as the dominating mechanism for solving the rates in a controlled multicomponent reaction system. The rate expression was based on the modified law of mass action, thus making it possible to simplify and couple it with the conservation equations. The results suggested that at high oxygen concentrations, most of the oxygen gas reacts with carbon to form CO and that equilibrium is reached after 0.06 s at the surface interface. The model was further developed to predict local variations in conditions such as total pressure, void fraction, bubble size, etc.\cite{13,14} In this model the activities were calculated based on the unified interaction parameter (UIP) model to acquire accurate information on the thermodynamic behavior.

A further extension to the reaction model in other studies\cite{12–14} was developed by Visuri et al.\cite{15} to include the reduction of top slag during the AOD reduction stage. The dominating reactions were assumed at the surface of the emulsifying slag droplets using thermodynamic submodels considering the activities of metal and slag. By including mass transfer reversible reactions and various additions to mass and heat balance, the model was able to predict the reduction stage in the AOD reasonably well.\cite{16}

Another method for existing kinetic process model predictions is the effective equilibrium reaction zone (EERZ)\cite{17–20} coupled with thermodynamic software such as FactSage or Thermo-Calc. With the help of thermodynamic databases, the local equilibrium calculation approach is applicable and the change of the chemical composition of bulk is controlled by interface reactions and the mass transfer coefficient. EERZ treats the reaction volume between two species as several finite number sections, first, calculating equilibrium at the interface which is followed by the homogenization reaction in the other finite sections.

Despite the earlier achievements in the cost-efficient satisfactory modeling of the AOD process, they rely on stagnant mathematical descriptions of the reaction surface interface. For this study, a more dynamical approach is required; hence, the coupling method between CFD and thermodynamic modeling developed\cite{21–25} is more suited. Ersson et al.\cite{21,22} developed a fundamental dynamic model of decarburization in a top-blown converter. The model integrated fluid dynamics with thermodynamic databases allowing thermodynamic reactions and continuous decarburization of molten steel surface over time. This was accomplished by achieving local cell equilibrium with the present chemical species. Andersson et al.\cite{24,25} developed a fluid flow and reaction model for the decarburization stage of the AOD including liquid, gas, and slag phases. The coupled model is also based on a single-cell local equilibrium between species elements. Furthermore, with a similar approach, Liu et al.\cite{23} developed a new multizoned reaction model that couples thermodynamics with CFD. The model predicted maximum hot spot temperature and decarburization rate in a bottom-blown electric arc furnace (EAF).

As seen earlier, numerical modeling of steel processes has grown over the years and is becoming more complex. Developed kinetic process models and coupled models can be used as a tool to understand more about the complex steelmaking process. The purpose of the present study was to develop a coupled fluid and thermodynamic model based on the local cell equilibrium concept. The focus was on the decarburization reactions taking place when an oxygen bubble rises in liquid steel. This was done to investigate fundamental phenomena such as where reactions take place, the effect of ferrostatic pressure, and the kinetics. This study is part of a larger research project to develop a dynamically coupled model of an AOD process and is important to further understand the complexity of the industrial decarburization process. The authors would like to stress that the objective of this study is not to present an overall AOD process simulation, but rather a model that provides the potential for transparency in decarburization reactions. Specifically, the effect of ferrostatic pressure on bubble decarburization is investigated.

2. Experimental Section

2.1. CFD Model

The model tracked the interface between the phases using the volume of fluid (VOF) model\cite{26} by solving the continuity equation of each phase volume fraction. The gas phase is solved with Equation (4)

$$\frac{\partial}{\partial t} \left( \alpha g \rho \right) + \nabla \cdot \left( \alpha g \rho \mathbf{v}_g \right) = S_{n_g} + \sum_{n=1}^n \left( m_{l_g} - m_{l_g} \right)$$

where \( \alpha \) is the volume fraction, \( \rho \) is the density, \( \mathbf{v} \) is the velocity vector with \( g \) and \( l \) as indices for gas and liquid phases, respectively, \( m_{l_g} \) is the mass transfer from gas to liquid phase, and \( m_{l_g} \) the mass transfer from liquid to gas phase. \( S_{n_g} \) is an additional source term.

In each control volume, the volume fraction of the liquid phase was computed based on the following constraint, as shown in Equation (5).

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*References*
\[ \alpha_g + \alpha_l = 1 \quad (5) \]

All phases were treated as incompressible Newtonian fluids with constant physical properties, where the model solves a set of mass and momentum conservation equations for the mixture phase in the following form.

\[ \frac{\partial}{\partial t} (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \nabla \cdot [\mu (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)] + \rho \mathbf{g} + \mathbf{F} \quad (6) \]

where \( \mu \) is the dynamic viscosity and \( p \) and \( \mathbf{g} \) are the pressure and gravitational acceleration respectively. Furthermore, \( \mathbf{F} \) represents the surface tension force, which was considered using the continuum surface force (CSF) model expressed as Equation (7) for a two-phase system:\[26]\]

\[ \mathbf{F} = \sigma \frac{\mu_0 \nabla \mathbf{m}}{0.5 (\rho_g + \rho_l)} \quad (7) \]

\( \sigma \) is the surface tension coefficient and \( \nu = \nabla \cdot \mathbf{m} \), \( \mathbf{n} = \frac{\nabla \mathbf{m}}{\text{div} \mathbf{m}} \).

In all bubble simulations, the flow was considered to be laminar, whereas the first system with water/air was isothermal and for the second system with steel/oxygen, the temperature was treated by sharing the energy equation among the phases according to Equation (8). The water/air system was investigated to establish a decent bubble evolution before applying the steel/oxygen system and reactions. This is explained more clearly in the next sections.

\[ \frac{\partial}{\partial t} (\rho E) + \nabla \cdot (\rho \mathbf{v} E + p) = \nabla \cdot (k_{\text{eff}} \nabla T) + S_n \quad (8) \]

The specific energy \( E \) and temperature \( T \) are treated as mass-averaged variables, \( k_{\text{eff}} \) is the effective thermal conductivity, and \( S_n \) is the source term that contains contributions from volumetric heat sources such as radiation.

A 2D axisymmetric computational domain was used under the simplification of a rectilinear bubble ascent to minimize the computational time. Previous work\[27\] has reported that for the current Eötvös (\( E_0 \)) and Galilei (\( G_0 \)) numbers, the bubble ascent will be stable, thus further justifying the usage of a 2D axisymmetric model. The wall and outflow boundaries were set to no-slip and pressure outlet conditions, respectively. The geometric reconstruction scheme was used to track the interface and the pressure-implicit with splitting of operators (PISO) scheme was used for the pressure-velocity coupling.\[28\] The parameters used for both systems are presented in Table 1.

Before coupling with the chemical reactions, the CFD model was tested for grid independence using the recommendations of previous work\[29–31\] as a starting point. To eliminate the effect of boundaries on the bubble behavior, the solution domain size should be a minimum of 8 times the bubble diameter \( (d_b) \) and 16–25 quadrilateral computational cells were required across the bubble to correctly predict the bubble characteristics. Therefore, an initial case in the water/air system was calculated with 12, 16, 20, and 25 cells across a 0.01 m bubble diameter. The bubble ascent and shape evolution were studied through the terminal velocity and size aspect ratio, as presented in Figure 1. The calculations with 20–25 cells across the bubble showed small deviations to terminal velocity and a maximum deviation of 8.2% for the size aspect ratio. Hence, 25 quadrilateral cells across the bubble were suited for the simulations.

### Table 1. Material properties, where \( g \) and \( l \) are subscripts for gas and liquid phase respectively.

| Calculation system | Unit | Water/air | Steel/oxygen |
|--------------------|------|-----------|--------------|
| \( \rho_g \) | [kg m\(^{-3}\) s\(^{-1}\)] | 1.79 \times 10\(^{-3}\) | 4.90 \times 10\(^{-3}\) |
| \( \rho_l \) | [kg m\(^{-3}\)] | 6.70 \times 10\(^{-3}\) | 1.30 |
| \( \mu_g \) | [kg m\(^{-3}\) s\(^{-1}\)] | 1.23 | 997 |
| \( \mu_l \) | [kg m\(^{-3}\)] | 7030 | 7.28 \times 10\(^{-3}\) |
| \( C_{pg} \) | [J kg\(^{-1}\) K\(^{-1}\)] | – | 1006 |
| \( C_{pl} \) | [J kg\(^{-1}\) K\(^{-1}\)] | – | 800 |
| \( K_g \) | [W m\(^{-1}\) K\(^{-1}\)] | – | 0.024 |
| \( K_l \) | [W m\(^{-1}\) K\(^{-1}\)] | – | 64 |
| \( T_{\text{initial}} \) | [K] | – | 1873 |
transient CFD solution. Thereafter, Thermo-Calc calculated equilibrium separately for each phase to account for the enthalpy and heat contents which served as inputs to calculate the total equilibrium. Finally, new temperatures, compositions, and masses were sent back to the CFD solution for the next timestep, as shown in the flowchart in Figure 2. The thermodynamic element quantities were treated with scalar transport locked to its fluid phase. The slag phase was included in the CFD solution. However, it was treated as an inert scalar in the liquid phase when formed. The reaction only takes place if the gas volume fraction is between 0.3 and 0.9 in the computational cell. This limit was set to decrease the number of equilibrium calculations that also would have only a minor impact on the results.

2.3. Numerical Procedure

All CFD simulations were performed using ANSYS Fluent R3 2019 with a convergence criterion of $1 \times 10^{-6}$ for all dependent variables except for energy, which was set to converge at $1 \times 10^{-10}$. The effect of the global Courant number ($C_{\text{global}}$) was tested prior to any calculations. Three different calculation methods were tested: 1) $C_{\text{global}} = 1$ with a fixed timestep of $1 \times 10^{-3}$ s, where equilibrium was calculated at each timestep, 2) $C_{\text{global}} = 0.1$ with a fixed timestep of $1 \times 10^{-4}$ s, where equilibrium was calculated every 10 timesteps, and 3) $C_{\text{global}} = 0.1$, with an adaptive timestep of $1 \times 10^{-4}$ s, where equilibrium was calculated every 10 timesteps. Figure 7 in the result section shows a negligible difference between a) $C_{\text{global}} = 1$ with a fixed timestep and c) $C_{\text{global}} = 0.1$ with an adaptive timestep; hence, an adaptive timestep up to $1 \times 10^{-3}$ s with the criterion to meet a global Courant number below 0.1 was used for the simulations. All simulations ran for 0.3 s.

The original approach referred to as Case I intended to investigate the effect of ferrostatic pressure on decarburization by patching a spherical oxygen bubble with a 0.06 m diameter into a volume of liquid steel. The pressure imposed on the bubble from a 1.3 m bath height was simulated by calculating the bubble ascent in a domain height of 0.3 m with an outlet gauge pressure. The outlet pressure represents the depth of the bath where three levels were calculated, referred to as P1, P2, and P3 corresponding to the bubble being released at the depths of 1.3, 1.2, and 0.3 m, respectively, Figure 3. The weight fraction of elements in each phase was monitored with user-defined scalars (UDS), which applied the convection and diffusion of their corresponding phases.

Previous studies\([27,29–31,36–39]\) of the shape evolution of a rising bubble in water/air systems have been experimentally characterized and mapped with dimensionless numbers. For instance, the $E_0$ number was a ratio of gravitational force to the surface tension force $E_0 \left( \frac{\rho g \pi}{\sigma} \right)$, with $\rho_1$ as liquid density, $g$ as gravitational

Table 2. Initial melt composition (case I).

| Mass % C | Mass % Cr | Mass % Fe | Mass % N | Mass % Ni | Mass % O |
|----------|-----------|-----------|----------|-----------|---------|
| 1.50     | 26.0      | 68.0      | 0.09     | 4.50      | 0.03    |

Figure 1. Mesh study over a) bubble width and height ratio and b) rising bubble velocity. Note that linear interpolation between the points has been used to increase readability. The legends $d/25$, $d/20$, $d/16$, and $d/12$ are the number of quadrilateral cells across the bubble.

Figure 2. Coupling flowchart between Fluent and Thermo-Calc.
acceleration, $R$ as initial radius, and $\sigma$ as surface tension coefficient. The $\text{Ga}$ number was the ratio of the gravitational force to the viscous force $\text{Ga} \equiv \sqrt{\frac{\rho l R}{\mu l}}$, where $\mu_l$ is the dynamic viscosity of the liquid and Morton number $\text{Mo} = \text{Eo}^3/\text{Ga}^4$. Hence, if the values from Table 1 are applied to these dimensionless numbers, the bubble shape behaviors for both water/air and steel/oxygen systems are predicted to be described in Table 3 according to the regimes, as shown in Figure 4.

The second approach referred to as Case II released the bubbles at the same depth corresponding to the pressure levels P1, P2, and P3. However, nitrogen and argon were added to the bubble according to Table 4 to resemble process gas at the first step of decarburization.

### 2.4. Mesh Sensitivity

When patching a circular bubble into a domain consisting of quadrilateral cells, the volume fraction will cover cells within the boundary of the bubble’s interface. However, some cells close to the boundary were excluded, as shown in Figure 5a. Therefore, when refining the grid, the size of the excluded cells close to the boundary differed, which affected the initial mass of the elements inside the bubble, as shown in Figure 5b. Hence, a traditional mesh sensitivity study is not applicable to study the grid dependence on the mass of the elements. Instead, a square bubble was patched to partly resolve this problem, as shown in Figure 5c,d. Three grids, 12,000 (25 cells across bubble), 16,000, and 22,000 cells, were used to investigate the grid independence for the coupled model. An unstructured mesh could be used, that conforms to the initial bubble shape. However, this would create a mesh that is not quadrilateral which is more ideal for this study since quadrilateral meshes are preferred for the VOF. Ideally, an adaptive quadtree mesh would be used, but it is out of scope for the current study.

### 3. Results and Discussions

This study focuses on the model coupling to predict the decarburization reaction of a rising bubble under different pressures. However, prior to coupling with the thermodynamic reactions, a bubble ascent pattern is required.

| Calculation System | Eo | Ga | Mo | Shape evolution |
|--------------------|----|----|----|----------------|
| Water–air          | 3.4 | 1104 | $2.5 \times 10^{-11}$ | sphere, ellipsoid cap, wobbly ellipsoid cap |
| Steel–oxygen       | 34  | 17076 | $4.6 \times 10^{-13}$ | sphere, spherical cap, breakup, toroid |

Figure 3. The domain and setup of different pressure levels P1, P2, and P3 with their respective outlet pressures to represent the depth of the injected bubble.

Table 3. Dimensionless numbers and corresponding shape evolution with inserted values from Table 1.

Table 4. Gas composition for case II where the released bubble also contains nitrogen and argon.

Mass % C | Mass % Cr | Mass % Fe | Mass % N | Mass % Ni | Mass % O | Mass % Ar
---|---|---|---|---|---|---
0  | 0  | 0.15 | 0 | 0.79 | 0.06

Figure 4. Different regimes of bubble shape and behavior. The different regions are: axisymmetric (circle); asymmetric (solid triangle); and breakup (square). The axisymmetric regime is called region I. The two colors within the asymmetric regime represent nonoscillatory region II (shown in green) and oscillatory region III (blue) dynamics. The two colors within the breakup regime represent the peripheral breakup region IV (light yellow) and the central breakup region V (darker yellow). The red dashed–dotted line is the $\text{Mo} = 10^{-10}$ line, above which oscillatory motion is not observed in experiments in other studies. Typical bubble shapes in each region are shown. In this and similar figures below, the bubble shapes have been made translucent to enable the reader to get a view of the internal shape. Reproduced with permission,²⁷ 2015, Nature Communications. Figure 1.
The bubble shape evolution in water/air systems has been previously studied and characterized with the dimensionless numbers mentioned in the Experimental Section.\(^{[27,29–31,36–39]}\) The topology of the bubble during ascent agrees well with the predicted bubble rise in the study by Tripathi et al.\(^{[27]}\) It is described as the asymmetric oscillatory region with a final state of a wobbly ellipsoidal shape, as shown in Figure 6a. The high \(E_o\) and \(G_a\) numbers in the steel/oxygen system (Case I) are not within the measured boundaries in the characterization map of Tripathi et al.\(^{[27]}\) However, it follows the pattern and behaves as the map suggests with a central breakup. In addition, it agrees with the statement that high \(E_o\) and \(G_a\) numbers result in a steady central breakup to a toroidal shape during the ascent, as shown in Figure 6b.

The axisymmetric simulation might not be suitable for this case due to the suppression of an unstable bubble ascent. However, due to the lack of experimental studies on the correlation between the bubble ascent and dimensionless numbers for a steel/oxygen system, the study relies on the statement of Xu et al.\(^{[30]}\) Gas bubbles with a diameter of 10–20 mm in steel rise in a stable linear path and hence, the CFD part of the coupled model is considered reasonable for the study.

Figure 7 shows a small effect of the different calculation setups on oxygen in the gas bubble. It can be seen that the global Courant number, that is, the timestep, has a very small impact on the results. The oxygen content in the bubble shows a similar trend as the other elements after the initial reactions; notice that the normalized mass is plotted in the figure. All further graphs presented in the article are normalized against the elements’ initial mass denoted as \(m_{\text{element}}/m_{\text{element}}^0\) on the Y-axis.

Figure 8 shows the normalized mass of oxygen in the square gas bubbles reacting while ascending in the steel for different grids. The mesh sensitivity study for reactive flow can be seen to differ at most by 4.5% between 12 and 22 k cells. Therefore, with these small differences, it was deemed reasonable to continue with the 12 k mesh, found in the previous mesh sensitivity study, to save computational time.

3.1. Case I: 60 mm Oxygen Bubble Ascending 0.3 m

The temperature at the bubble–liquid interface and its distribution, controlled by convection during the ascent, is illustrated in Figure 9 for the 60 mm bubble. The temperature is initially set to 1873 K and rises to 1890 K due to the exothermic reactions at the interface. The instantaneous rise in temperature is also found by...
Järvinen et al. and the level agrees with the operating temperature span in the AOD process during decarburization.

The normalized mass of carbon in gas and steel is presented in Figure 10 for the pressure levels P1 and P2. It appears that the oxygen bubble reacts drastically with carbon and nitrogen in steel melt to produce off-gases. However, as the mass of the steel surrounding the bubble is remarkably larger than the bubble mass, the initial local equilibrium in the bubble dynamically adjusts toward a global equilibrium in the system. This is visually represented in Figure 11, where the mass fraction of gas is seen to disappear over time.

To further investigate the possible final state, single-point equilibrium calculations were performed for the cases P1, P2, and P3. P1 and P2 could not sustain any gas at THE final thermodynamic equilibrium. On the other hand, at lower pressure levels such as P3, gas becomes more stable, which resulted in both liquid and gas as stable phases in the system. This is seen in both single-equilibrium and coupled model calculations. The difference in the elements during the bubble ascent is presented in Figure 12 and 13 and a visual representation of the carbon gradient in the bubble over time is illustrated for the P3 level in Figure 14. It can be seen from Figure 12 and 13 that the pressure has a large effect on decarburization and nitrogen removal. It is also possible that the kinetics are fast enough to admit decarburization calculations at pressures close to surface pressure. However, with larger gas flow rates, there will be a larger concentration gradient in the plume region that may admit decarburization at higher pressures.

It is not possible to provide a quantitative validation due to the lack of experimental data. In this study, a qualitative comparison has been done. For this case, the results show that the most active elements are carbon and nitrogen, as illustrated in Figure 15, with the normalized mass of elements in steel for P3. The carbon is drastically increased in the gas bubble before 0.2 s and seems to level out due to saturation of the bubble. This behavior is visually illustrated in Figure 14, where the carbon gradient appears to diminish between the frame 0.2 and 0.25 s. This trend is common in the AOD process and is also predicted in the previous work. The period for a fully saturated CO bubble may be affected by the ascending shape evolution (breakup or no breakup), supply of oxygen (size of bubble), and/or mass transfer of carbon to the interface (bubble rising velocity).

Furthermore, as presented in previous works, oxidation of elements such as iron and chromium is inevitable in the AOD process. Despite this, no oxidation of Cr and Fe appears in Case I. This can be explained by the scale difference of the simulations between this case and previous work. The previous studies calculate the decarburization of a full AOD converter ranging from 5 min to full process while this case is calculated for a single bubble. Another explanation is connected to the initial conditions such as the amount of dissolved oxygen or carbon in the melt. In the bubble simulation by Järvinen et al., they found that the major fraction of oxygen oxidizes the carbon in the melt due to the high initial carbon content of 1 mass-%. This was also found by Andersson et al. with 0.6 mass-%. The initial dissolved carbon and oxygen content for this case is 1.5 and 0.03 mass-%, respectively, which implies that the oxygen from the gas bubble is dissolved into the steel instead of oxidizing chromium or iron. Basically, this case
represents the first injected oxygen bubble into a freshly taped melt that has progressed from the earlier step in the production line, for example, the EAF. This context is important to note as it could indicate that the melt is yet to reach the critical conditions required for chromium oxidation. The reactions for different initial conditions will be presented and discussed in Case III.

3.2. Case II: 60 mm Bubble with Oxygen, Nitrogen, and Argon Bubble Ascending 0.3 m

The results for the bubble consisting of oxygen, argon, and nitrogen are presented in Figure 16 and 17. Due to the inert argon gas in the bubble, a gas phase will always be stable in the present system. Looking at Figure 16a, it is understood that the carbon that has entered the bubble does not fully dissolve back into the steel at higher pressure levels such as for P1 and P2 in Case I. However, with lower pressure, more carbon in the steel reacts with oxygen to form off-gases, as shown in Figure 16b. In addition, the time for carbon saturation in the bubble is extended. This is explained in Figure 17. As the bubble partly consists of nitrogen, it will dissolve into the steel at higher pressure levels (P1 and P2). On the other hand, at lower pressure levels (P3), the lowered partial pressure of N₂ increases nitrogen solubility in the bubble. The time to saturate the bubble with carbon is never reached for the low-pressure case (P3). However, after 0.2 s, there is a clear change in the rate at which carbon enters the bubble.

The difference in pressure for P1 and P2 does not appear to have a large effect on decarburization. However, it appears that
the saturation level is increased when the bubble is released at higher bath levels and that a bubble released close to the bath surface has the most efficient decarburization. This is due to the increased solubility of the elements in the gas at higher bath levels, which decreases the partial pressures in the bubble. In addition, the single-cell equilibrium calculations in the Thermo-Calc software agreed with the end results of the coupled model. This means that for a semiclosed system such as these cases with a single bubble release, the bubble in the coupled model will inevitably reach the state that is calculated with a single-cell equilibrium calculation. In practice, the plume in an AOD consists of interactions between multiple bubbles. With this in mind, it is difficult to describe how pressure affects the decarburization reactions in a continuous oxygen supply by modeling a single bubble. However, with the coupled model, it is possible to eliminate the closed system effect by modeling a continuous jet with the inlet positioned at different heights to include the pressure differences. This is important to better represent the practical operation and is planned for future work.

3.3. Case III: 60 mm Bubble Ascending 0.3 m with Different Initial Melt Conditions

In the cases discussed before, the initial composition of the steel represented a newly taped melt with high carbon and low oxygen content. In these cases, there was no slag formation during the calculations. In Case III, the initial steel melt composition was adjusted to fit a charge further into the decarburization step, as shown in Table 5, and the model was tested for the pressure case P3. The results show that a small amount of slag was formed with the elements: chromium, iron, and oxygen. The slag formation is illustrated as the mass of chromium during the bubble ascent, as shown in Figure 18. It is seen that the slag is being dragged along with the bubble. It is important to note that the slag which forms in these calculations is treated as inert and has the same physical properties as the liquid steel. This topic will also be included in further studies. In Case I and II, the supply of oxygen is restricted to the single bubble introduced. The model showed that at first contact with the melt it was more favorable to decarburize and oxidize the steel than to form slag. As the bubble occupies a small fraction of the domain compared with the steel, it did not affect the composition of the steel to the point of slag formation before
the bubble was saturated with carbon. In the industrial process, the supply of oxygen is much higher than a single bubble and is not comparable to this study. A jet oxygen supply is therefore well suited as the next step of this project. The current method is based on the assumption of very high reaction rates, limited only by local mass transfer. This is reasonable considering the very high temperatures of the process. However, to develop the method further, the next suggested step is to incorporate a reaction rate that is limited by the local cell turbulence. Furthermore, it is not fully understood how solid oxides behave in regard to formation as well as dissolution. The current approach to let the oxides form and afterward be treated as inert (nonreacting) should be seen as a first step to investigate the effect of pressure on the dynamic formation of oxides in the AOD process.

4. Conclusion

A coupled thermodynamic and fluid transport model on a dynamic oxygen bubble in a steel melt was developed to fundamentally investigate pressure differences in decarburization reactions. The successful software coupling has led to some promising development areas. 1) The reactions take place rapidly in the bubble was saturated with carbon. In the industrial process, the supply of oxygen is much higher than a single bubble and is not comparable to this study. A jet oxygen supply is therefore well suited as the next step of this project. The current method is based on the assumption of very high reaction rates, limited only by local mass transfer. This is reasonable considering the very high temperatures of the process. However, to develop the method further, the next suggested step is to incorporate a reaction rate that is limited by the local cell turbulence. Furthermore, it is not fully understood how solid oxides behave in regard to formation as well as dissolution. The current approach to let the oxides form and afterward be treated as inert (nonreacting) should be seen as a first step to investigate the effect of pressure on the dynamic formation of oxides in the AOD process.

Table 5. Initial melt composition (case III).

| Mass % C | Mass % Cr | Mass % Fe | Mass % N | Mass % Ni | Mass % O |
|---------|-----------|-----------|----------|-----------|---------|
| 0.5     | 25.2      | 69.84     | 0.16     | 4.2       | 0.1     |

Figure 16. Normalized mass of carbon in gas (case II). The left graph a) is adjusted to fit the data acquired from levels P1 and P2 whereas the right graph b) presents the whole range to include all pressure levels.

Figure 17. Normalized mass of nitrogen in gas (case II).

Figure 18. Chromium mass in inert slag formation over 0.28 s during bubble rise (case III).
and saturate the gas bubble with carbon as well as increase the temperature. The saturation time is affected by the pressure and the elements of the injected gas bubble. For a 60 mm oxygen bubble injected at the surface, the time to saturate the bubble with carbon is $\approx 0.2-0.25$ s, while a bubble consisting of oxygen, nitrogen, and argon requires more than 0.3 s. 2) The impact of ferrostatic pressure on the reactions was more significant at larger depth differences of the injected bubble. A bubble injected closer to the surface is saturated at higher carbon levels due to the low static pressure on the reactions was more significant. Even with an inert gas present, the ending oxygen supply of a single bubble poses difficulties in analyzing the effect of pressure on decarburization. This may be eliminated by modeling a continuous oxygen jet and will be investigated in further studies. The slag formation is dependent on the initial steel melt composition where melts representing early decarburization stages did not form any slag by the small amount of oxygen supplied from a bubble. 4) Further studies will involve a coupled model of a jet oxygen supply to investigate the effect of pressure on the decarburization reactions and study the critical point of chromium oxidation.

Acknowledgements

The authors wish to express their gratitude to the members of Jernkontoret committee, project 23033, as well as the innovative program Metalliska Material for all the creative and productive discussions, and the relevant insight into the industry. Special thanks to VINNOVA for financial support.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords

argon–oxygen decarburization process, bubbles, computational fluid dynamics, coupled models, decarburization reactions

Received: February 28, 2022
Revised: May 27, 2022
Published online: June 30, 2022

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