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The objective of this work was to develop a process model for the CAS-OB (Composition Adjustment by Sealed argon bubbling-Oxygen Blowing). The CAS-OB is designed to homogenize and control the steel composition and temperature before the casting. In the heating mode (OB) studied here, a refractory bell is lowered and submerged 30 cm below the liquid steel surface of the ladle and under this well-defined sealed volume, oxygen gas is injected to oxidize solid aluminum particles that are fed and molten at the surface. Under consideration were the melting of the solid aluminum particles, the oxidation of pure molten aluminum, and the oxidation of dissolved species, in this case Al, Mn, C and Si, and the solvent Fe. We also considered the formation and oxidation of steel droplets formed in the blowing when they pass through and react with the surface slag and also the reaction of pure aluminum on the top of the slag layer. Based on our simulations, only 30–40% of the chemical energy can be used to heat up the steel. A fraction of 0.8–0.85 of the $O_2$ can be utilized in the process; these values correspond to those obtained in previous work. The main part of the heating energy comes from the oxidation of the fed Al. FeO is primarily an intermediate product of the reactions. The model was tested against industrial trials for steel temperature and compositions of slag and steel, and it succeeded in capturing correct trends and absolute accuracy within the analyzing accuracy.

KEY WORDS: CAS-OB; numerical modeling; heat-up stage.

1. Introduction

The CAS-OB (Composition Adjustment by Sealed Argon Bubbling with Oxygen Blowing) process was developed in the 1980s by Nippon Steel Corporation to improve on the existing argon rinsing stations used for deoxidizing and alloying molten steel. The CAS-OB process enables consistently high alloy recoveries and the reheating of steel using the exothermic reaction between oxygen and aluminum. With this capability of good chemical composition control, steel homogeneity, and reheating, the CAS-OB becomes an ideal buffer station in the secondary metallurgy of steelmaking. The objective of the CAS-OB process is to homogenize and control the steel composition and temperate. It has been reported that the CAS-OB process enables a better scheduling, improved temperature control, and higher inclusion purity.1) Figure 1 presents a typical process treatment schedule; the oxygen blowing stage is highlighted.

In the heating mode (OB) studied here, the refractory bell is lowered and submerged 30 cm below the liquid steel surface of the ladle and under this well-defined volume, oxygen gas is typically injected at the rate of 2 300 m$^3$/h (29 mol/s) at the Ruukki Metals Oy, Raahen Works CAS-OB stations. At the same time, solid aluminum particles are typically fed at the rate of 40 kg/min (25 mol/s) (see Fig. 2). The molar ratio of $O_2$ to Al is then 1.16. The stoichiometric $O_2$/Al ratio is 0.75, and therefore this means that there is some $O_2$ left over to oxidize other species as well. Of course, some residual $O_2$ will escape the system together with the dust and Ar via the de-dusting duct. Typically, heating rates of 10 K/min can be obtained. This value is limited by the thermal stresses developed in the wall structures in the ladle and bell. Therefore, accurate control of the heating is essential.

As far as the authors are aware, there are no process models available in the open literature for CAS-OB. There are some papers published on flow simulations in the process...
characteristics for the process. Structures in order to have accurate heat-up and cooling at the surface. We also consider heat transfer in the bell and ladle number of equations to be solved. Chemical reactions may occur at the jet hit depression area, the molten aluminum-slag surface, the aluminum-oxide particles, and oxidation/reduction of dissolved species (in this case, Al, Mn, C and Si, and the dissolvent Fe) were to be considered. Energy equations for the gas volume, liquid melt and different sections of the gas-liquid interface will be solved to get their temperatures. Because a significant fraction of the generated heat can be transferred and accumulated into the ladle and bell structures, we also developed simplified heat transfer models for these.

2. Description of the Model

Our simulation model is based on the numerical solution of the time-dependent differential equations of species and energy in the CAS-OB process. These are formulated for all species and temperatures in all the important volumes and reaction surfaces, including volumes of gas in the bell, liquid steel bath, top slag layer, and metal droplets dispersed in the slag, for a total of 48 unknown variables and an equal number of equations to be solved. Chemical reactions may occur at the jet hit depression area, the molten aluminum-gas surface, the molten aluminum-slag surface, the aluminum particle oxygen surface, and the metal droplet-slag surface. We also consider heat transfer in the bell and ladle structures in order to have accurate heat-up and cooling characteristics for the process. Figure 3 presents the principles of the model.

2.1. Modeling the Operation of the Top Lance

The driving force for the process is the injection of oxygen via a supersonic oxygen top lance. The supersonic gas jet produces a depression on the surface of the steel bath. The depth and diameter of the depression are defined by the momentum flux in the jet, lance distance \( H \), and material properties on both sides of the surface. We assume here that the surface in the depression is kept clean by the jet, referred to as the free surface \( f \), and any slag formed is pushed to the surrounding ring surface, the occupied surface \( o \) (see Fig. 3). As the liquid aluminum is lighter than the slag, we assume that it stays on the top of the slag layer.

The correlations proposed by Koria and Lange\(^5\) were used here to calculate the dimensions of the depression. The gas jet was assumed to be perpendicular to the surface. The flow rate of the blown gas is measured and the jet velocity available based on our CFD simulations.\(^6\) These were calculated for an AOD lance, but a similar approach was used for the CAS-OB lance. The momentum flux leaving the nozzle can be calculated as follows.

\[
M = \frac{\dot{m}_G u_G}{\rho_L H^3}............................ (1)
\]

In our case, \( d_0 = 30.5 \text{ mm} \) and the velocity at the nozzle exit was obtained with CFD simulations, \( u_L = 475 \text{ m/s} \). From these, the non-dimensional momentum flow rate can be calculated as follows.\(^3\)

\[
\frac{M}{\rho_L g H^3} = \frac{M}{\rho_g H^3}........................... (2)
\]

The depth and diameter of the depression are then calculated as follows.\(^3\)

\[
\frac{h_f}{H} = 4.469 M^{0.66} ................................ (3)
\]

\[
\frac{d_f}{H} = 2.813 M^{0.282} .......................... (4)
\]

Based on the findings of Sharma et al.,\(^7\) it was assumed that the geometry of the depression is unaffected by reactions and the interference of top slag. A typical lance height is 1.5 m, and as the bell diameter under the bell is 1.28 m, we then have the typical geometry of the depression: \( h_f = 104 \text{ mm} \) and \( d_f = 712 \text{ mm} \). We consider the increase in surface area of the open eye due to the convex surface assuming the spherical cap geometry here, and therefore \( S_e = \pi (a_e^2 + h_e^2) \) where \( a_e \) is the radius of the depression perimeter \( a_e = 0.5d_e \).

The surface under the bell is divided into two parts: free surface \( S_f \) (open eye) and occupied area \( S_o \) by liquid; the surface slag and aluminum are on the top of it. The free liquid steel surface has no mass. The area covered by liquid slag is assumed to have a constant thickness, \( h_s \). Based on the
slag layer area and mass, the thickness of the liquid layer can be calculated as follows.

\[ h_s = \frac{m_s}{\rho_s S_s} \] .......................... (5)

Metal droplets are formed at the gas jet impact area while blowing, and these eject from the bath and land on the surrounding slag surface. The degree and mode of spattering is defined by the blowing number \( N_b \):

\[ N_b = \frac{\rho_g u_0^2}{2 \sqrt{\gamma_s g \rho_L}} \] .......................... (6)

The initial gas velocity \( u_0 \) for this specific CAS-OB geometry was taken from CFD simulations. Based on these, the centerline gas velocity attenuates from the nozzle level to the surface vicinity before the flow turns, in this case by a factor of 0.432. In addition, only a fraction of 0.447 can be utilized to spatter the liquid. Therefore, the critical gas velocity is equal to \( u_c = 0.432 \times 0.447 \times u_1 = 0.193 \times u_1 \). The rate of droplet formation \( R_b \) (kg/s) is defined as follows:

\[ R_b = \frac{N_b^{1.2}}{V} \] .......................... (7)

wherein \( V \) is the lance blow rate in Nm\(^3\)/s. At this point, we only consider the constant blowing rate and the mass of droplets in the slag-metal emulsion at time \( t \) is then calculated as

\[ m_p = \min(\tau_D, t) R_b \] .......................... (8)

wherein \( \tau_D = \frac{h_s}{u_{c,D}} \) is the residence time of droplets in the slag and \( h_s \) is the slag layer thickness. The terminal velocity of the droplets \( u_{c,D} \) was solved from the droplet force balance analytically as follows. All numeral values are combined for simplicity here:

\[ u_{c,D} = 0.153 \times \left( \frac{d_p \rho \mu \rho_s}{\mu_s} \left( \frac{d_p \rho_s}{\mu_s} \right)^{0.6} \right)^{1/4} \] .......................... (9)

This equation is applicable in the range \( Re_D = 1–1000 \). From the mass, we can solve the overall surface area of the emulsified steel droplets as follows.

\[ S_D = \frac{6m_p}{d_p \rho_L} \] .......................... (10)

2.2. Chemical Reactions

We consider the melting of pure solid aluminum, primary oxidation reactions of pure liquid and dissolved aluminum (Al and Al\(_L\), respectively), and oxidation of Si, Mn, C, and Fe. In addition to these, the secondary reactions of the metal droplets in the slag are considered. Our main objective is to develop an effective model to consider parallel surface reactions with mass transfer limitations. (s), (l), and (S) refer to solid, liquid, and slag, respectively. The following reactions are considered in the gas jet impact area.

\[ \text{Al(s)} \leftrightarrow \text{Al(L)} \] .......................... R0

\[ 2 \text{Al(L)} + 3/2 \text{O}_2 \leftrightarrow \text{Al}_2\text{O}_3(S) \] .......................... R1

\[ 2\text{Al(L)} + 3/2 \text{O}_2 \leftrightarrow \text{Al}_2\text{O}_3(S) \] .......................... R2

\[ \text{Si(L)} + \text{O}_2 \leftrightarrow \text{SiO}_2(S) \] .......................... R3

\[ \text{Mn(L)} + 1/2 \text{O}_2 \leftrightarrow \text{MnO(S)} \] .......................... R4

\[ \text{Fe(L)} + 1/2 \text{O}_2 \leftrightarrow \text{FeO(S)} \] .......................... R5

\[ \text{C} + 1/2 \text{O}_2 \leftrightarrow \text{CO(g)} \] .......................... R6

The surface slag is formed in the above reactions R1–5. In addition to steel droplets forming in the blowing, Al is assumed to form droplets as soon as it is molten. We assume that the rate of Al droplet formation is equal to the difference between the rate of melting and dissolution. As the density of the Al is lower than that of the top slag, liquid Al is assumed to stay on the top of slag layer surface. The following reactions take place across the area \( S_0 \) formed by the steel droplets when they fall through the surface slag layer.

\[ \text{FeO(S)} + 2/3 \text{Al(L)} \leftrightarrow \text{Fe} + 1/3 \text{Al}_2\text{O}_3(S) \] .......................... R8

\[ \text{FeO(S)} + 1/2 \text{Si(L)} \leftrightarrow \text{Fe} + 1/2 \text{SiO}_2(S) \] .......................... R9

\[ \text{FeO(S)} + \text{Mn}(L) \leftrightarrow \text{Fe} + \text{MnO(S)} \] .......................... R10

In addition to these, important reactions are reduction of FeO, SiO\(_2\), and MnO when pure liquid Al is “sprayed” on the top of the slag layer. We assumed that these are immediate and are limited by the delivery rate of Al and equilibrium.

\[ \text{FeO(S)} + 2 \text{Al(L)} \leftrightarrow 3 \text{Fe} + \text{Al}_2\text{O}_3(S) \] .......................... R12

\[ 3/2 \text{SiO}_2(S) + 2 \text{Al(L)} \leftrightarrow 3/2 \text{Si} + \text{Al}_2\text{O}_3(S) \] .......................... R13

\[ \text{MnO(S)} + 2 \text{Al(L)} \leftrightarrow 3 \text{Fe} + \text{Al}_2\text{O}_3(S) \] .......................... R14

The rates of all chemical reactions were calculated by the method presented in our previous publications. \(^{10–12}\) The rate is derived based on the modified law of mass action using activities. Unknown forward rate coefficients are used as free variables that are set to sufficiently high values to guarantee mass transfer control and chemical equilibrium at the reaction surface. As an example, the rate of reaction 1 is calculated as follows and a similar approach is used for all the others. Please see our previous work\(^{10–12}\) for more details on this method.

\[ R_i = k_{f,i} \left( d_{a_i} a_{O_2} - \frac{d_{a_i} D_{a_i}}{K_i} \right), \text{where } k_{f,i} \rightarrow \infty. \] .......................... (11)

It is known that the rate of CO post-oxidation, R7 (not considered here), is highly dependent on the H\(_2\)/H\(_2\)O content of the gas. In typical hydro-carbon combustion applications, there is always H\(_2\)/H\(_2\)O present. But here, pure O\(_2\) is used, and in principle these catalyzing gases are not present. Under fully dry conditions, the rate of this reaction is very slow, and therefore it is not reasonable to assume infinite reaction kinetics. Instead, actual rate expression is required. At the moment, as far as the authors are aware of, there is no such equation available, so this reaction is not included here. However, the role of the post-combustion of CO will be studied later when validating the model with experiments. Based on our previous experimental work\(^{14}\) only a small amount of C is released, so this reaction has no significant importance for the process operation, and at the moment, we assume that only CO is present in the system.

2.3. Conservation of Gaseous Species

Conservation equations of the gaseous oxygen in the gas volume defined by the snorkel and liquid steel surface are given below. Positive flow direction is towards the reaction surface. There is also a flow of Ar out from the surface, but as it is much smaller than the O\(_2\) flow, its effect on the gas side bulk flow rate is neglected. However, the net flow of O\(_2\) (i.e., the Stefan flow) is considered. We have used the first-order upwind method to model the convective flux here. Total mass flow rates are simply calculated by summing up the contributions from all reactions.
Based on the force balance of a spherical Al particle floating in steel, only a fraction of 0.42 of the particle’s surface is below the liquid steel surface. Therefore, the surface area of a sphere should be multiplied by a factor of 0.42 to correct this effect. The fraction of the particle above the surface is exposed to thermal radiation and melts, but as the gas blow rate is high, the molten Al is rapidly blown away and we assume that this fraction does to contribute to Al dissolution. The analytical solution for the melting time of the Al sphere is equal to

\[ t_m = \frac{\rho \Delta H}{8} \lambda (T - T_m) \]  \tag{18} \]

\( \lambda \) is the effective steel conductivity, assumed 60 W/mK here. \( T_m \) is the melting temperature of Al 660°C, \( T_l \) is the melting heat of Al, and \( T \) is the local temperature, here \( T_l \). There is also a solid steel crust formed in some cases during the early stages of melting, as the melting temperature of Al is lower than of steel. As the mixing here is very effective and all molten material is rapidly blown away, the effect of crust formation is neglected. There are particles at different stages of melting in the process at the same time. To be precise, the population balances of different sizes of particles should be solved. However, the melting time of a single Al particle is relatively small when compared with the whole process time (5–15 min). We could therefore assume that the average melting rate of solid Al per unit mass, \( r_m \), is equal to \( r_m = 1/t_m \). The rate of solid Al accumulation is defined as the difference between the input flow and the rate of melting.

\[ \dot{m}_{Al} = \dot{m}_{Al,s} - \dot{r}_m m_{Al,l} = \frac{dm_{Al,l}}{dt} \] \tag{19} \]

Molten Al is dissolved and blown away to the top of the slag layer where it is then oxidized by gaseous \( O_2 \), \( FeO(S) \), or \( MnO(S) \). The amount of molten Al on the top of the slag layer is as follows; we assumed here that liquid Al does not accumulate in the open eye area.

\[ r_m m_{Al,l} - h_{Al} S_{Al} \rho_{Al} (1 - y_{Al}) + S_{Ri} R_{12,Al} + S_{Ri} R_{13,Al} + S_{Ri} R_{14,Al} = \frac{dm_{Al,l}}{dt} \] \tag{20} \]

where \( S_{Al} \) is the total surface area of the Al particles that float on the surface. It is calculated from the mass of solid Al as

\[ S_{Al} = \frac{6 m_{Al}}{d_{Al} \rho_{Al}} \] \tag{21} \]

Accumulation rate of dissolved Al is defined as the difference between the rate of pure Al dissolution from the surface of Al particles and the rate of mass transfer to free surface where it is oxidized.

\[ -h_{Al} S_{Al} \rho_{Al} (y_{Al} - 1) - h_{Al} S_{Al} \rho_{Al} (y_{Al} - y_{Al,f}) - \max \left( m_{L,f} - 0 \right) S_{Al} y_{Al,f} - h_{Al,f} S_{Al} \rho_{Al} (y_{Al} - y_{Al,f}) - \max \left( m_{L,D} - 0 \right) S_{Al} y_{Al,f} + \max \left( -m_{L,D} - 0 \right) S_{Al} y_{Al,f} \] \tag{22} \]

\[ + \max \left( -m_{L,D} - 0 \right) S_{Al} y_{Al,f} \]

\[ = \frac{d (m_{Al,l})}{dt} \]

\[ h_{Al} \rho_{Al} (y_{Al} - y_{Al,f}) + \max \left( m_{L,f} - 0 \right) y_{Al} - h_{Al,f} S_{Al} \rho_{Al} (y_{Al} - y_{Al,f}) - \max \left( m_{L,D} - 0 \right) y_{Al} + \max \left( -m_{L,D} - 0 \right) y_{Al} \] \tag{23} \]

\[ + \max \left( -m_{L,D} - 0 \right) y_{Al} + y_{Al,f} R_{2} = 0 \]

\[ + \max \left( -m_{L,D} - 0 \right) y_{Al} + y_{Al,f} R_{2} = 0 \] \tag{24} \]

The mass conservation equations of Si, Mn, C, and Fe at the steel bath and at the free metal surface all have the same
format. Only Si is presented here.

\[-h_{\text{Sl}} \rho L_{\text{Sl}} \left( y_{\text{Sl}} - y_{\text{Sl}, f} \right) - \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) y_{\text{Sl}} + m_{\text{Sl}, -, 0} S_{\text{ySl}} y_{\text{Sl}} - h_{\text{Sl}} \rho L_{\text{Sl}} \left( y_{\text{Sl}} - y_{\text{Sl}, f} \right) - \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) y_{\text{Sl}} + m_{\text{Sl}, -, 0} S_{\text{ySl}} y_{\text{Sl}} = \frac{d\left( m_{\text{Sl}} y_{\text{Sl}} \right)}{dt} \]  

\[h_{\text{Sl}} \rho L_{\text{Sl}} \left( y_{\text{Sl}} - y_{\text{Sl}, f} \right) - \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) + \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) = \frac{d\left( m_{\text{Sl}} y_{\text{Sl}} \right)}{dt} \]  

The overall mass balance of the liquid steel can be solved simultaneously by summing all individual mass balances of components. It is assumed that there is only one volume of each slag component in the system, which means that Al2O3 that is formed (either at the free surface or at the free liquid Al surface) ends up in the same place and only one single value of activity is required. Conservation equations of the slag species are given as follows. Equations for MnO and FeO are similar to SiO2, and therefore are not presented here. The total mass of the slag can be calculated by summing all slag components.

\[v_{\text{Al}, O, 1} R_{\text{Sl}, O} + v_{\text{Al}, O, 12} R_{\text{Sl}, O} + v_{\text{Si}, O, 3} R_{\text{Sl}, D} = \frac{dm_{\text{Sl}}} dt \]  

2.5. Energy Balances

One of the main objectives of the CAS-OB process is to chemically heat up the steel melt effectively. Therefore, the accurate prediction of the reactor temperature is an essential requirement for the model. For this, energy equations for the system are derived and implemented in the following. Reaction enthalpies were taken from.18,19) Thermal radiation between surfaces in the bell is considered; the effect of volumetric radiation of the gas and dust is here excluded, but could be considered later. The energy conservation equation for gas in the bell is as follows.

\[m_{\text{Ar, in}} c_{\text{p, Ar}} \left(T_{\text{in, Ar}} - T_{\text{L}}\right) = -h_{\text{Sl}} \rho L_{\text{Sl}} \left( y_{\text{Sl}} - y_{\text{Sl}, f} \right) - \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) y_{\text{Sl}} + m_{\text{Sl}, -, 0} S_{\text{ySl}} y_{\text{Sl}} - h_{\text{Sl}} \rho L_{\text{Sl}} \left( y_{\text{Sl}} - y_{\text{Sl}, f} \right) - \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) y_{\text{Sl}} + m_{\text{Sl}, -, 0} S_{\text{ySl}} y_{\text{Sl}} = \frac{d\left( m_{\text{Sl}} y_{\text{Sl}} \right)}{dt} \]  

\[h_{\text{Sl}} \rho L_{\text{Sl}} \left( y_{\text{Sl}} - y_{\text{Sl}, f} \right) - \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) + \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) = \frac{d\left( m_{\text{Sl}} y_{\text{Sl}} \right)}{dt} \]  

The first two terms describe the heat-up of oxygen and argon to bulk gas temperature, respectively. All argon is assumed to pass through the open eye. The 3, 4, and 5 terms present the convective heat transfer to the slag surface, the open eye, and the bell walls, respectively, and the 6 term is the heat-up of the CO formed to bulk temperature. The right-hand side is the accumulation of heat in the gas. The energy equation for the liquid bulk melt was formulated as follows.

\[m_{\text{Ar, in}} c_{\text{p, Ar}} \left(T_{\text{in, Ar}} - T_{\text{L}}\right) = -h_{\text{Sl}} \rho L_{\text{Sl}} \left( y_{\text{Sl}} - y_{\text{Sl}, f} \right) - \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) y_{\text{Sl}} + m_{\text{Sl}, -, 0} S_{\text{ySl}} y_{\text{Sl}} - h_{\text{Sl}} \rho L_{\text{Sl}} \left( y_{\text{Sl}} - y_{\text{Sl}, f} \right) - \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) y_{\text{Sl}} + m_{\text{Sl}, -, 0} S_{\text{ySl}} y_{\text{Sl}} = \frac{d\left( m_{\text{Sl}} y_{\text{Sl}} \right)}{dt} \]  

\[h_{\text{Sl}} \rho L_{\text{Sl}} \left( y_{\text{Sl}} - y_{\text{Sl}, f} \right) - \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) + \max \left( m_{\text{Sl}, -, 0} S_{\text{ySl}} \right) = \frac{d\left( m_{\text{Sl}} y_{\text{Sl}} \right)}{dt} \]  

where \( \eta_D = 1 - \exp \left[ -\frac{6\pi \rho \tau_D}{d_{\text{p, Al}}} \right] \) is the droplet heat transfer efficiency, i.e., how much of the available temperature difference \( T_{\text{L} - T_{\text{B}}} \) can be utilized when the droplet passes the slag. The larger the heat transfer coefficient and the smaller the droplet size and residence time, the better the efficiency. The 1 term is the heat-up of argon to bulk liquid temperature. The 2 term describes the heat consumption for fed Al particles to heat up and melt, and we assume here that the required energy is taken from the liquid melt. The next three terms are the convective heat flux to the surrounding surfaces. The 6 term is very important; it describes the heat loss from the free steel/slag surface exposed to the surroundings, \( S_{\text{e}} \) is the surface area outside the bell and when the bell is raised; \( S_{\text{e}} \) equals the overall ladle surface area. 7 term is the heat loss to bell when it is submerged. The following five equations present the cooling of dissolved elements in the case of a backwards reaction. The 13, 14, and 15 terms describe the incoming heat from the reduced iron, silicon, and manganese, respectively. The last term on the left is the incoming heat from hot metal droplets exiting the slag. The term on the right side is the accumulation of heat. The energy balance for the free liquid steel surface, i.e., the open eye, is as follows; we assume here that slag species are not returned to the free surface from the top slag layer.

\[\alpha_L \left(T_{\text{L} - T_{\text{f}}}\right) + \alpha_{\text{Fe}} \left(T_{\text{L} - T_{\text{f}}}\right) - \left(J_1 - J_{\text{B1}}\right) - \sum_{k=2}^{6} \sum_{l=0}^{B_k} \left(R_k v_{\text{f}, k} S_{\text{ySl}} \right) = \frac{d\left( m_{\text{Sl}} y_{\text{Sl}} \right)}{dt} \]  

\[\alpha_L \left(T_{\text{L} - T_{\text{f}}}\right) + \alpha_{\text{Fe}} \left(T_{\text{L} - T_{\text{f}}}\right) - \left(J_1 - J_{\text{B1}}\right) - \sum_{k=2}^{6} \sum_{l=0}^{B_k} \left(R_k v_{\text{f}, k} S_{\text{ySl}} \right) = 0 \]  

\[J_1 \text{ and } J_{\text{B1}} \text{ are the radiosities of the free liquid surface and the internal wall area of the bell, respectively. These are solved from a separate thermal radiation model, presented later. Energy equation for the surface slag element is a bit more complex. We assume that both surface slag and the liquid Al layer on the top of it are at the same temperature } T_{\text{v}}.\]
and pure aluminum surfaces as follows:

\[
-k_{B1} \frac{\partial T}{\partial x} = \alpha_{B1} \varepsilon \sigma T^4 \left( T_{B1} - T_{B1} \right) + S_o \left( J_f - J_{B1} \right)
\]

where \(S_o = \varepsilon_o \sigma T_o^4 \) and as a result, the melt will be mixed. The liquid rise velocity is equal to 0.8 m/s. 3) We use the surface penetration model proposed by Higby\(^{35}\) to calculate the mass transfer during this contact period. Heat transfer coefficients can be obtained by replacing \(Sh\) with \(Nu\) and \(D_i\) with thermal diffusivity. Equation (41) is used for metal side mass transfer for metal-gas (f), metal-slag (o), and metal droplets-slag (D).

\[
h_{i,metal} = 2 \sqrt{\frac{D_i}{\pi \tau_{i,metal}}} \]

Heat and mass transfer coefficients are similar for falling liquid steel droplets in the slag. We assume that liquid side mass transfer controls the metal droplet-slag reactions R8–11. On the slag side, oxides are present with high mass frac-
tions, while on the liquid side mass fractions are at the ppm level. As the droplet falls, an internal circulation is created in the steel. The surface of the droplet is renewed the rate defined by the slip velocity and droplet size and residence time is calculated as follows.

\[ \tau_D = \frac{d_D}{u_D} \]  

(42)

Slip velocity is calculated by Eq. (9). Heat and mass transfer coefficients can then be calculated from Eq. (41) for the droplets.

Heat and mass transfer around the melting Al particles is different from the metal droplets in slag or gas bubbles. This is a case of liquid passing a solid sphere calotte. The mass transfer coefficient was calculated from the Ranz-Marshall correlation as follows

\[ Sh_d = \frac{h_d d_{Al}}{D_{Al}} = 2 + 0.6 \text{Re}^{0.5} \text{Sc}_{Al}^{0.333} \]  

(43)

The heat transfer coefficient can be obtained by the analogy replacing \( Nu \) with \( Sh \) and \( Sc \) with \( Pr \), respectively. The Reynolds number is calculated from the rise velocity 0.8 m/s.

### 2.8. Activity of the Species

Our system of species conservation equations was derived on the mass fraction basis. It is therefore necessary to write all activities based on mass fractions. The ideal gas law is assumed to be valid for gases.

\[ a_i = \gamma_i \frac{M_i}{P_n} \]  

(44)

Activity coefficients of dissolved species were calculated based on the Unified Interaction Parameter (UIP) Model. Wagner’s interaction model was first tested, but it was found to be non-suitable, as a numerical solution often jumps to non-dilute regions during the initial steps of iterations where a non-physical trend is predicted. Interaction parameters \( \varepsilon_{ij} \) are given in Table 1; the references for these are given in the Table 1.

Activity coefficients were defined as follows.

\[ \ln(y_i) = \ln(y_{FeO}) + \ln(y_{O_2}) + \sum_{j=1}^{N_{species}} (\varepsilon_{ij} y_j) \]  

(45)

The key difference from Wagner’s model is the first term on the right, i.e., the activity coefficient of the solvent, which in this case is iron. It is defined as follows.

\[ \ln(y_{FeO}) = -0.5 \sum_{j=1}^{N_{species}} (\varepsilon_{ij} y_j) \]  

(46)

Substituting this into (45) and re-arranging gives us.

\[ \ln(y_i) = \ln(y_{O_2}) + \sum_{j=1}^{N_{species}} (\varepsilon_{ij} y_j - 0.5 \sum_{k=1}^{N_{species}} \varepsilon_{ik} y_k) \]  

(47)

Representing mole fractions in the terms of mass fractions.

\[ \ln(y_i) = \ln(y_{O_2}) + \sum_{j=1}^{N_{species}} (\varepsilon_{ij} M_j y_j - 0.5 \sum_{k=1}^{N_{species}} \varepsilon_{ik} M_k y_k) \]  

(48)

For the slag phase, the Ban-Ya regular solution model is used. The activity coefficient of species \( i \) is defined by

\[ RT \ln(y_{RS}_{i}) = RT \ln(y_{RS}_{FeO}) + \Delta G_{RS-i} \]  

(49)

\[ \Delta G_{RS-i} = \sum_{j=1}^{N_{species}} \left( \gamma_{RS_{ij}} - \sum_{j=1}^{N_{species}} \gamma_{RS_{ij}} \right) \]  

(50)

\( \gamma_{RS} \) is equal to inverse Kronecker delta, \( X \) is equal to the cation fraction defined as the ratio of anions in species \( i \) and anions in all slag species. \( N_{O_i} \) is equal to the number of O atoms in one molecule of species.

\[ X_i = \frac{X_i N_{O_i}}{\sum_{j=1}^{N_{species}} \frac{N_{O_j}}{M_j}} \]  

(51)

and activities are calculated as \( a_i = y_{RS_{i}} X_i \). Our system of slag species are defined below, giving the interaction energies and conversion Gibbs energies. The slag species are FeO, Al2O3, MnO, SiO2, and CaO. Table 2 presents the properties.

### 2.9. Physical and Thermo-dynamical Properties

Physical and thermo-dynamical data was obtained from [15,19,23]. We used the effective diffusion model approach, \( D_i = 4 \times 10^{-10} \text{m}^2/\text{s} \), \( D_{O_2} = 0.21 \times 10^{-2} \text{(T/298 K)}^{1.5} \text{(p/101325) m/s} \). The viscosities of steel and slag were 0.0061 Pa s and 0.0709 Pa s, respectively.[23]

### 2.10. Numerical Solution

The model for the CAS-OB process has a set of non-linear differential equations defined above. The equations are integrated with respect to time using the implicit Euler method. The system is well-defined by 36+12 unknown variables and 36+12 non-linear equations. The full Newton method was used to maximize the numerical efficiency. For the best stability, the energy equations were solved semi-explicitly, which means that when mass transfer and reactions are solved, temperatures are kept constant, but the solution method was implicit itself. In the real industrial CAS-OB process, Al particles, O2, and Ar are fed with different time periods, mostly overlapping, but also partly at different times and with varying rates. As we wanted to validate the model with these real batches, we needed to consider the feed rates and times accurately. In the model, feed rates are modeled with linear trends, marking the point where changes are made. Examples of these are presented below.

<table>
<thead>
<tr>
<th>Table 2. Slag activity model parameters,17–30 conversion energy is between the regular solution state and Raoult state.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interaction energies ( \alpha_{ij} ) of cations, J</td>
</tr>
<tr>
<td>Al2O3</td>
</tr>
<tr>
<td>MnO</td>
</tr>
<tr>
<td>SiO2</td>
</tr>
<tr>
<td>CaO</td>
</tr>
</tbody>
</table>

* Calculated from the activity data available in slag atlas[29]

### Table 1. First order molar interaction parameters for the UIP model, Henry’s law constants, Raoult reference state.14,26

<table>
<thead>
<tr>
<th>( \varepsilon_{ij} )</th>
<th>Fe</th>
<th>Al</th>
<th>Si</th>
<th>Mn</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>6</td>
<td>6.9</td>
<td>2.8</td>
<td>6.7</td>
<td>-104</td>
</tr>
<tr>
<td>Si</td>
<td>0</td>
<td>6.9</td>
<td>37</td>
<td>8.3</td>
<td>-173</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0</td>
<td>2.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.5</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>6.7</td>
<td>8.3</td>
<td>-0.5</td>
<td>11.4</td>
<td>-22.2</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>-104</td>
<td>-173</td>
<td>0</td>
<td>-22.2</td>
<td>-13.4</td>
</tr>
</tbody>
</table>

\( \gamma_{RS} = 1 \) | 0.029 | 0.0013 | 1.3 | 0.57 | 1 |

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3. Results

The model is compared with process measurements obtained from the CAS-OB process at Ruukki Metals Oy, Raahe Works, Finland. Initial steel temperature is typically ~1 600°C. O2 flow is 2 300–2 600 m3/h, Al feed is 40–80 kg/min, and Ar flow is 400–800 l/min. Initial Al particle size was 38 mm, based on the measured average mass of used particles.

Although the distribution of steel droplets at their place of birth contains relatively large droplets in excess of 10 mm, these droplets are likely to disintegrate due to contact with the gas jet. The droplet break-up correlation proposed by Koria and Lange31) yields that the upper size limit of the non-disintegrating metal droplets is approximately 2–3 mm. Moreover, the residence time of large droplets in the slag is very short, and the mass-transfer rate within the droplet is relatively slow in comparison to small droplets. It may be expected that the effective average size of the droplets residing in the slag is on the order of few millimeters. In this work, a value of 1.5 mm was employed.

Throat diameter of the lance nozzle was 30.5 mm, and gas exit velocity was 475 m/s. Height of the ladle was 2.655 m and liquid surface diameter 2.665 m. Height and diameter of the bell were 1.5 and 1.28 m, respectively. In this work, we used the process data measured during January 2014 at Ruukki Metals Oy Raahe Works in Finland and simulated three Al killed steels. At first, a comparison and temperature measurements. The predictions in steel and slag composition, Table 4, are really good and errors are smaller than the accuracy of the analysis of the slag is extremely difficult.

3.1. Heating Rates

One of the main objectives of the CAS-OB process is to control the steel temperature before the continuous casting. The heat-up rate is typically limited to ~10–15 K/min due to the risk of thermal cracking of the ladle or bell refractories.13) Figure 5 presents the heat-up rate and fed Al remaining on the surface for the case A1 as an example.

As can be seen from Fig. 5, the heat rate rapidly reaches a maximum level when O2 blowing is started, then keeps a constant level of ~10–12 K/min. There is also a peak in the heating rate at the end of the blowing, as the cooling effect of Al melting rapidly disappears. After the Al feed is stopped, the cooling begins and a cooling rate of 1.2–1.5 K/min is reached with no Al melting effects. This corresponds well to the observations from the real process, where typical free cooling rates were 1.5–2 K/min.22)

3.2. Contribution Analysis

In this part, we study the main heat generating reactions and where the energy is consumed. Figure 6 presents the

<table>
<thead>
<tr>
<th>Table 3. Input data and temperature predictions, feed periods are given as time intervals when materials are fed.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperatures</strong></td>
</tr>
<tr>
<td><strong>Time min</strong></td>
</tr>
<tr>
<td>A1</td>
</tr>
<tr>
<td>Exp. 10</td>
</tr>
<tr>
<td>Model 10</td>
</tr>
<tr>
<td>A2</td>
</tr>
<tr>
<td>Exp. 10</td>
</tr>
<tr>
<td>Model 10</td>
</tr>
<tr>
<td>A3</td>
</tr>
<tr>
<td>Exp. 12</td>
</tr>
<tr>
<td>Model 12</td>
</tr>
</tbody>
</table>

119/86 and 144/82. The errors resulting from these are 32%, 27%, and 43% in Al balance. Of course in the model, all Al can be found. Experiments and the model show that FeO is only an intermediate product and is reduced very effectively from the slag. It must be noted that the representative analysis of the slag is extremely difficult.

<table>
<thead>
<tr>
<th>Table 4. Melt and slag compositions before and after the heat-up, A = Al-killed steel.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Batch</strong></td>
</tr>
<tr>
<td><strong>tmin</strong></td>
</tr>
<tr>
<td>A1</td>
</tr>
<tr>
<td>Exp. 10</td>
</tr>
<tr>
<td>Model 10</td>
</tr>
<tr>
<td>A2</td>
</tr>
<tr>
<td>Exp. 9</td>
</tr>
<tr>
<td>Model 9</td>
</tr>
<tr>
<td>A3</td>
</tr>
<tr>
<td>Exp. 12</td>
</tr>
<tr>
<td>Model 12</td>
</tr>
</tbody>
</table>

A: assumed that measured slag masses are correct, b: assumed that end steel composition is correct.

Fig. 5. Heat-up rate and fed Al at the surface, A1. 0–330 s: Ar-stirring/sampling, 330–450 s: Al feeding and O2 blowing and 450–600 s: Ar-stirring/sampling.
3.3. Energy and O₂ Efficiency

As soon as Al feeding and blowing is stopped, the heat accumulated in the steel is lost. Most of the energy is lost through the slag surface, the bell structure, and the ladle walls. To minimize these, thicker insulations would be required and the slag surface should be covered with an insulated lid whenever possible and, obviously, to keep the free cooling periods to a minimum. It is known from practice that the average free cooling rate is 1.5–2 K/min, and the longer the waiting time, the larger the heat loss. Simulated oxygen efficiencies A1–3 were 0.81, 0.84, and 0.85, respectively.

4. Conclusions

This paper presented a new approach to the model CAS-OB process. More specifically, the oxygen blowing mode (OB) was considered. Melting of the solid aluminum particles, oxidation of pure molten aluminum, and oxidation of dissolved species, here Al, Mn, C, and Si, and the solvent Fe were considered. We also implemented energy equations for the liquid melt, the gas in the bell, and different sections of the gas-liquid interface to be solved to get their temperatures. As a significant fraction of the generated heat can be transferred and accumulated into the ladle and bell structures, simplified heat transfer models were developed to take this into account. The new model gives information on the heat-up rate and temperatures of the steel melt, gas, reaction surfaces, and refractory walls. The model yielded accurate predictions for steel composition, heating rate, and O₂ efficiency. For the studied heats, the predicted heating rate was 8–12 K/min versus the ~10 K/min measured average.

Based on our simulations, thermal efficiency of the process is greatly affected by the length of the free cooling period; typically 30–40% of the chemical energy can be used to heat the steel. Only a fraction of 0.8–0.85 of the O₂ can be utilized in the process; these correspond to the values observed in previous work. Most of the energy comes from the oxidation of the fed Al, and FeO is primarily an intermediate product of the reactions. The model was tested against industrial trials, and it succeeded to capture both main trends and high absolute accuracy. More validation experiments will be carried out in the future. On-line gas analysis measurements are also being planned.

Acknowledgements

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List of symbols

- \( a_t \) radius of the depression, m
- \( c_p \) specific heat capacity, J/kg K
- \( d \) diameter, m
- \( D \) diffusion coefficient, m²/s
- \( f \) activity coefficient, –
- \( g \) gravitational acceleration, 9.81 m/s²
- \( G \) geometry factor, –

As can be seen in Fig. 7, thermal efficiency of the CAS-OB treatment varies between 30–40%, and thus 60–70% of the chemical energy is lost. Most of the energy is lost through the slag surface, the bell structure, and the ladle walls. To minimize these, thicker insulations would be required and the slag surface should be covered with an insulated lid whenever possible and, obviously, to keep the free cooling periods to a minimum. It is known from practice that the average free cooling rate is 1.5–2 K/min, and the longer the waiting time, the larger the heat loss. Simulated oxygen efficiencies A1–3 were 0.81, 0.84, and 0.85, respectively.
\( \Delta G \) Gibbs free energy, J/mole
\( F \) view factor, flow factor, –
\( h \) specific enthalpy, J/kg
\( h \) mass transfer coefficient, m/s
\( h_t \) depth of the lance depression, m
\( H \) lance height, m
\( J \) radiosity, W/m²
\( k \) reaction rate coefficient, –
\( K \) equilibrium constant, –
\( m \) mass, kg
\( m \) mass flow rate, kg/s
\( M \) momentum flow rate, N
\( M \) non-dimensional momentum flow rate, –
\( \nu_0 \) blowing number, –
\( \nu \) Nusselt number, –
\( \alpha \) interaction coefficient, –
\( \epsilon \) emissivity, –
\( \delta \) Kronecker delta, –
\( \gamma \) activity coefficient, –
\( \lambda \) thermal conductivity, W/mK
\( \eta \) heat transfer efficiency, –
\( \rho \) density, kg/m³
\( \sigma \) surface tension, N/m
\( \tau \) melting time, s
\( \tau_0 \) residence time, s
\( \nu \) stoichiometric coefficient, –

Greek symbols
\( \alpha \) convective heat transfer coefficient, W/m²K
\( \alpha_{ij} \) interaction energy, J
\( \varepsilon \) emissivity, –
\( \epsilon_{ij} \) interaction coefficient, –
\( \delta_{ij} \) Kronecker delta, –
\( \gamma \) activity coefficient, –
\( \lambda \) thermal conductivity, W/mK
\( \eta \) heat transfer efficiency, –
\( \rho \) density, kg/m³
\( \sigma \) surface tension, N/m
\( \tau \) melting time, s
\( \tau_0 \) residence time, s
\( \nu \) stoichiometric coefficient, –

Subscripts symbols
\( b \) black body
\( B \) bell
\( D \) droplet
\( f \) open eye
\( G \) gas
\( J \) jet
\( L \) liquid
\( \text{NTP} \) normal temperature 298 K and pressure 101325 Pa
\( s \) surface, solid
\( \text{sub} \) submerged
\( S \) slag
\( o \) slag surface
\( w \) wall
\( \infty \) bulk condition

REFERENCES