Relationship between motion of bubbles and agglomeration of inclusions into clusters during solidification of continuously cast steel

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Abstract

The possibility of cluster formation during solidification of steel is explored to explain structures that are seen on the fracture surface of the steel. A hypothesis is built that postulates porosities provide favourable locations for inclusions to agglomerate and form clusters. A thermodynamic model is constructed to describe precipitation of porosity and inclusions. Formation of inclusions follow a nucleation and growth mechanism. Porosities on the other hand are the product of pressure balance in the liquid. Motion of pores and inclusions is analysed based on the drag force and surface stresses. Gradient of surface tension is also identified as a driving force which acts on the pore surface and would cause motion. It is shown that relative motion of pores and inclusions coupled with the inclusion tendency to get attached on pore surface makes for a viable mechanism explaining agglomeration of inclusion particles to clusters.
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Supplement 1:
A. S. Nick, H. Fredriksson,
On the Relationship Between Inclusions and Pores, Part I: Precipitation,

Supplement 2:
A. S. Nick, H. Fredriksson,
On the Relationship between Inclusions and Pores, Part II: Dendritic Structure,
Pressure Drop in the Liquid and Pore Precipitation,

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Contribution from the author to the supplements:

- **Supplement 1**: Literature survey, Experiments and Major part of the writing.
- **Supplement 2**: Literature survey, Experiments and Major part of the writing.
- **Supplement 3**: Part of literature survey, Numerical simulation, Thermodynamic analysis and part of the writing.
1 Introduction

Inclusions in metals are particles that differ from the metallic matrix in composition. The difference in composition, in most cases means difference in properties. Hence the structure of the metals is not uniform on and around inclusions. Inclusions, based on their properties are known to be the cause for different phenomena in metals. Inclusions are used as nucleating agents to decrease grain size in multi crystalline materials. Inclusions are recognized as barriers to dislocation movement hence increasing creep life. Fatigue life of metallic materials on the other hand is shortened due to cracks forming around inclusions. Surface homogeneity of metals are sometimes disrupted due to strings of inclusions on the surface.

Inclusions could be divided based on their origin into groups of exogenous and indigenous. Exogenous inclusions are introduced to the structure from surroundings. Surface of the crucible in contact with the melt can get eroded due to melt convection. Detached parts of the crucible solidifies with the melt as part of the structure and constitute as exogenous inclusion. Indigenous inclusions have their source of formation inside the material and are usually formed following a nucleation and growth procedure. Thermodynamics is the tool metallurgist use to describe the formation of indigenous inclusions.

In terms of continuous casting of metals indigenous inclusions could be discriminated as whether forming before or during solidification. Inclusions precipitate before solidification mostly due to alloying or interaction with the atmosphere and container walls. During solidification inclusions form in general due to temperature change and segregation of elements associated with solidification. After solidification inclusions can form also as second phase particles.

Inclusions that form in the liquid move in relation with the liquid and inclusions in the solid move in relation with the solid. Inclusions have been known to cluster as a results of motion. Clustering of inclusions in continuous casting of steel which happens before solidification could lead to nuzzle clogging. Clusters involved in clogging mechanism are in the scale of millimetres [1]. It is recently postulated that clustering of inclusions could also happen during solidification. Clustering of inclusions during solidification is affected by porosities that also form during solidification. Clusters that form during solidification are shown to be in the scale of micrometers [2].

Formation of porosity (referred to as bubbles here on out) is related to gas content of the system (composition), systems capacity to hold gas elements in solution (solubility) and volume change (shrinkage) in the system during phase change. In steels, bubbles could be divided in two categories based on their origin. One is the bubble that enters steel in gas phase, the other is one that precipitates from liquid. Precipitation is said to occur when the content of the dissolved gas in the phase, solid or liquid, is larger than solubility of the phase and is also large enough to overcome the barriers for formation, e.g. surface tension and ambient pressure. Solubility is dependent on temperature and composition. For steels, solubility mostly decreases with temperature in liquid and solid phases. During phase change, melting or solidification, there is
a great difference between the solubility values. Solubility of liquid steel is larger than solid steel. Coupling the difference in solubility values with shrinkage and segregation, steels are most susceptible to bubble formation during solidification [3–5].

Bubbles move in the liquid but are stationary in the solid state. The motion of a bubble in liquid is governed by gravity (buoyancy force) and surface tension, among others. The motion of a bubble due to gravity is caused by the difference between the density of gas and liquid. Bubbles move due to gravity in the vertical direction; however, the motion of the bubble due to surface tension does not have a predefined direction. In steels, surface tension is dependent on temperature and concentration of surface active elements. Hence, a gradient in temperature or composition creates a gradient in surface tension. The gradient of surface tension acts as the force for the movement of the bubble. The direction of the motion would be along the direction of the gradient.

The dominant surface-active element that is present in most steels is sulphur. Surface tension and surface-tension gradients are functions of sulphur concentration and temperature in steels [6]. The temperature derivative of surface tension changes sign, from negative to positive, by increasing sulphur content above around 30 ppm. The change in the direction of temperature component of surface tension gradient is speculated to cause a change in the direction of bubble motion [7]. In this study, it is shown that the change in the direction of temperature derivative of surface tension does not cause a change in the direction of a bubble moving through the mush area. Liquid motion could also affect the motion of bubbles.

Another aspect of bubble motion in molten steel is the interaction with the solid. A bubble could become engulfed or be pushed by the solidification front. Small solid particles can get attached in/on bubbles, as in froth flotation during mineral beneficiation [5]. It is here postulated that bubbles which precipitate in the liquid drift towards inclusions and incorporate them to form clusters.

Figure 1: Two examples of inclusions, shown by arrows, and pores, shown by the dashed circles, on a fracture surface
Engulfment of these pore/inclusion clusters in the solid steel would be one explanation for the structure in Fig. 1.

In order to test the viability of this hypothesis, we combine experimental work with a mathematical model. First, in section 2, observations are made of pore/inclusion clusters that are present in a continuously cast austenitic stainless steel bloom; the material is then subject to DTA and DSC-testing, in order to determine its solidus and liquidus temperatures, which are required as input for a subsequent mathematical model. In section 3, a three-part mathematical model is constructed for how the pores and inclusions could have formed and clustered during casting: the first part constitutes the thermal problem and gives, as output, the temperature and sulphur concentration distributions; the second part uses these distributions to determine where in the mushy region pores and inclusions will precipitate and what their subsequent velocities will be; the third part tracks their trajectories in the mush region until they are absorbed into the solid. The results are presented in section 4, and conclusions are drawn in section 5.
2 Experimental

22 samples, each of size $10 \times 10 \times 70 \text{ mm}^3$ were made, covering the symmetry axes of a continuously cast austenitic stainless steel bloom with the profile size $265 \times 320 \text{ mm}^2$. Fig. 2. The symmetry axes divides the bloom profile in half, to give dimensions $265 \times 160 \text{ mm}^2$. The samples are oriented so that the 70 mm edge is aligned with the casting direction. Grain structure is composed of columnar crystals on each side, 80 mm and 50 mm in length with equiaxed crystals in between. 5 mm deep notch was cut on each sample in the middle of the $10 \times 70 \text{ mm}^2$ face. Samples were fractured by a 15 kg pendulum hammer at liquid nitrogen temperature. The fracture surface was studied under scanning electron microscope. Fractured samples were cut on one side, 10 mm below fracture surface, polished and etched with V2A solution for LOM and SEM. DSC sample was 0.365 g. The sample was heated to 1743 K with heating rate of 10 K/min. The melt was kept at 1743 K for 10 minutes and then cooled down to 1273 K with 10 K/min and kept at 1273 K for 20 min. This cycle was repeated twice for accuracy, as well as to investigate if there would be any residual effect registered. The DTA sample was 6 g. The heating cycle for DTA and DSC was the same.

Figure 2: (a) Bloom (b) Sampling
2.1 Inclusions on fracture surface

Inclusions that appeared on the fracture surface (Figures 1, 3 and 4) could be categorized in different ways. Based on their shape, Inclusions are set in two groups i.e. faceted (Figures 1 and 3a) and non-faceted (Figures 3b and 4). Based on the location inclusions appear on the fracture surface relative to grains, inclusions are set in two groups i.e. sub granular or grain boundaries (Figures 3b and 4b) and inter granular (Figures 1, 3a and 4a). Sub granular locations are in between two or more grains while inter granular locations are situated inside one grain. It can readily be seen that faceted inclusions appear primarily on inter granular locations while non faceted inclusions can be found on inter granular or sub granular locations. Mere difference in shape of inclusions, being faceted or non faceted, does not indicate a difference in composition of said inclusions. Factors like growth velocity, temperature gradient, supersaturation or substrate could cause a change in the shape of an inclusion as well as a difference in composition can. It should be noted that inclusions with similar shape and size on the fracture surface could very well be of different compositions. It is also possible to categorize inclusions based on being a single uniform particle (figs. 3a and 4) or rather a cluster of particles (Figure 1). Here a cluster indicates agglomeration of several discrete particles as oppose to a growth mechanism. Clusters are primarily made of faceted inclusions.

(a) Faceted inclusion on inter granular space
(b) Precipitates on sub granular space (grain boundaries)

Figure 3: Inclusion and precipitates are shown by arrows and sub granular space is marked by dashed lines

2.2 Energy dispersive spectroscopy (EDS)

In order to analyse the composition of inclusions in the stainless steel samples, EDS analysis was employed. EDS analysis proved impossible on fracture surface due to surface non uniformity which in turn caused diffraction of the x rays omitted from the sample hence obscuring the results.
(a) Intergranular, Inclusions shown by arrow

(b) Subgranular, Inclusions shown by arrows on subgranular space (grain boundaries) marked by dashed line

Figure 4: Non-Faceted inclusions

(a) Titanium nitride with aluminium oxide as nucleus

(b) Molybdenum Sulphide

(c) Titanium carbide

Figure 5: Faceted inclusions
It was possible to identify the composition of inclusions and precipitates on polished surfaces. Inclusions and precipitates in the stainless steel are shown in Figures 5 and 6. Details of the quantitative compositional analysis corresponding to Figures 5 and 6 is in appendix A.

(a) Titanium molybdenum carbide  
(b) Titanium molybdenum nitride

Figure 6: Non faceted inclusions and precipitates

Through similarities in morphology and location of the inclusions relative to the matrix, between inclusions and precipitates on fracture surface and on polished samples, an assumption is made for the composition of the inclusions on fracture surfaces. It is postulated that inclusions in Figures 1 and 3a correspond to inclusions in Figure 5. Precipitates in Figure 3b would correspond to precipitates in Figure 6a. Inclusions in Figure 4 could correspond to inclusions in Figure 6b. Correspondence is made based on inclusions being faceted (Figures 1, 3a and 5) or non faceted (Figures 4 and 6b) or to be located on grain boundaries (Figures 3b and 6a). It is worth mentioning that inclusions on fracture surface and polished surface are not from the same specimen.

2.3 Dendrite arm spacing (DAS)

Dendrite arm distance has been counted on the etched metallographic surface. The distance measurement is done through an intercept method with bias for parallel stems Fig. 7. The procedure is as follows: At a fixed distance from the surface of the bloom a line with 10 mm in length parallel to the surface of the bloom is considered (dashed line in fig. 7). The width of the parallel primary stems (double sided white arrow in Fig. 7) is divided by the number of the stems in the set (solid black lines in Fig. 7). Weight average of the measured values on the dashed line represents PDAS in Fig. 8. The results show an increase in the dendrite arm distance from the surface of the bloom to the end of the columnar crystal zone.
Figure 7: DAS measurement protocol

Figure 8: DAS
3 Modelling

In order to explain the formation of pores and clusters theoretically, modelling work was undertaken; this is documented in detail in Supplements 1-3, but here a short overview is given.

3.1 Supplement 1

Here, the focus is on determining thermodynamically when pores and different types of inclusions specifically inclusions which could be inside the clusters in Fig. 1 are formed. TiN is a faceted inclusion (Fig 5a) which could be among the particles in Fig. 1 and Al$_2$O$_3$ could act as a substrate for precipitation.

Formation of TiN and Al$_2$O$_3$ is considered based on reactions [8,9]

$$\text{Ti}(1\text{wt%}) + \text{N}(1 \text{ wt%}) = \text{TiN}^{(s)}, \quad \Delta G^0 = -308799 + 114.35T,$$

$$\text{2Al}(1 \text{ wt%}) + 3\text{O}(1 \text{ wt%}) = \text{Al}_2\text{O}_3^{(s)}, \quad \Delta G^0 = -1202000 + 386.3T,$$

where TiN and Al$_2$O$_3$ are stoichiometric solids (activity equal to one) and both values for $\Delta G^0$ are in joules.

Solubility of the elements are governed by the thermodynamic properties of the system. The thermodynamic properties are the activity of the elements and temperature which is formulated through the Gibbs energy. Gibbs energy is defined as:

$$\Delta G = RT\ln \frac{a_{TiN}}{a_TiN} + \Delta G^0$$

where $R$ is the gas constant, $T$ is the temperature in kelvin $a$ is the activity of the substance. Activity follows Henry’s law for dilute solutions as:

$$a_i = f_i(pct.i)$$

where $f$ is activity coefficient and $i$ represents the element. Activity coefficient is calculated based on Wagner’s formalism [10] as:

$$\log f_i = \sum_{j=1}^{n} e_i^j \text{ (pct.}j\text{)}$$

where $e$ is the interaction coefficient and $i$ and $j$ are the concentration of the elements. Formation of inclusions are considered at equilibrium which entails by definition, no change in Gibbs energy. The solid compounds have no solubility in liquid.

Nucleation precedes supersaturation of the melt. Supersaturation needed for homogeneous nucleation is calculated as [11]

$$RT \ln \left( \frac{SS_{solubility}}{EQ_{solubility}} \right) = \sqrt{\frac{16\pi}{3}} \frac{\gamma^3 V_n^2}{60k_B T},$$
where \( V_m \) is molar volume of the stoichiometric solids and \( k_B \) is the Boltzmann constant \( (1.3806 \times 10^{-23} \text{ m}^2\text{kg}^{-1}\text{K}^{-1}) \). The surface tension coefficient, \( \gamma \), is calculated according to [6]

\[
\gamma = 10^{-3} \left\{ 1840 - 0.4(T - 1823) - 0.056T \ln \left( 1 + 0.68e^{8.5647 - 28798/TK} \right) \right\}.
\]

A Material balance is set up to calculate the size of particles. Analysis for TiN and Al\(_2\)O\(_3\) follows:

\[
N \times \frac{4 \pi}{3} r^3 = (x_{ss} - x_{eq}) \times V_M
\]

where \( N \) is the number of particles, \( r \) cm is particle radius, \( x_{ss} \), \( x_{eq} \) mol is supersaturated and equilibrium concentration and \( V_M \text{ cm}^3/\text{mol} \) is molar volume.

Supersaturated and equilibrium concentrations has been calculated as weight percentage. To change the supersaturated value to number of moles the following procedure is taken:

According to random walk in one dimension, melt in between dendrite arms is uniform in concentration at constant solid fractions. Al\(_2\)O\(_3\) and TiN precipitates at 92% solid. Thickness of the liquid at this solid fraction ranges between \( 5 \times 10^{-3} \) cm to \( 5 \times 10^{-4} \) cm based on DAS which changes between 90 \( \mu \text{m} \) to 600 \( \mu \text{m} \) (Fig. 8). Number of moles at supersaturated and equilibrium concentrations can only be calculated at a certain defined volume. Hence a sphere with the thickness of the liquid is considered since random walk is instantaneous at constant solid fractions. The volume fraction of Fe, Cr and Ni in the sphere is calculated according to

\[
Fe_{\text{Volume fraction}} = \frac{\text{wt.}\% \text{Fe}}{\rho_{\text{Fe}}} + \frac{\text{wt.}\% \text{Cr}}{\rho_{\text{Cr}}} + \frac{\text{wt.}\% \text{Ni}}{\rho_{\text{Ni}}}
\]

Number of moles in the sphere is

\[
Total \text{ number of moles} = \frac{V_{\text{sphere}}}{V_M(\text{Fe}) + V_M(\text{Ni}) + V_M(\text{Cr})}
\]

Concentration of sphere is assumed to be composed of Fe, Ni and Cr since other alloying elements exist in dilute amounts. Mole fraction Al, O, Ti and N is calculates as

\[
O_{\text{mole fraction}} = \frac{SSwt.\% \text{O}}{\rho_O \times V_M(\text{O})} + \frac{\text{wt.}\% \text{Ni}}{\rho_{\text{Ni}} \times V_M(\text{Ni})} + \frac{\text{wt.}\% \text{Cr}}{\rho_{\text{Cr}} \times V_M(\text{Cr})}
\]

where SSwt.%O is supersaturated concentration of oxygen, \( \rho_O \) is oxygen density (gr/cm\(^3\)), \( V_O \) is oxygen molar volume (cm\(^3\)/mol). Number of moles for Al, O, Ti and N is calculated as

\[
\text{Oxygen moles} = \text{Mole fraction Oxygen} \times \text{Total numebr of moles}
\]

10
Table 1: Data used for material balance calculations

<table>
<thead>
<tr>
<th></th>
<th>wt.%</th>
<th>ρ (gr/cm³)</th>
<th>$V_M$ (cm³/mol)</th>
<th>SS wt.%</th>
<th>EQ wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>0.001429</td>
<td>11200</td>
<td>0.026</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0012</td>
<td>11200</td>
<td>0.019</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td>2.7</td>
<td>10</td>
<td>1.26</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>4.5</td>
<td>10.6</td>
<td>2.65</td>
<td>2.59</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>50</td>
<td>7.8</td>
<td>7</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>30</td>
<td>8.9</td>
<td>6.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>20</td>
<td>7.19</td>
<td>7.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>26.28</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TiN</td>
<td>-</td>
<td>-</td>
<td>11.808</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Formation of Al₂O₃ is controlled by concentration of aluminium since fraction of oxygen over aluminium in the sphere is 1.09 while molar fraction of oxygen to aluminium in Al₂O₃ is 1.5. Formation of TiN is controlled by concentration of titanium since fraction of nitrogen to titanium in TiN is one while 1.2 in the sphere. The number of moles from Eq. 12 for aluminium and titanium is used in Eq. 8 as $x_{ss} - x_{eq}$. The radius of one particle of TiN which forms at 92% solid where DAS is 90 µm is $r = 2.8 \times 10^{-5}$ cm and where DAS is 600 µm is $r = 1.8 \times 10^{-4}$ cm. The radius of one particle of Al₂O₃ which forms at 92% solid where DAS is 90 µm is $r = 3.4 \times 10^{-5}$ cm and where DAS is 600 µm is $r = 2.2 \times 10^{-4}$ cm.

3.2 Supplement 2

This paper studies how the solidified dendrite structure affects pore precipitation in austenitic stainless steel. An analysis is given that couples the heat transfer in the interdendritic melt between two dendrites to the pressure variation along the dendrite arm.

Heat transfer is one dimensional as:

$$\frac{dq}{dt} = -k \frac{T_L - T_i}{x} = -(-\Delta H)\rho V.$$

where $k$ is the heat conductivity coefficient, $T_L$ and $T_i$ are liquidus and interface temperature respectively, $x$ is the position of the dendrite tip, $\Delta H$ is enthalpy, $\rho$ is density and $V$ is solidification rate. The model is based on solidification heat being released at the tip of the dendrite and travelling in one direction towards the side of the bloom. Heat conductivity of the mush is the same as solid. Liquidus temperature and enthalpy is measured through thermal analysis. Interface temperature is assumed to be constant (1200 K).

The position of the solidification front $Y_S$ and width of the mush $L$ against the position of the tip (horizontal axes) calculated according to Eq. 13. Width of the mush increases as solidification proceeds, indicating higher velocity of the tip rather than the root (previously called solidification front). One dimensional heat transfer hold for columnar zone but loses validity in the equiaxed zone. One
would expect to get even larger velocities when the bloom is in contact with the mould wall. The model does not take the mould into account.

**Pore formation** is evaluated based on pressure balance in the interdendritic area [3]. Gas inside the pore comes from the segregation of gas elements (nitrogen, hydrogen and oxygen) in the melt. Curvature of the porosity exerts pressure on the pore in form of the surface tension on unit length. Atmospheric and hydrostatic pressures are applied through the melt. Friction between the melt and the dendritic structure and shrinkage during solidification cause the pressure to decrease in the interdenritic melt. Local pressure balance can be written as:

\[
P_G = P_{\text{atm}} + P_{\rho gh} + P_{st} + \Delta P_{\text{den}}.
\]

where \( P_G \) is gas pressure, \( P_{\text{atm}} \) is atmospheric pressure, \( P_{\rho gh} \) is metallostatic pressure, \( P_{st} \) is pressure caused by surface tension and \( \Delta P_{\text{den}} \) is pressure change due to the melt motion inside the interdendritic area and shrinkage. Expansion and phase change is compensated by the existing melt in front of the dendrite tip so they are neglected.

Gas pressure \( P_G \) is the partial pressure of the gas elements in the melt and is calculated based on Sivert’s law as:

\[
C = k \sqrt{P_C}
\]

where \( C \) is the concentration of the gas component inside the melt, \( k \) is a constant and \( P_C \) is the partial pressure of the gas component. Sivert’s law is a different interpretation of Gibbs energy Eq. 3 where temperature and activity coefficient contribution for a reaction containing a gas phase is shown with a constant \( k \).

Atmospheric pressure \( P_{\text{atm}} \) is equal to 1 atm. Metallostatic pressure \( P_{\rho gh} \) is the pressure exerted by the liquid column. Roughly 1 meter of liquid steel exerts 1 atm pressure. Pressure exerted by the curvature or surface tension pressure \( P_{st} \) for a bubble is calculated as:

\[
P_{st} = \frac{2\gamma}{r}
\]

where \( \gamma \) is the surface tension and \( r \) is the radius of the bubble.

Pressure change due to the dendritic structure \( P_{\text{den}} \) exists in the mushy zone. Mushy zone consists of solid dendrites and enriched liquid. Dendritic structure create friction between solid and liquid. The friction between solid and liquid causes the pressure to decrease from the tip towards the root of the dendrite. Pressure decrease in the presence of friction is formulated based on Darcy’s law. Flemings have adopted Darcy’s law for solidification of metals according to Eq.
\[
\frac{dP_{den}}{dl} = 8\mu v r^2
\]  
(17)
\[
v = \frac{\beta V}{1 - \beta}
\]  
(18)
\[
r = \frac{l}{L} \lambda
\]  
(19)
\[
\frac{dP_{den}}{dl} = 8\mu \frac{\beta L^2 V}{1 - \beta \overline{l^2} \overline{\lambda}^2}
\]  
(20)

In Eq. 17 the left hand side shows pressure change along a distance, \(\mu\) is liquid viscosity, \(v\) is the liquid velocity and \(r\) is the radius of Darcy’s pores. Velocity of the liquid is related to the solidification rate \(V\) based on Eq. 18 where \(\beta\) is solidification shrinkage. The mushy zone as approximated to Darcy’s porous media according to Eq. 19 where \(l\) is a distance variable, \(L\) is width of the mush and \(\lambda\) represents DAS. Substituting Eq. 18 and 19 in Eq. 17 will change the differential equation to Eq. 20. By integrating Eq. 20 over the width of the mush (\(l\) from 0 to \(L\)) total pressure decrease in the mush is calculated as Eq. 21.

\[
\Delta P = -8\mu \frac{\beta L^2 V}{1 - \beta \overline{l^2} \overline{\lambda}^2}
\]  
(21)

The system can accommodate pores when the equality in Eq. 14 is true.

### 3.3 Supplement 3

Here, a more complete model which takes into account the formation and motion of pores and inclusions in a continuous casting process is constructed. The mathematical model that we consider consists of three components:

1. First, we compute the temperature field in the caster as a whole; this gives us the location of the mushy zone. Moreover, the solid fraction is used to give the location of where in the caster pores will first form, as well as the local sulphur concentration in the mushy zone.

2. Once these pores form, it is necessary to understand how they will move prior to solidifying into the final sample. To do this, basic fluid mechanics, scaling arguments and asymptotic methods are used on the microscale of the pore; the same methods can be used to determine the motion of inclusions.

3. The sub-models in 1) and 2) above are combined to determine the trajectories of pores and inclusions through the mush prior to final solidification.

Here, some details are given of the sub-models.
Figure 9: 2D schematic for the vertical continuous casting of steel
3.3.1 Sub-model 1

We consider a steady state two-dimensional (2D) problem, as shown in Fig. 9, in which an alloy melt at temperature $T_{\text{cast}}$, which is greater than or equal to the liquidus temperature, $T_{\text{liq}}$, enters a mould region at $z = 0$. Mush begins to form at the inner mould surface at $z = z_{\text{liq}}$ when the temperature reaches $T_{\text{liq}}$, whereas complete solidification occurs at $z = z_{\text{sol}}$, where $z_{\text{sol}} > z_{\text{liq}}$, when the temperature reaches the solidus temperature, $T_{\text{sol}}$; on the centreline at $y = W$, mush begins to form at $z = z_{l,\text{mid}}$ and complete solidification occurs at $z = z_{s,\text{mid}}$. Heat transfer in the solid, liquid and mush regions is expressed through

$$\rho c_p V_{\text{cast}} \frac{\partial T}{\partial z} = \frac{\partial}{\partial y} \left( k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) + V_{\text{cast}} \frac{\partial}{\partial z} \left( \rho \Delta H_f \chi \right), \quad (22)$$

where $T$ is the temperature,

$$k = (1 - \chi)k_l + \chi k_s, \quad (23)$$

$$c_p = (1 - \chi)c_{pl} + \chi c_{ps}, \quad (24)$$

and $\chi = \chi(T)$ denotes the solid fraction, which satisfies

$$\chi(T_{\text{sol}}) = 1, \quad \chi(T_{\text{liq}}) = 0; \quad (25)$$

here, we will use [12]

$$\chi = \begin{cases} 
1, & T \leq T_{\text{sol}} \\
\frac{T_{\text{liq}} - T}{T_{\text{liq}} - T_{\text{sol}}} + \frac{\chi(T_{\text{liq}} - T_{\text{sol}})}{(1 - \chi)(T_{\text{liq}} - T_{\text{sol}})} \left( 1 - \cos \left( \frac{\pi}{2} \frac{T - T_{\text{liq}}}{T_{\text{sol}} - T_{\text{liq}}} \right) \right), & T_{\text{sol}} < T < T_{\text{liq}} \\
0, & T \geq T_{\text{liq}}
\end{cases} \quad (26)$$

In equation (22), $\rho$ denotes the density, which we shall assume to be the same for both solid and liquid phases, $\Delta H_f$ denotes the latent heat of fusion and $V_{\text{cast}}$ denotes the casting speed. In equations (23) and (24), and $c_{ps}$ and $k_s$ denote the specific heat capacity and thermal conductivity, respectively, of the solid phase, and $c_{pl}$ and $k_l$ denote the specific heat capacity and thermal conductivity, respectively, of the liquid phase.

The boundary conditions for equation (22) are:

$$k \frac{\partial T}{\partial y} = \varepsilon \sigma (T^4 - T_{\text{amb}}^4) \quad \text{at } y = 0, \quad (27)$$

$$\frac{\partial T}{\partial y} = 0 \quad \text{at } y = W, \quad (28)$$

$$T = T_{\text{cast}} \quad \text{at } z = 0, \quad (29)$$

$$\frac{\partial T}{\partial z} = 0 \quad \text{at } z = L, \quad (30)$$

where $T_{\text{amb}}$ is the ambient temperature, $\varepsilon$ is the emissivity of steel and $\sigma$ is the Stefan-Boltzmann constant ($5.6704 \times 10^{-8}$ W m$^{-2}$ K$^{-4}$). Physically, equations (27)-(30) express, respectively, the following:
• heat loss due to radiation at the outer surface of the strand;
• $y = W$ is an axis of symmetry;
• the inlet temperature is equal to the casting temperature;
• heat transfer due to conduction at $z = L$ is negligible.

Note that, since the purpose of this sub-model is to provide a temperature field for the analysis of pore motion, we have made several simplifications as compared to the actual situation in a continuous caster. In using equation (27), we have neglected the details of the mould cooling, as well as the water spray cooling at the surface of the strand. In addition, we have neglected the curvature of the strand. Thus, the model is similar in spirit, although not exactly identical, to that in [12].

In the model, element concentration changes with alloy composition during solidification due to segregation. The concentration of small elements, for example nitrogen, oxygen and hydrogen, change with $\chi$ according to the lever rule as

$$C = \frac{C^0}{1 - \chi(1 - k_{\text{part}})},$$

where $C^0$ is initial concentration and $k_{\text{part}}$ is the partition coefficient given by

$$k_{\text{part}} = \frac{C_s}{C_l},$$

where $C_s$ and $C_l$ are the equilibrium concentration in solid and liquid steel, respectively. $P_G$ in equation (14) is the sum of the oxygen, nitrogen and hydrogen partial pressures.

Moreover, using Scheil’s equation for the local sulphur concentration in the mush, $c$, we have

$$c = \frac{c_0}{(1 - \chi)^{-k_S}},$$

where $c_0$ is the initial sulphur concentration and $k_S$ is its partition coefficient. Thus, we will be able to determine the spatial gradients of $T$ and $c$, which will be necessary for determining the motion of any pores that form.

Consider now the motion of a pore that forms at $(y_0, z_0)$, where $y_0$ and $z_0$ are such that $\chi(y_0, z_0) = \chi_{\text{crit}}$. Typically, such a pore has a radius that is an order of magnitude or more smaller than the interdendritic spacing, which may be as large as 700 $\mu$m [4]. It is therefore convenient to think of the pore in the interdendritic melt as being akin to a bubble in a fluid of infinite extent; moreover, such a pore should move analogously. Here, we consider a pore that is subjected to temperature and sulphur concentration gradients that will act on it and cause it to move, relative to its background motion, i.e. downward translation with the casting speed, $V_{\text{cast}}$, as well as the possible effect of buoyancy. It is necessary to consider the effect of each of these in turn.
3.3.2 Sub-model 2

We re-derive the formulae for the velocity of the bubble given in Young et al. [13] and Kuznetsov et al. [14], and verify that diffusion dominates convection when parameters for the casting of steel are used; in fact, it turns out that equation (9) in [13] and equation (7) in [14] do not agree with each other. The steady-state axisymmetric governing equations for conservation of mass, momentum and heat in spherical polar $(r, \theta, \phi)$ coordinates, as shown in Fig. 10, and in the frame of reference in which the bubble is fixed at the origin are, for $j = g, l$,

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 u_r^{(j)} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( u_\theta^{(j)} \sin \theta \right) = 0, \quad (32)
\]

\[
0 = -\frac{\partial p^{(j)}}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \tau_{rr}^{(j)} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \tau_{r\theta}^{(j)} \sin \theta \right) - \frac{\left( \tau_{\theta\theta}^{(j)} + \tau_{\phi\phi}^{(j)} \right)}{r}, \quad (33)
\]

\[
0 = -\frac{1}{r} \frac{\partial p^{(j)}}{\partial \theta} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \tau_{r\theta}^{(j)} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \tau_{\theta\theta}^{(j)} \sin \theta \right) + \frac{\left( \tau_{r\theta}^{(j)} - \tau_{\phi\phi}^{(j)} \cot \theta \right)}{r}, \quad (34)
\]

\[
\rho^{(j)} c_p^{(j)} \left( u_r^{(j)} \frac{\partial T^{(j)}}{\partial r} + \frac{u_\theta^{(j)}}{r} \frac{\partial T^{(j)}}{\partial \theta} \right) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T^{(j)}}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial T^{(j)}}{\partial \theta} \right), \quad (35)
\]

where $u_r^{(j)}$ and $u_\theta^{(j)}$ are the radial and angular velocity components, $p^{(j)}$ is the pressure, $c_p^{(j)}$ is the specific heat capacity of the fluid of phase $j$ and $k^{(j)}$ is its
thermal conductivity. In equations (33) and (34), \( \tau_{rr}^{(j)} \), \( \tau_{r\theta}^{(j)} \), \( \tau_{\theta\theta}^{(j)} \) and \( \tau_{\phi\phi}^{(j)} \) denote components of the stress tensor, which are given by

\[
\tau_{rr}^{(j)} = 2 \mu^{(j)} \left( \frac{\partial u_r^{(j)}}{\partial r} \right),
\]

\[
\tau_{r\theta}^{(j)} = \frac{2 \mu^{(j)}}{r} \left( \frac{\partial u_\theta^{(j)}}{\partial \theta} + \frac{u_\theta^{(j)}}{r} \right),
\]

\[
\tau_{\theta\theta}^{(j)} = 2 \mu^{(j)} \left( \frac{\partial u_\theta^{(j)}}{\partial \theta} \right), \quad \tau_{\phi\phi}^{(j)} = \frac{2 \mu^{(j)}}{r} \left( \frac{u_\theta^{(j)}}{r} \cot \theta \right),
\]

The boundary conditions are as follows. At \( r = a \),

\[
\begin{align*}
    u_r^{(g)} = u_r^{(l)} = 0, \\
    u_\theta^{(g)} = u_\theta^{(l)},
\end{align*}
\]

\[
\begin{align*}
    \mu^{(g)} \left( \frac{\partial}{\partial r} \left( \frac{u_\theta^{(g)}}{r} \right) + \frac{1}{r} \frac{\partial u_r^{(g)}}{\partial \theta} \right) - \mu^{(l)} \left( \frac{\partial}{\partial r} \left( \frac{u_\theta^{(l)}}{r} \right) + \frac{1}{r} \frac{\partial u_r^{(l)}}{\partial \theta} \right) = \frac{1}{r} \frac{\partial \gamma}{\partial \theta},
\end{align*}
\]

\[
\begin{align*}
    p^{(g)} - 2 \mu^{(g)} \frac{\partial u_r^{(g)}}{\partial r} - p^{(l)} + 2 \mu^{(l)} \frac{\partial u_r^{(l)}}{\partial r} = \frac{2 \gamma}{r},
\end{align*}
\]

\[
\begin{align*}
    T^{(g)} = T^{(l)},
\end{align*}
\]

\[
\begin{align*}
    k^{(g)} \frac{\partial T^{(g)}}{\partial r} = k^{(l)} \frac{\partial T^{(l)}}{\partial r},
\end{align*}
\]

where \( \gamma \) is the surface tension. As \( r \to \infty \), we have

\[
\begin{align*}
    u_r^{(l)} &\to -V \cos \theta, \\
    u_\theta^{(l)} &\to V \sin \theta, \\
    T^{(l)} &\to T^0 + T_1 r \cos \theta,
\end{align*}
\]

where \( V \) is the thermocapillary drift speed. If \( \gamma = \gamma \left( T \right) \), we can linearize about \( T = T^0 \) so that

\[
\gamma = \gamma^0 + \gamma_T \left( T - T^0 \right),
\]

where \( \gamma^0 = \gamma \left( T^0 \right) \), and \( \gamma_T := \left( \frac{d\gamma}{dT} \right)_{T=T_0} \) is a constant.

Thermocapillary drift velocity derived from Eqs 32 to 45 is:

\[
V_{d,T} = -\frac{\gamma_T a T_1}{2 \mu^{(l)}}.
\]

It is often overlooked, but nevertheless deserves to be noted, that the solutions obtained above made no use of the normal stress condition (41); indeed, we find that the left-hand side of (41) is

\[
\mu \left( P^{(g)}_\infty - 9 \cos \theta \right) - \left( P^{(l)}_\infty + 8 \cos \theta \right),
\]

whereas the right-hand side is

\[2 \left( C_0 - 3 \cos \theta \right).\]
This is explained by the fact the original equations (32)-(44) should be formulated so that the location of the gas-liquid interface is not known, but should be determined as part of the problem; hence the bubble would, in general, not be spherical. This issue has been considered by Levan [15], and requires us to determine how unspherical it might become. In our case, where $\mu \ll 1$, we require

$$-(P^{(l)}_\infty + 8 \cos \theta) \approx 2(C_0 - 3 \cos \theta),$$

which implies that $P^{(l)}_\infty = -2C_0$; thence, the bubble will be spherical if $C_0 \gg 1$, i.e. if the $\cos \theta$ terms are negligible with the leading-order terms. Thus, we see that the spherical approximation is valid provided that $|C_0| \gg 1$.

From our computations, we find that, for the mushy region, $8.3 \times 10^4 \leq |C_0| \leq 1.8 \times 10^8$, as required.

For solutocapillary drift, the formulation is slightly different from (32) to (45), since the sulphur concentration is only defined for the liquid, i.e. $r \geq a$; however, the governing equations for $u^{(l)}_r, u^{(l)}_\theta, p^{(l)}_r, p^{(l)}_\theta, u^{(g)}_r, p^{(g)}_r$ remain unchanged. Consequently, (35) is replaced by

$$\rho^{(l)} \left( u^{(l)}_r \frac{\partial c}{\partial r} + \frac{u^{(l)}_\theta}{r} \frac{\partial c}{\partial \theta} \right) = D \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial c}{\partial \theta} \right) \right\}. \quad (47)$$

The boundary conditions for $c$ are

$$\frac{\partial c}{\partial r} = 0 \quad \text{at} \ r = a, \quad (48)$$

$$c \to c_0 + c_1 r \cos \theta \quad \text{as} \ r \to \infty; \quad (49)$$

thus, (48) replaces (42) and (43). The remaining boundary conditions are as before, except that here we consider $\gamma = \gamma(c)$, and linearize about $c = c^0$ so that

$$\gamma = \gamma^0 + \gamma_c (c - c^0), \quad (50)$$

where $\gamma^0 = \gamma(c^0)$, and $\gamma_c := (d\gamma/dc)_{c=c^0}$ is a constant.

Solutocapillary drift velocity is then derived as:

$$V_{d,c} = -\frac{\gamma_c a c_1}{2 \mu^{(l)}}. \quad (51)$$

From our computations, we find that, for the mushy region, $10^{-3} \leq |Le| \leq 10$, meaning that $V$ will not be as given by (51) for all of the mushy region. To resolve this would require a more sophisticated approach to the governing equations, whereby the left-hand side of (47) is not neglected. This is beyond the scope here, but see, for example, [16–19]. It should be noted that although (46) and (51) are very similar, there are differences in how they are derived.

First, consider the effect of the temperature and sulphur concentration gradients. As we will see in Section 4, $|T_y| \gg |T_z|$, and we will therefore need only
to focus on the horizontal temperature gradient. It is evident that \(|T_y| \gg |T_z|\) will also imply that \(|c_y| \gg |c_z|\), since equation (31) implies

\[
\nabla c = \frac{c_0 (1 - k_S)}{(1 - \chi)^2 - k_S} \frac{d\chi}{dT} \nabla T, \tag{52}
\]

where, from (26),

\[
\frac{d\chi}{dT} = \begin{cases} 
0, & T \leq T_{sol} \\
-\sin\left(\frac{\pi}{2} \frac{T - T_{sol}}{T_{liq} - T_{sol}}\right) \left(\frac{T}{T_{liq} - T_{sol}} - 1\right), & T_{sol} < T < T_{liq} \\
0, & T \geq T_{liq}
\end{cases}, \tag{53}
\]

Secondly consider that surface tension is simultaneously affected by temperature and concentration gradients as:

\[
\gamma = \gamma^0 + \gamma_T (T - T^0) + \gamma_c (c - c^0), \tag{54}
\]

where

\[
\gamma_T = \left(\frac{\partial \gamma}{\partial T}\right)_{T^0, c^0}, \quad \gamma_c = \left(\frac{\partial \gamma}{\partial c}\right)_{T^0, c^0}, \tag{55}
\]

and \(T^0\) and \(c^0\) are a reference temperature and concentration, respectively.

Furthermore, we arrive at the overall drift velocity, \(V_d\), as the sum of \(V_{d,T}\) and \(V_{d,c}\),

\[
V_{d,T} = -\frac{a}{2\mu(l)} (\gamma_T T_1 + \gamma_c c_1). \tag{56}
\]

As regards the possible effect of buoyancy, it is well-known [20–22] that the rise velocity of a bubble would be given by

\[
V_{rise} = \frac{2a^2 g (\rho^{(l)} - \rho^{(g)}) (\mu^{(l)} + \mu^{(g)})}{3\mu^{(l)} (2\mu^{(l)} + 3\mu^{(g)})}, \tag{57}
\]

which, since \(\mu^{(l)} \gg \mu^{(g)}\) and \(\rho^{(l)} \gg \rho^{(g)}\), reduces to

\[
V_{rise} = \frac{a^2 g \rho^{(l)}}{3\mu^{(l)}}, \tag{58}
\]

The rise velocity, \(V_{rise}\), for bubbles can be as high as 0.0003 ms\(^{-1}\). It shows that \(V_{rise} \ll V_{cast}\), so that pores will simply be taken down with the casting speed.

For inclusions, we can use (57), with \(\mu^{(g)} \gg \mu^{(l)}\), to obtain

\[
V_{rise} = \frac{2a^2 g (\rho^{(l)} - \rho^{(i)})}{9\mu^{(l)}},
\]

where \(\rho^{(i)}\) denotes the density of the inclusions. The rise velocity, \(V_{rise}\), for inclusions can be as high as 0.001 ms\(^{-1}\) and yet one order smaller than casting speed.
3.3.3 Sub-model 3

The location of a bubble will be given by

\[
\frac{dy_b}{dt} = V_d, \quad (59)
\]

\[
\frac{dz_b}{dt} = -V_{cast}, \quad (60)
\]

where \( t \) is the time measured from the instant of precipitation. For a bubble precipitating at \((y_0, z_0)\) at \( t = 0 \), we have

\[
y_b(0) = y_0, \quad (61)
\]

\[
z_b(0) = z_0. \quad (62)
\]

\( V_d \) has to be recomputed for every \((y_b, z_b)\) that the bubble finds itself at whilst it is still in the mush. The problem for \( V_d \), involves the temperature gradient and concentration gradient. Although it is perhaps more intuitive to introduce \( t \), it is actually not entirely necessary, since we can combine (59) and (60) as

\[
\frac{dy_b}{dz_b} = -\frac{V_d}{V_{cast}}, \quad (63)
\]

where \( V_d = V_d(y_b, z_b) \); hence, (63) is a first-order ordinary differential equation, having the initial condition

\[
y_b(z_0) = y_0. \quad (64)
\]
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>(a)</td>
<td>(10^{-5} - 10^{-4}) m</td>
</tr>
<tr>
<td>(c_p^{(g)})</td>
<td>1000 J kg(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>(c_p^{(l)})</td>
<td>500 J kg(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>(c_p^{(s)})</td>
<td>900 J kg(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>(D)</td>
<td>(10^{-6} - 10^{-7}) m(^2)s(^{-1})</td>
</tr>
<tr>
<td>(k^{(g)})</td>
<td>0.1 W m(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>(k^{(l)})</td>
<td>30 W m(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>(k^{(s)})</td>
<td>19 W m(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>(L)</td>
<td>9 m</td>
</tr>
<tr>
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</tr>
<tr>
<td>(T_{\text{liq}})</td>
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</tr>
<tr>
<td>(T_{\text{sol}})</td>
<td>1600 K</td>
</tr>
<tr>
<td>(V_{\text{cast}})</td>
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</tr>
<tr>
<td>(W)</td>
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</tr>
<tr>
<td>(\Delta H_f)</td>
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</tr>
<tr>
<td>(\mu^{(g)})</td>
<td>(10^{-5}) kg m(^{-1})s(^{-1})</td>
</tr>
<tr>
<td>(\mu^{(l)})</td>
<td>0.007 kg m(^{-1})s(^{-1})</td>
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<td>(\rho^{(g)})</td>
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<tr>
<td>(\rho^{(l)})</td>
<td>7000 kg m(^{-3})</td>
</tr>
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</table>

Table 2: Model parameters
4 Results and discussion

4.1 Temperature and solid fraction

The temperature field was computed using the finite-element software Comsol Multiphysics. Linear triangular elements were used for equation (22) on an unstructured mesh having around 3367208 elements, corresponding to around 1686865 degrees of freedom. Meshes that were finer and coarser than this were also tried, without any discernible difference in the results. The convergence criterion used was

$$\left( \frac{1}{N_{dof}} \sum_{i=1}^{N_{dof}} |E_i|^2 \right)^{1/2} < \varepsilon,$$

where $N_{dof}$ is the number of degrees of freedom, $E_i$ is the estimated error in the latest approximation to the $i$th component of the true solution vector and $\varepsilon = 10^{-6}$.

Results for the temperature fields are shown in Figs. 11-13. The bloom is completely solidified after 8.1 m, as shown in Fig. 11. The mushy zone increases in width from the top of the strand to the bottom. The thickness of the mush increases both along the length and the width. Inside the mush, the temperature decreases as the solid fraction increases from 0 to 1.

Temperature gradients are larger in the lateral direction (width of the bloom) compared to the longitudinal direction (length of the bloom), as was discussed in Section 3. Fig. 12 shows the temperature gradients in longitudinal direction...
Figure 12: Temperature gradients along length

Figure 13: Temperature gradients along width
along the length of the strand, 0.065 m from the cooled surface. The temperature gradient increases almost uniformly from top to bottom. At 0.065 m from the cooling surface, 2.2 m at the top is liquid, there is the mush between roughly 2.2 m and 4.7 m and the rest is solid. The temperature gradient increases linearly in the liquid from top downwards. There is a visible change in the linearity of the temperature gradient’s behaviour from the beginning of the mush at around 2.2 m to the bottom of the strand in Fig. 12. Fig. 13 shows temperature gradients along the width at one third of the length of the strand from the top. The temperature gradient in the lateral direction is greater than the temperature gradient in the longitudinal direction along the width. At one third of the length from the top of the strand, solid extends from the cooled surface to around 0.043 m; there is mush between 0.043 m and 0.08 m and liquid between 0.08 m and 0.13 m. Temperature gradients decrease uniformly from the surface to the middle of the bloom. There is a visible change in the temperature gradient behaviour at around 0.08 m, which coincides with the liquidus line. The temperature gradient in the lateral direction is greater than that in longitudinal direction, except for 2 mm or less from the middle of the bloom. The middle of the bloom represents a symmetry line for the temperature field; hence, the temperature gradient in lateral direction becomes small at distances closer to the middle.

![Figure 14: $\chi_{\text{crit}}$ (dashed line)](image)

### 4.2 Bubble formation

Analysis of bubble formation show that bubbles could form in the mush all along the width of the bloom, as shown in Fig. 14. Bubbles form for solid
fractions between 0.55 and 0.94. Atmospheric and metallostatic pressure work against bubble formation, according to equation (14). The atmospheric pressure is constant. The metallostatic pressure increases from top to bottom along the length of the strand. Hence, the partial pressures of the gas components need to be larger for bubbles to form at the bottom of the strand rather than the top. In Fig. 14, bubbles form at a solid fraction of around 0.55 close to the surface of the bloom, corresponding to the top of the strand, and at a solid fraction of around 0.94 closer to the middle of the bloom, corresponding to bottom of the strand.

4.3 Inclusion formation

Analysis of inclusion formation shows that multiple inclusion particles can form along the dendrite from 0 to 100% solid (Fig. 15). Figure for formation of TiN is not presented because of the similarity with Fig. 15. Melt gets enriched during solidification due to segregation. When enrichment surpasses equilibrium value for solubility of the compound, the melt is supersaturated. Inclusions precipitate when the supersaturation is enough to overcome surface tension. Upon precipitation, concentration of the dissolved elements of the inclusion reduce according to the weight percentage of the elements in the inclusion. The concentrations decrease until the composition of the solubility curve for the particular inclusion is reached. From the composition of the equilibrium solubility, segregation has to increase the concentration of the elements to reach the nucleation supersaturation in order to precipitate another inclusion particle.

Equilibrium and supersaturated solubilities are numerically calculated for the mush region in a temperature interval from 1600 K to 1670 K. The precipitation of the particles are based on the mass percentage of the elements included in the inclusion component according to the stoichiometric ratios. Seven particles of Al2O3 can precipitate in the region where the solid fraction is greater than 0.92. Two particles of TiN can precipitate in the region 0.91 to 1 solid fraction. Maximum size of Al2O3 and TiN particles respectively are $1.8 \times 10^{-4} \text{ cm}$ and $2.2 \times 10^{-4} \text{ cm}$. Particle sizes are calculated based on a material balance, details of which are given in section 3.1.

Fig. 16 shows inclusions precipitated in the mush at different solid fractions. Pressure is assumed not to affect particle formation; hence, particles are formed at constant solid fractions from top to the bottom of the strand.

Fig. 17 shows inclusions and bubbles forming in the mush. Bubbles move according to equation (63). It can be seen that bubble motion in horizontal direction is dominant compared to bubble motion in vertical direction. Temperature gradient of surface tension changes sign in the interdendritic melt but bubble motion is constantly towards the solid from where bubbles nucleate inside the mesh to where bubbles incorporate in the solid. At each point where bubbles, denoted by circles in Fig. 17 pass an inclusion, denoted by dashed lines, inclusions get incorporated in/on the bubble. The bubble moves with the inclusion attached. Inclusions do not have an effect on the velocity of the
Figure 15: Precipitation of Al$_2$O$_3$

Figure 16: Precipitation of inclusions
bubble. Bubbles stop moving and get incorporated to the solid when bubble
diameter is same as distance between dendrite arms. Bubble incorporation into
solid happens at a solid fraction of around 0.99. Bubbles are considered not to
deform and change shape; hence, a spherical bubble can only move in a space
bigger than its own diameter.
5 Conclusions

The calculations show that bubbles and inclusions can form in the mush area of a continuously cast bloom. In continuous casting, bubbles inside the mush would move towards the solid under the influence of soluto-thermocapillary forces. A bubble can come into contact with several inclusions from the place that it forms to the point that it is incorporated into the solid. Since inclusions can become absorbed by the surface of the bubble, the lateral motion of the bubble in the mush could explain the formation of clusters of inclusions in steel as was presented in Fig. 1.
6 Future work

A scientific journal article is expected to be published based on this thesis. In this work bubble motion is not understood in regions with medium or large Lewis number. In order to have a more comprehensive understanding of bubble motion the possibilities for larger Lewis number has to be considered. In some perspective separation of time scales might not be possible. Hence derivation of the drift velocity with consideration of acceleration would make for some interesting analysis. Whether the analysis would hold if the bubble is not situated in infinite fluid is also of great interest.
Appendix A: EDS results

EDS was performed at 20 kV and 8.22 kcps.
Figure A1: Quantitative compositional analysis for titanium nitride with aluminium oxide as nucleus (Figure 5a)
Figure A2: Quantitative compositional analysis for molybdenum sulphide (Figure 5b)
Figure A3: Quantitative compositional analysis for titanium-molybdenum nitride (Figure 6b)
Figure A4: Quantitative compositional analysis for titanium carbide (Figure 5c)
Figure A5: Quantitative compositional analysis for titanium molybdenum carbide (Figure 6a)
References


On the Relationship Between Inclusions and Pores, Part I: Precipitation

Arash Safavi Nick · Hasse Fredriksson

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Abstract Formation mechanism and clustering of TiN–Al2O3 inclusions precipitated during solidification of austenitic stainless steel is analyzed in this paper. Steel sample are taken from a continuously cast bloom. Clustering of inclusions was examined with a hypothesis that inclusions gather inside the pores. Precipitation of the inclusions occurs through segregation in the residual melt in the interdendritic area. Size and mean distance of the inclusion particles are calculated with mass balance. Impact fracture test in cryogenic temperature reveals clusters of inclusions inside pores on the fracture surface. Size and distribution of the inclusions are examined using light optical microscopy and scanning electron microscopy. Inclusion’s composition is investigated with energy dispersive X-ray spectroscopy analysis. Differential thermal analysis and differential scanning calorimetry Tests determined the transformation temperatures. Results of the experiments are in good agreement with theoretical analysis.

Keywords Solidification · Inclusions · Steel · Nucleation · Cluster

1 Introduction

In string shape, anisotropy in upper shelf energy [1] and lamination defect [2] are among deleterious effects of clusters. It has also been shown that cracks propagate through inclusions [3]. Accordingly impact fracture test in liquid nitrogen temperature is utilized to study inclusions on the fracture surface.

Interaction between inclusions and pores has also been a heated discussion for decades. Inclusions have been reported to nucleate pores [4, 5]. Also the common use of inserting bubbles in melt in order to “clean” the melt from inclusions is another indicator of the strong interaction between gas pores and inclusions.

This work is based on a hypothesis that clusters of inclusions are gathered inside pores. In this article formation of inclusions is calculated based on familiar thermodynamic relations. The movements of pores and the mechanism of inclusion incorporation inside pores are yet to be determined.

2 Materials and Methods

The material used in this study is a continuously cast austenitic stainless steel bloom with the dimensions of 260 × 320 mm. The samples are taken in traverse direction relative to casting direction. Samples with the size of 70 × 10 × 10 mm with a notch in the middle were fractured in liquid nitrogen temperature with a 15 kg pendulum impact test. Fracture surface was studied under SEM. These samples were cut 10 mm below fracture surface and polished for LOM and SEM.

DSC sample was 0.365 g. The sample was heated to 1,743 K with heating rate of 10 K/min. Melt was kept at 1,743 K for 10 min and then cooled down to 1,273 K with 10 K/min and kept at 1,273 K for 20 min. The cycle was
repeated two times for accuracy and to investigate if there would be any residual effect registered. DTA sample was 6 g. The heating cycle for DTA and DSC was the same.

3 Results

3.1 Fracture Surface Analysis

Fracture mode was mostly ductile as expected from austenitic structure. Facets with different morphologies were observed on the fracture surface. Analysis of fracture facets is out of the scope of this work. Multiple types of inclusions were revealed on the fracture surface.

Inclusion particles of interest were categorized in two groups: Single particles Fig. 1 and clusters Fig. 2. Single particles were observed on planes or in shallow pits or inside cracks. Size of single inclusion particles varied between ~3 and 20 μm. Clusters on the other hand only contained particles with sizes ≤7 μm and almost always were found in deep pits that is postulated to be pores. Number of particles in each pore differs enormously.

3.2 Composition Analysis

Nominal composition of the material is Fe, 30 pct. Ni, 20 pct. Cr, 0.45 pct. Al, 0.51 pct. Ti, 0.01 pct. N. O concentration is estimated to be 20 ppm from the producer. Samples were cut, polished and studied with LOM and SEM. Composition analysis on inclusions was done with EDX. Complex {Ti, Mo}C particles were mostly found as plates on grain boundaries. The compact faceted inclusions in Figs. 1 and 2 were identified as TiN. Aluminum Oxide was found in most of the nitride particles as shown in Fig. 3. It seems that oxide particles are nucleating TiN.

3.3 Thermal Analysis

DTA/DSC was performed on the samples. Melting point of the alloy was found to be at 1,670 K and the solidification interval was about 50 K.

3.4 Thermodynamic Analysis

Thermodynamic analysis starts with the equilibrium for formation of TiN and Al₂O₃ [6–8].

\[
\begin{align*}
\text{Ti} + \text{N} & \rightleftharpoons \text{TiN} & \Delta G^0 & = -308799 + 114.35 T \text{ J} \\
2\text{Al} + 3\text{O} & \rightleftharpoons \text{Al₂O₃} & \Delta G^0 & = -1202000 + 386.3 T \text{ J}
\end{align*}
\]

Standard state for the underlined elements are 1 wt% solubility in liquid iron. It is assumed that the solid products are pure and do not have any solubility in liquid
From Eqs. 1 and 2 the equilibrium value of the solubility product was calculated at 1873 K, 1761 K (ladle), 1716 K (tundish) and 1670 K (solidification) temperatures.

Activity follows Henry’s Law (i in weight percentage) and activity coefficient (f) is calculated using Wagner’s interaction parameter (e) [9] according to:

$$a_i = f_i(\text{pct.} i)$$ (3)

$$\log f_i = \sum_{j=1}^{n} e_i^j(\text{ pct.} j)$$ (4)

Wagner’s interaction parameter is postulated to be constant over the temperature and composition interval. The next step is to calculate the supersaturation for nucleation. Supersaturation or activation energy for homogeneous nucleation is calculated according to Fredriksson [5] as:

$$-\Delta G_m = RT\ln \frac{a_{Ti} \times a_N}{(a_{Ti} \times a_N)^{eq}} = \sqrt{\frac{16\pi}{3} \times \frac{\sigma^2(V_{m}^{TiN})^2}{60k_BT}}$$ (5)

$\Delta G$ is the driving force of nucleation, $k_B$ is the Boltzmann’s constant, $\sigma$ is the surface tension between the particle and the surrounding melt, $V_m$ molar volume of the particle and $T$ is the critical nucleation temperature. Surface tension is assumed to be 1 J/m$^2$ [10]. Molar volume of TiN and Al$_2$O$_3$ is $11.8 \times 10^{-6}$ and $25.68 \times 10^{-6}$ m$^3$/mol respectively [11]. Nucleation temperature was set to solidification temperature. The procedure was repeated for Al$_2$O$_3$. Microsegregation of Ti, Al, N and O was calculated. Initial concentration of the elements is calculated according to the equilibrium at the ladle temperature (1,761 K). Ti and Al segregations are described through Scheil’s model and O and N segregations are described with lever rule. Microsegregation calculations revealed that supersaturation for precipitation of TiN and Al$_2$O$_3$ will be reached at 84 and 41 % solid fraction respectively. Initial oxygen concentration is calculated in equilibrium with aluminum. Initial nitrogen concentration is calculated in equilibrium with titanium. Particle distribution was calculated according to mass conservation as it is shown in Eq. 6:

$$N \times \frac{4\pi}{3} r^3 = \frac{x^{ss} - x^{eq}}{V_m}$$ (6)

Distance between two particles of various sizes is calculated according to Eq. 6 and is shown in Table 1. Table 2 contains constants and parameters used throughout this article.

### 4 Discussion

Samples have been fractured in order to reveal the inclusions inside. Fracture initiated from the tip of the notch that was placed in the middle of each sample and propagated through the inclusions and surfaced the inclusions as in Figs. 1 and 2. The clusters were found inside pores as in Fig. 2.

Initial concentration of elements before segregation has been calculated according to the equilibrium in the ladle (1,761 K). This assumption is based on the fact that melt stays in the ladle for quite some time during which a considerable amount of stirring and turbulence happens in the melt.

Measurement of the distances is done inside the melt and in between dendrite arms. According to our hypothesis inclusions will move before getting incorporated in the solid phase. Our presumption is that the controlling factor on maximum size of the particle is dendrite arm spacing (DAS). Supersaturation controls when the particles are nucleated and DAS determines the final size. The average size of the TiN particles in the clusters is about 7 µm in diameter. According to the calculations these particles would be at a distance of ~ 300 µm from each other in the melt. This distance relates to DAS. The distances are calculated based on spherical particles because of the mathematical convenience while the inclusions observed in Figs. 1, 2 and 3 are highly faceted. Therefore the sizes mentioned are on an average bases measured based on a spherical particle.

TiN particle in Fig. 3 is agglomerated out of multiple particles due to the multiple aluminum oxides (two on the arrow) which can be seen. The size of the particle...
corresponding to the aluminum oxide in the middle is roughly measures to a sphere with \( \sim 7 \) \( \mu \)m radius (Fig. 3 bottom left). According to Table 1, a TiN particle with \( 7 \) \( \mu \)m radius are at \( 638 \) \( \mu \)m from each other. This distance corresponds to aluminum oxide with \( \sim 2 \) \( \mu \)m radius while the oxide particle in Fig. 3 has only \( 1 \) \( \mu \)m radius. Although homogeneous nucleation explains oxides acting as nucleation sites for nitrides it does not explain the size of the particle in Fig. 3. Particle size in Fig. 3 can be due to heterogeneous nucleation of TiN on oxides. TiN precipitates on the oxides which hinder oxides growth. Due to this, supersaturation of Al and O happens again further during the solidification and more oxide particles will nucleate. These new oxide particles will be smaller in size and they in turn will have TiN precipitated on them. Eventually these particles will collide and agglomerate like the one in Fig. 3. Big TiN particles similar to Fig. 3 were not seen in the clusters inside pores and were found almost always as a single particle or agglomerate.

Another reason for size deviation from Table 1 could be movement of the particles. Inclusion particles can nucleate pores and then they could move according to the pressure profile around them and marangoni forces applied on them and gravity. This movement could put these particles in a different concentration profile. At this point will move toward a new equilibrium and size of the particle will change accordingly.

This article is based on the hypothesis that a pore/inclusion in between dendrite arms will move to create the clusters. The mechanism is not yet fully developed but it involves the existence of the inclusions in reasonably close vicinity, existence of the pores, motion of the pores and incorporation of the inclusions inside the pores. The first part has been the objective of this article.

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References

Supplement 2
On the relationship between inclusions and pores, Part II: dendritic structure, pressure drop in the liquid and pore precipitation

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Abstract. There is a relationship between pores and inclusions. Inclusions and pores are both formed during solidification inside the interdendritic melt. As hypothesis goes, porosity moves to absorb inclusions and form clusters. Focus of this paper is how solidified dendritic structure affects pore precipitation in austenitic stainless steel. Steel sample is a continuously cast bloom. Temperature profile and width of the mushy zone of the strand is modeled according to a constant temperature at the strands surface. Thermal analysis has been performed with differential thermal analysis (DTA) and differential scanning calorimeter (DSC). Primary dendrite arm spacing (PDAS) is measured with light optical microscopy (LOM) and scanning electron microscopy (SEM). PDAS is represented as the weight average of the distance between parallel sets of primary dendrite stems. Pressure field is calculated based on Darcy’s law. Pore formation is described through segregation of the gas components and pressure field in the liquid.

Introduction

Pore formation has been a subject of discussion for decades. Pores are seen in different sizes and shapes. A number of deleterious effects have been attributed to pores e.g. lower fatigue life. Pore formation seems to be related to gas partial pressure inside the melt and shrinkage.

Although there is no generally accepted comprehensive mechanism for pore formation, experimental data regarding to the subject is not rare. Experimental evidence shows that there is a relationship between solidification rate and porosity. Increasing solidification rate seems to decrease porosity and/or minimize the size of the porosity. Initial concentration of gaseous elements has been shown to have direct effect, as higher initial gas concentration promotes pore formation [1]. Pore formation seems to be sensitive to applied pressure. Therefore, an increased applied pressure inhibits porosity formation [2].

Clustering of inclusions in continuous casting has been only considered to happen inside the ladle or in the nozzles between the ladle, tundish and the mold. Only recently it has been suggested that clustering could also take place inside the interdendritic melt during solidification of the metal [3]. Fig. 1 shows an example of the cluster which is expected to have been formed during solidification.
Experimental Investigation

The material investigated in this study is a continuously cast austenitic stainless steel bloom with the dimensions of $260 \times 320 \text{ mm}$. Nominal composition of the material is Fe, 30 pct. Ni, 20 pct. Cr, 0.45 pct. Al, 0.51 pct. Ti, 0.01 pct. A piece of the bloom 18 mm in thickness is taken in traverse direction relative to casting direction. The profile of the bloom is macro etched to reveal the different zones i.e. columnar and equiaxed. The length of the columnar zone along the shorter side of the sample (260 mm) was 100 mm. 7 samples with the size of $70 \times 10 \times 10 \text{ mm}$ with a 5 mm deep notch in the middle were made from the columnar crystal zone and were fractured in liquid nitrogen temperature with a 15 kg pendulum impact test. Fracture was just utilized in order to reveal the inclusions and clusters. Fracture surface was studied under SEM. These samples were cut 10 mm below fracture surface, polished and etched with V2A solution for LOM and SEM. DSC sample was 0.365 g. The sample was heated to 1743 K with heating rate of 10 K/min. Melt was kept at 1743 K for 10 min and then cooled down to 1273 K with 10 K/min and kept at 1273 K for 20 min. This cycle was repeated 2 times for accuracy as well as to investigate if there would be any residual effect registered. DTA sample was 6 g. The heating cycle for DTA and DSC was the same.

Results and discussion

**Pore formation** is evaluated based on pressure balance in the interdendritic area [2]. Gas inside the pore comes from the segregation of gas elements (nitrogen, hydrogen and oxygen) in the melt. Curvature of the porosity exerts pressure on the pore in form of the surface tension. Atmospheric and hydrostatic pressures are applied through the melt. Friction between the melt and the dendritic structure and shrinkage during solidification cause the pressure to decrease in the interdendritic melt. Local pressure balance can be written as:

$$P_G = P_{atm} + P_{pgh} + P_{st} + \Delta P_{den}. \quad (1)$$

where $P_G$ is gas pressure, $P_{atm}$ is atmospheric pressure, $P_{pgh}$ is metallostatic pressure, $P_{st}$ is pressure caused by surface tension and $\Delta P_{den}$ is pressure change due to the melt motion inside the interdendritic area and shrinkage. Expansion and phase change is compensated by the existing melt in front of the dendrite tip so they are neglected.

Pressure difference caused by the melt flow inside the interdendritic area is based on the Darcy’s law interpreted by Flemings [4]. The interdendritic pressure change is represented by:

$$\frac{dP_{den}}{dl} = 8\mu \frac{\beta}{1 - \beta} \frac{L^2 V}{\lambda^2}. \quad (2)$$

where $\mu$ is the liquid viscosity, $\beta$ is the solidification shrinkage, $L$ is the length of the mushy zone, $V$ is the solidification rate, $\lambda$ is primary dendrite distance and $l$ is the distance along the dendrite stem. Integration of Eq. 2 will give the desired pressure change in the interdendritic area. Material constants in Eq. 2 are given in Table 1. However, it is not possible to calculate the pressure change without knowing the corresponding values for the length of the mushy zone, the solidification rate and the dendritic arm distance.

**Length of the mushy zone and solidification rate.** Solidification is modeled through the heat balance with constant temperature on the surface of the strand. Heat conduction is in one direction [5]. 1D heat conduction holds for the columnar crystals but loses accuracy in the equiaxed zone. The heat balance is written as:

$$\frac{dq}{dt} = -k \frac{(T_L - T_i)}{x} = -(\Delta H)\rho V. \quad (3)$$

where $k$ is the thermal conductivity, $T_L$ is the liquid temperature, $T_i$ is the interface temperature, $x$ is the position of the dendrite tip, $H$ is the enthalpy, $\rho$ is the density and $V$ is the solidification rate.
Fig. 2: (a) Length of the solid shell (Ys) and mushy zone (L) along the width of the bloom, (b) Solidification rate V along the width of the bloom.

Furthermore a linear temperature gradient is assumed through the solid. The liquidus and solidus temperatures are measured with DTA and DSC equal to 1670 and 1603 K, respectively. The surface temperature is taken to be 1270 K. Values for constants in Eq. 3 are given in Table 1. The model predicts that during solidification length of the mushy zone increases from zero at the beginning of the solidification to almost 17 mm at the end of the columnar zone (Fig. 2a). Ys in Fig. 2a represents the solidified shell thickness and L is the mushy zone thickness. Vertical axe is a length scale and horizontal axe x shows the distance from the surface of the bloom until the end of the columnar zone (100 mm). Fig. 2b shows solidification rate which decreases rapidly in the beginning of the solidification and stays almost constant afterwards.

**Primary dendrite arm distance** has been counted on the etched metallographic surface. The distance measurement is done through an intercept method with bias for parallel stems Fig. 3a. The procedure is as follows: At a fixed distance from the surface of the bloom a line with 10 mm in length parallel to the surface of the bloom is considered (dashed line in Fig. 3a). The width of the parallel primary stems (double sided white arrow in Fig. 3a) is divided by the number of the stems in the set (solid black lines in Fig. 3a). Weight average of the measured values on the dashed line represents PDAS in Fig. 3b. The results show an increase in the dendrite arm distance from the surface of the bloom to the end of the columnar crystal zone. The growth criteria based on the solidification rate $V$ (Fig. 2b) and the dendrite arm distance $\lambda$ (Fig. 3b) is calculated as:

$$V\lambda^2 \approx 1.5 \times 10^{-11} \frac{\eta^3}{s}. \quad (4)$$

Eq. 4 gives confidence to the proposed solidification model and the dendritic arm distance measurements [5].

**Pressure decrease in the mushy zone.** Eq. 2 has been integrated over two directions. One is along the length of a dendrite and normal to the surface of the bloom called constant dendrite arm distance direction. The second domain is along the width of the bloom and virtually connects the dendrite tips and/or roots in the casting direction and shows the pressure change over an increasing dendrite arm distance direction. Constant dendrite arm distance points to constant length in the mushy zone. There is only one variable which changes along the dendrite arm ($l$ in Eq. 2). Integration of Eq. 2 on the constant dendrite arm distance direction gives the pressure drop as:

$$\Delta P = -8\mu \frac{\beta}{1-\beta} \frac{L^2 V}{l \lambda^2}. \quad (5)$$

The only variable in Eq. 5 is $l$ which changes from zero to $L$. The pressure drop measured from Eq. 5 is shown in Fig. 3c. So while strand moves down from the top of the mold PDAS is increasing. In the beginning the amount of pressure drop increases and reaches a maximum. Hence the largest amount of pressure drop exists close to the top of the strand.
Fig. 3: (a) Length of the solid shell (Ys) and mushy zone (L) along the width of the bloom, (b) Solidification rate V along the width of the bloom.

Fig. 4: (a) Pressure drop from the tip to the root of the dendrites in constant dendrite arm distance direction, (b) Pressure drop in increasing dendrite arm distance direction.

Integration on the second direction adds three more dependent variables to the constant dendrite arm distance direction in Eq. 5. These dependent variables are the length of the mushy zone L, the solidification rate V and the dendrite arm distance λ. In order to integrate, all the variables are reduced to one variable which is the distance along the width of the bloom x. The relationship between L, l, V and λ with the distance along the width of the bloom x is deduced from a fitting method (Fig. 2 and 3b).

Replacing the parameters (L, l, dl, V and λ) in Eq. 2 with x in Fig. 2 and 3b will provide the necessary differential equation to be integrated over the width of the bloom. Result for the pressure change over the width of the bloom is seen in Fig. 3d. Pressure decrease along the dendrite arm promotes porosity according to Eq. 1.
Gas pressure. Segregation during solidification can increase the partial pressure of dissolved gaseous elements. Fig. 5. Partial pressure in the melt has the capacity to compensate the total pressure (right hand side in Eq. 1). Initial concentration for O and N is calculated according to the equilibrium at the ladle temperature (1761 K). Initial concentration of H is from the plant data. O, H and N segregations are described with lever rule. The partial pressures of the gaseous elements are calculated based on the Sivert’s law as:

\[
C = k \sqrt{P_C}
\]  \\
(6)

where \(C\) is the concentration of the gas component inside the melt, \(k\) is a constant and \(P_C\) is the partial pressure of the gas component. The system can accommodate pore growth only after the accumulated partial pressures has gone at least above 1 atm in order to overcome atmospheric pressure. Gas pressure inside the melt is necessary for pore formation and growth but it is not enough for nucleation.

Nucleation of pores. Fig. 5 shows that the gas component segregation provides the supersaturation required for precipitation of gas pores above 0.6 solid fractions. However, it is difficult to nucleate pores in the interdendritic region due to the surface tension described by the following relation:

\[
P = \frac{2\sigma_{L/G}}{r}.
\]  \\
(7)

Where \(\sigma_{L/G}\) is the surface energy between liquid and gas, \(r\) is the radius of the surface between liquid and gas and \(P\) is the pressure exerted by the surface. Due to this difficulty pores are nucleated heterogeneously. A possibility can be as follow. Aluminum oxides can form homogeneously at a solid fraction equal to 0.4 [3]. The oxides grow to a size of 2 μm. Gas wets the oxides and the relationship between the oxide, the gas and the liquid is described as:

\[
P = \frac{2}{r} \left(\sigma_{L/G} + \sigma_{G/S} - \sigma_{L/S}\right).
\]  \\
(8)

Where \(\sigma_{L/G}\) is the surface energy between liquid and gas, \(\sigma_{G/S}\) is the surface energy between the gas and the solid inclusion and \(\sigma_{L/S}\) is the surface energy between the liquid and the solid inclusion. It could be expected that \(\sigma_{L/G} + \sigma_{G/S} < \sigma_{L/S}\) which gives a negative pressure for pore formation.

Pore growth. Dissolved gas in the melts is activated on the surface of the porosity absorbing the surface energy. The larger the surface the larger amount of the gas will precipitate inside of the pore. When the solidification rate is large, the primary and the secondary arm spaces quickly become narrow which leave smaller surface on the pore front. In turn, the gas accumulation inside the porosity will decrease; hence the pore growth would be slow compared to solid growth which will end in a solid with a large amount of microporosity. When the solidification rate is small gas accumulation inside the pore will increase pore surface faster than the thickening dendrite arms can close pore contact with the melt.

Hence pore will absorb the gas at a larger rate which in turn will cause a faster pore growth. At large enough pore growth rate (small enough solidification rate) pore surface will migrate towards the lower solid fraction which can significantly increase the surface area of the pore and in turn, increases the gas absorption ability. Therefore, a low solidification rate can promote larger pores.

The surface energy provides the activation energy for formation of gas molecules. Alloying elements that increase the surface energy should in principle promote pore formation. Moreover, alloying elements that decrease the surface energy will have the opposite effect.
### Table 1: Constants and parameters used in calculation

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<th>Value</th>
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</tr>
<tr>
<td>Shrinkage ($\beta$)</td>
<td></td>
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<td>Thermal conductivity (k)</td>
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<tr>
<td>Enthalpy ($\Delta H$)</td>
<td>$\frac{J}{g}$</td>
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<td>Density ($\rho$)</td>
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<td>Partition coefficient K(N)</td>
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### Summary

This article belongs to a series that discuss clustering of inclusions during solidification. In this article, pressure decrease along the dendrite arm is shown as a promoting factor for porosities. Surface of the pore control the growth. Next step will be to analyze motion of the pores and inclusions and clustering and incorporation of the inclusions inside the pores.

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### References


Supplement 3
Pores and clustering of inclusions in the continuous casting of steel

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Abstract
A mathematical model is derived to predict the trajectories of pores and inclusions that are nucleated in the interdendritic region during the continuous casting of steel. Using basic fluid mechanics and heat transfer, scaling analysis and asymptotic methods, the model accounts for the possible lateral drift of the pores as a result of the dependence of the surface tension on temperature and sulphur concentration. Moreover, the soluto-thermocapillary drift of such pores prior to final solidification, coupled to the fact any inclusions present can only have a vertical trajectory, can help to interpret recent experimental observations of pore-inclusion clusters in solidified steel castings.

1 Introduction
Formation of porosity (referred to as bubbles here on out) is related to gas content of the system (composition), systems capacity to hold gas elements in solution (solubility) and volume change (shrinkage) in the system during phase change. In steels, bubbles could be divided in two categories based on their origin. One is the bubble that enters steel in gas phase, the other is one that precipitates from liquid. Precipitation is said to occur when the content of the dissolved gas in the phase, solid or liquid, is larger than solubility of the phase and is also large enough to overcome the barriers for formation, e.g. surface tension and ambient pressure. Solubility is dependent on temperature and composition. For steels, solubility gradually decreases with temperature in liquid and solid phases. During phase change, melting or solidification, there is a great difference between the solubility values. Solubility of liquid steel is larger than solid steel. Coupling the difference in solubility values with shrinkage and segregation, steels are most susceptible to bubble formation during solidification [1–3].

Bubbles move in the liquid but are stationary in the solid state. The motion of a bubble in liquid is governed by gravity (buoyancy force) and surface tension,
among others. The motion of a bubble due to gravity is caused by the difference between the density of gas and liquid. Bubbles move due to gravity in the vertical direction; however, the motion of the bubble due to surface tension does not have a predefined direction. In steels, surface tension is dependent on temperature and concentration of surface active elements. Hence, a gradient in temperature or composition creates a gradient in surface tension. The gradient of surface tension acts as the force for the movement of the bubble. The direction of the motion would be along the direction of the gradient.

The dominant surface-active element that is present in most steels is sulphur. Surface tension and surface-tension gradients are functions of sulphur concentration and temperature in steels [4]. The temperature derivative of surface tension changes sign, from negative to positive, by increasing sulphur content above around 30 ppm. The change in the direction of temperature component of surface tension gradient is speculated to cause a change in the direction of bubble motion [5]. In this study, it is shown that the change in the direction of temperature derivative of surface tension does not cause a change in the direction of a bubble moving through the mush area. Liquid motion could also affect the motion of bubbles.

Another aspect of bubble motion in molten steel is the interaction with the solid. A bubble could become engulfed or be pushed by the solidification front. Small solid particles can get attached in/on bubbles, as in froth flotation during mineral beneficiation [3]. It is here postulated that bubbles which precipitate in the liquid drift towards inclusions and incorporate them to form clusters. Engulfment of these pore/inclusion clusters in the solid steel would be one explanation for the structure in Fig. 1.

Figure 1: Two examples of inclusions, shown by arrows, and pores, shown by the dashed circles, on a fracture surface

In order to test the viability of this hypothesis, we combine experimental work with a mathematical model. First, in section 2, observations are made of pore/inclusion clusters that are present in a continuously cast austenitic stainless steel bloom; the material is then subject to DTA and DSC-testing, in order to
determine its solidus and liquidus temperatures, which are required as input for a subsequent mathematical model. In section 3, a three-part mathematical model is constructed for how the pores and inclusions could have formed and clustered during casting: the first part constitutes the thermal problem and gives, as output, the temperature and sulphur concentration distributions; the second part uses these distributions to determine where in the mushy region pores and inclusions will precipitate and what their subsequent velocities will be; the third part tracks their trajectories in the mush region until they are absorbed into the solid. The results are presented in section 4, and conclusions are drawn in section 5.

2 Experimental

22 samples, each of size $10 \times 10 \times 70$ mm$^3$ were made, covering the symmetry axes of a continuously cast austenitic stainless steel bloom with the profile size $265 \times 320$ mm$^2$. The symmetry axes divides the bloom profile in half, to give dimensions $265 \times 160$ mm$^2$. The samples are oriented so that the 70 mm edge is aligned with the casting direction. Grain structure is composed of columnar crystals on each side, 80 mm and 50 mm in length with equiaxed crystals in between. 5 mm deep notch was cut on each sample in the middle of the $10 \times 70$ mm$^2$ face. Samples were fractured by a 15 kg pendulum hammer at liquid nitrogen temperature. The fracture surface was studied under scanning electron microscope. Fractured samples were cut on one side, 10 mm below fracture surface, polished and etched with V2A solution for LOM and SEM. DSC sample was 0.365 g. The sample was heated to 1743 K with heating rate of 10 K/min. The melt was kept at 1743 K for 10 minutes and then cooled down to 1273 K with 10 K/min and kept at 1273 K for 20 min. This cycle was repeated twice for accuracy, as well as to investigate if there would be any residual effect registered. The DTA sample was 6 g. The heating cycle for DTA and DSC was the same.

3 Model

The mathematical model that we consider consists of three components.

1. First, we compute the temperature field in the caster as a whole; this gives us the location of the mushy zone. Moreover, the solid fraction is used to give the location of where in the caster pores will first form, as well as the local sulphur concentration in the mushy zone.

2. Once these pores form, it is necessary to understand how they will move prior to solidifying into the final sample. To do this, basic fluid mechanics, scaling arguments and asymptotic methods are used on the microscale of the pore; the same methods can be used to determine the motion of inclusions.
3. The sub-models in 1) and 2) above are combined to determine the trajectories of pores and inclusions through the mush prior to final solidification.

![Figure 2: 2D schematic for the vertical continuous casting of steel](image)

### 3.1 Sub-model 1

We consider a steady state two-dimensional (2D) problem, as shown in Fig. 2, in which an alloy melt at temperature $T_{\text{cast}}$, which is greater than or equal to the liquidus temperature, $T_{\text{liq}}$, enters a mould region at $z = 0$. Mush begins to form at the inner mould surface at $z = z_{\text{liq}}$ when the temperature reaches $T_{\text{liq}}$, whereas complete solidification occurs at $z = z_{\text{sol}}$, where $z_{\text{sol}} > z_{\text{liq}}$, when the temperature reaches the solidus temperature, $T_{\text{sol}}$; on the centreline at $y = W$, mush begins to form at $z = z_{l,mid}$ and complete solidification occurs at $z = z_{s,mid}$. Heat transfer in the solid, liquid and mush regions is expressed through

$$
\rho c_p V_{\text{cast}} \frac{\partial T}{\partial z} = \frac{\partial}{\partial y} \left( k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) + V_{\text{cast}} \frac{\partial}{\partial z} (\rho \Delta H_f \chi),
$$

(1)
where $T$ is the temperature,

$$k = (1 - \chi)k_l + \chi k_s, \quad (2)$$

$$c_p = (1 - \chi)c_{pl} + \chi c_{ps}, \quad (3)$$

and $\chi = \chi(T)$ denotes the solid fraction, which satisfies

$$\chi(T_{sol}) = 1, \quad \chi(T_{liq}) = 0; \quad (4)$$

here, we will use [6]

$$\chi = \begin{cases} 
1, & T \leq T_{sol} \\
\frac{T_{liq} - T + \frac{\pi}{2}(T_{sol} - T_{liq})\left(1 - \cos\left(\frac{\pi}{2} \frac{T - T_{liq}}{T_{sol} - T_{liq}}\right)\right)}{(T_{liq} - T_{sol})(1 - \frac{\pi}{2})}, & T_{sol} < T < T_{liq} \\
0, & T \geq T_{liq}.
\end{cases} \quad (5)$$

In equation (1), $\rho$ denotes the density, which we shall assume to be the same for both solid and liquid phases, $\Delta H_f$ denotes the latent heat of fusion and $V_{cast}$ denotes the casting speed. In equations (2) and (3), and $c_{ps}$ and $k_s$ denote the specific heat capacity and thermal conductivity, respectively, of the solid phase, and $c_{pl}$ and $k_l$ denote the specific heat capacity and thermal conductivity, respectively, of the liquid phase.

The boundary conditions for equation (1) are:

$$k \frac{\partial T}{\partial y} = \varepsilon \sigma (T^4 - T_{amb}^4) \quad \text{at } y = 0, \quad (6)$$

$$\frac{\partial T}{\partial y} = 0 \quad \text{at } y = W, \quad (7)$$

$$T = T_{cast} \quad \text{at } z = 0, \quad (8)$$

$$\frac{\partial T}{\partial z} = 0 \quad \text{at } z = L, \quad (9)$$

where $T_{amb}$ is the ambient temperature, $\varepsilon$ is the emissivity of steel and $\sigma$ is the Stefan-Boltzmann constant ($5.6704 \times 10^{-8}$ W m$^{-2}$ K$^{-4}$). Physically, equations (6)-(9) express, respectively, the following:

- heat loss due to radiation at the outer surface of the strand;
- $y = W$ is an axis of symmetry;
- the inlet temperature is equal to the casting temperature;
- heat transfer due to conduction at $z = L$ is negligible.

Note that, since the purpose of this sub-model is to provide a temperature field for the analysis of pore motion, we have made several simplifications as compared to the actual situation in a continuous caster. In using equation (6), we have neglected the details of the mould cooling, as well as the water spray cooling at the surface of the strand. In addition, we have neglected the curvature of the strand. Thus, the model is similar in spirit, although not exactly identical, to that in [6].
3.1.1 Bubbles/pores

On solving equation (1) subject to (6)-(9), we find $T$ and $\chi$. Attention now turns to mushy zone, where $0 < \chi < 1$. In particular, it is known that pores can precipitate when the pressure of the dissolved gas elements, $P^{(g)}$, satisfies [1]

$$P^{(g)} = P_{\text{atm}} + P_{\text{st}} + P_{\text{shr}} + P_{\gamma},$$

(10)

where $P_{\text{atm}}$ is the atmospheric pressure, $P_{\text{st}}$ is the metallostatic pressure, $P_{\text{shr}}$ is the pressure difference caused by shrinkage and $P_{\gamma}$ is the pressure due to surface tension. For $P_{\text{st}}$, we have

$$P_{\text{st}} = \rho gz,$$

where $g$ is the acceleration due to gravity; in addition, we neglect $P_{\text{shr}}$, since it is believed to be small compared to the other terms [2] and, moreover, since we have not included the effects of shrinkage in sub-model 1. For $P_{\gamma}$, we have

$$P_{\gamma} = \frac{2\gamma}{a},$$

where $\gamma$ is the surface tension coefficient for a gas bubble in liquid steel and $a$ is the bubble radius; with $a \sim 10^{-5}$ m and $\gamma \sim 1$ N/m [7], we have $P_{\gamma} \sim 10^5$ Pa, which will be comparable with $P_{\text{atm}}$. So, the local pressure balance becomes

$$P^{(g)} = P_{\text{atm}} + \rho gz + \frac{2\gamma}{a}.$$  

(11)

$P_{g}$ in equation (11) can be calculated according to Sievert’s law,

$$P_{g} = K C^2,$$  

(12)

where $K$ is temperature and composition dependent and $C$ is the concentration of the gas elements dissolved in the liquid. Oxygen and hydrogen partial pressures are calculated according to Sievert’s law. The constant $K$ in equation (12) for oxygen and hydrogen in iron respectively is 0.2130 and 0.0026 [3]. Gas partial pressure can also be calculated based on the equilibrium of the reaction with gas products. We consider nitrogen forming gas molecules according to [8]

$$\frac{1}{2} N_2^{(g)} = N \text{ (1wt%)}, \quad \Delta G^0 = 3598 + 23.89T,$$  

(13)

where $\Delta G^0$ is the standard free energy of the reaction (in Joules) and the standard state for dissolved nitrogen is 1wt% solution in iron. The partial pressure of nitrogen from the reaction in equation (13) is related to standard free energy according to

$$\Delta G = RT\ln\frac{a_N}{P_g} + \Delta G^0,$$  

(14)

where $\Delta G$ is free energy change for the equilibrium in equation (13), $R$ is the gas constant, $P_g$ is the partial pressure of gas phase nitrogen and $a_N$ is the activity
of the dissolved nitrogen. The change in free energy of a reaction is negative for spontaneous reactions and zero for the equilibrium state. $a_N$ is related to concentration of the dissolved nitrogen, $C_N$, by

$$a_N = f_N C_N,$$

(15)

where $f_N$ is the activity coefficient. The activity coefficient for multicomponent systems can be calculated according to Wagner’s formalism by

$$\log f_N = \sum_j c^j_N C_j,$$

where $j$ are the alloying elements in steel, $c^j_N$ are the interaction coefficients and $C_j$ are the concentration of element $j$ in weight percentage. The interaction coefficients used in this paper are given in Table 1. Activity coefficient is approximated constant. The partial pressure of the gas element and activity change with concentration in equations (12) and (15). Element concentration changes with alloy composition during solidification due to segregation. The concentration of small elements, for example nitrogen, oxygen and hydrogen, change with $\chi$ according to the lever rule as

$$C = \frac{C^0}{1 - \chi(1 - k_{part})},$$

where $C^0$ is initial concentration and $k_{part}$ is the partition coefficient given by

$$k_{part} = \frac{C_s}{C_l},$$

where $C_s$ and $C_l$ are the equilibrium concentration in solid and liquid steel, respectively. Values for partition coefficients and initial compositions are given in Table 1. $P_g$ in equation (11) is the sum of the oxygen, nitrogen and hydrogen partial pressures.

Moreover, using Scheil’s equation for the local sulphur concentration in the mush, $c$, we have

$$c = \frac{c_0}{(1 - \chi)^{1-k_S}},$$

(16)

where $c_0$ is the initial sulphur concentration and $k_S$ is its partition coefficient. Thus, we will be able to determine the spatial gradients of $T$ and $c$, which will be necessary for determining the motion of any pores that form.

Consider now the motion of a pore that forms at $(y_0, z_0)$, where $y_0$ and $z_0$ are such that $\chi(y_0, z_0) = \chi_{crit}$. Typically, such a pore has a radius that is an order of magnitude or more smaller than the interdendritic spacing, which may be as large as 700 $\mu$m [2]. It is therefore convenient to think of the pore in the interdendritic melt as being akin to a bubble in a fluid of infinite extent; moreover, such a pore should move analogously. Here, we consider a pore that is subjected to temperature and sulphur concentration gradients that will act on
Table 1: Composition (wt.%), interaction ($e$) and partition coefficients ($k_{part}$)

<table>
<thead>
<tr>
<th>$i$</th>
<th>wt.%</th>
<th>$e_{Al}$</th>
<th>$e_{H}$</th>
<th>$e_{Mn}$</th>
<th>$e_{N}$</th>
<th>$e_{O}$</th>
<th>$e_{S}$</th>
<th>$e_{Ti}$</th>
<th>$k_{part}$ $[^9]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.45</td>
<td>0.048 $^{[10]}$</td>
<td>0.013 $^{[10]}$</td>
<td>0.027 $^{[11]}$</td>
<td>-0.028 $^{[10]}$</td>
<td>-0.83 $^{[12]}$</td>
<td>0.035 $^{[13]}$</td>
<td>0.93 $^{[11]}$</td>
<td>0.6</td>
</tr>
<tr>
<td>C</td>
<td>0.67</td>
<td>0.11 $^{[10]}$</td>
<td>0.06 $^{[10]}$</td>
<td>-0.07 $^{[13]}$</td>
<td>0.13 $^{[10]}$</td>
<td>-0.45 $^{[13]}$</td>
<td>0.11 $^{[13]}$</td>
<td>-0.21 $^{[11]}$</td>
<td>0.34</td>
</tr>
<tr>
<td>Co</td>
<td>0.033</td>
<td>-$^{b}$</td>
<td>0.0018 $^{[10]}$</td>
<td>-</td>
<td>0.011 $^{[10]}$</td>
<td>0.007 $^{[10]}$</td>
<td>0.0026 $^{[13]}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>20.33</td>
<td>0.0096 $^{[12]}$</td>
<td>-0.0022 $^{[13]}$</td>
<td>0.0039 $^{[12]}$</td>
<td>-0.045 $^{[14]}$</td>
<td>-0.08 $^{[15]}$</td>
<td>-0.011 $^{[13]}$</td>
<td>0.032 $^{[16]}$</td>
<td>0.86</td>
</tr>
<tr>
<td>Cu</td>
<td>0.095</td>
<td>-</td>
<td>0.0005 $^{[10]}$</td>
<td>-</td>
<td>0.009 $^{[10]}$</td>
<td>-0.009 $^{[10]}$</td>
<td>-0.0084 $^{[13]}$</td>
<td>-</td>
<td>0.88</td>
</tr>
<tr>
<td>H</td>
<td>0.0020</td>
<td>0.24 $^{[10]}$</td>
<td>0 $^{[10]}$</td>
<td>-0.31 $^{[13]}$</td>
<td>-3.1 $^{[13]}$</td>
<td>0.12 $^{[13]}$</td>
<td>-1.1 $^{[13]}$</td>
<td>0.3 $^{[3]}$</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.53</td>
<td>0.035 $^{[11]}$</td>
<td>-0.0014 $^{[10]}$</td>
<td>0.002 $^{[15]}$</td>
<td>-0.02 $^{[10]}$</td>
<td>-0.182 $^{[15]}$</td>
<td>-0.026 $^{[13]}$</td>
<td>-0.043 $^{[11]}$</td>
<td>0.785</td>
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<tr>
<td>Mo</td>
<td>0.22</td>
<td>-</td>
<td>0.0022 $^{[13]}$</td>
<td>-</td>
<td>-0.011 $^{[10]}$</td>
<td>0.0035 $^{[10]}$</td>
<td>0.0027 $^{[13]}$</td>
<td>0.01 $^{[17]}$</td>
<td>0.585</td>
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<tr>
<td>N</td>
<td>0.010</td>
<td>0.033 $^{[18]}$</td>
<td>-</td>
<td>-0.091 $^{[13]}$</td>
<td>0 $^{[10]}$</td>
<td>0.057 $^{[10]}$</td>
<td>0.01 $^{[13]}$</td>
<td>-3.8 $^{[10]}$</td>
<td>0.48</td>
</tr>
<tr>
<td>Nb</td>
<td>0.01</td>
<td>-</td>
<td>-0.0023 $^{[13]}$</td>
<td>-</td>
<td>-0.06 $^{[13]}$</td>
<td>-0.14 $^{[13]}$</td>
<td>-0.013 $^{[13]}$</td>
<td>0.155 $^{[17]}$</td>
<td>0.22</td>
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<tr>
<td>Ni</td>
<td>30.30</td>
<td>-0.029 $^{[12]}$</td>
<td>0 $^{[10]}$</td>
<td>-0.0085 $^{[12]}$</td>
<td>0.012 $^{[20]}$</td>
<td>0.006 $^{[13]}$</td>
<td>0 $^{[10]}$</td>
<td>-0.0115 $^{[20]}$</td>
<td>0.95</td>
</tr>
<tr>
<td>O</td>
<td>0.0027$^{c}$</td>
<td>-1.98 $^{[11]}$</td>
<td>-0.19 $^{[10]}$</td>
<td>-0.637 $^{[15]}$</td>
<td>0.05 $^{[13]}$</td>
<td>-0.20 $^{[13]}$</td>
<td>-0.27 $^{[13]}$</td>
<td>-1.8 $^{[13]}$</td>
<td>0.03 $^{[21]}$</td>
</tr>
<tr>
<td>P</td>
<td>0.010</td>
<td>-</td>
<td>0.011 $^{[10]}$</td>
<td>-0.0035 $^{[13]}$</td>
<td>0.051 $^{[10]}$</td>
<td>0.07 $^{[10]}$</td>
<td>0.29 $^{[13]}$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.0006</td>
<td>0.049 $^{[10]}$</td>
<td>0.008 $^{[10]}$</td>
<td>-0.0048 $^{[13]}$</td>
<td>0.013 $^{[10]}$</td>
<td>-0.133 $^{[13]}$</td>
<td>-5.8 $^{[11]}$</td>
<td>-0.11 $^{[13]}$</td>
<td>0.035</td>
</tr>
<tr>
<td>Si</td>
<td>0.63</td>
<td>0.056 $^{[11]}$</td>
<td>0.027 $^{[10]}$</td>
<td>-0.0327 $^{[11]}$</td>
<td>0.023 $^{[22]}$</td>
<td>-0.066 $^{[15]}$</td>
<td>0.063 $^{[11]}$</td>
<td>-0.009 $^{[22]}$</td>
<td>0.52</td>
</tr>
<tr>
<td>Ti</td>
<td>0.51</td>
<td>0.004 $^{[11]}$</td>
<td>-0.08 $^{[10]}$</td>
<td>-0.05 $^{[11]}$</td>
<td>-0.593 $^{[20]}$</td>
<td>-0.6 $^{[13]}$</td>
<td>-0.072 $^{[13]}$</td>
<td>0.47 $^{[16]}$</td>
<td>0.33</td>
</tr>
</tbody>
</table>

$^{a}$The square brackets refer to the reference from which the value is taken

$^{b}$Where data is not given, it was not found in the literature and assumed zero

$^{c}$Initial composition for oxygen is calculated based on equilibrium with aluminium according to equation (27)
it and cause it to move, relative to its background motion, i.e. downward trans-
lation with the casting speed, \( V_{\text{cast}} \), as well as the possible effect of buoyancy.
It is necessary to consider the effect of each of these in turn.

First, consider the effect of the temperature and sulphur concentration gra-
dients. As we will see in Section 4, \(|T_y| \gg |T_z|\), and we will therefore need
only to focus on the horizontal temperature gradient. A pore at \((y,z)\) will be
subject to \( T_y \) at that point. Assuming that the pore instantaneously reaches its
terminal horizontal velocity, \( V_d \), we will have \[23\]
\[
V_d = -\frac{\gamma_T a T_1}{2\mu(l)^2},
\]
where \( T_1 = T_y(y,z) \) and
\[
\gamma = \gamma^0 + \gamma_T (T - T^0) + \gamma_c (c - c^0),
\]
where
\[
\gamma_T = \left( \frac{\partial \gamma}{\partial T} \right)_{T_0,c_0}, \quad \gamma_c = \left( \frac{\partial \gamma}{\partial c} \right)_{T_0,c_0},
\]
and \( T^0 \) and \( c^0 \) are a reference temperature and concentration, respectively. It
is evident that \(|T_y| \gg |T_z|\) will also imply that \(|c_y| \gg |c_z|\), since equation (16)
implies
\[
\nabla c = c_0 (1-k_S) \frac{d\chi}{(1-\chi)^2-k_S} \frac{d\chi}{dT} \nabla T,
\]
where, from (5),
\[
\frac{d\chi}{dT} = \begin{cases} 
0, & T \leq T_{\text{sol}} \\
-\frac{1-\sin\left(\frac{T-T_{\text{sol}}}{T_{\text{liq}}-T_{\text{sol}}}(1-\frac{T_{\text{sol}}}{T_{\text{liq}}})\right)}{(T_{\text{sol}}-T_{\text{liq}})(1-\frac{T_{\text{sol}}}{T_{\text{liq}}})}, & T_{\text{sol}} < T < T_{\text{liq}} \\
0, & T \geq T_{\text{liq}}
\end{cases},
\]
so that, focusing again on the horizontal gradient, we can nominally arrive at
\[
V_{d,c} = -\frac{\gamma_c a c_1}{2\mu(l)^2},
\]
where \( V_{d,c} \) is the drift velocity induced by the horizontal temperature gradient
and \( c_1 = c_y(y,z) \). Note that although (17) and (22) are very similar, there
are differences in how they are derived; the details are documented in full in
Appendixes A-C, in order to demonstrate clearly the assumptions made. Fur-
thermore, we arrive at the overall drift velocity, \( V_d \), as the sum of \( V_{d,T} \) and
\( V_{d,c} \),
\[
V_{d,T} = -\frac{a}{2\mu(l)^2} (\gamma_T T_1 + \gamma_c c_1).
\]

As regards the possible effect of buoyancy, it is well-known \[24–26\] that the
rise velocity of a bubble would be given by
\[
V_{\text{rise}} = \frac{2a^2 g \left( \rho(l) - \rho(g) \right) \left( \mu(l) + \mu(g) \right)}{3\mu(l) \left( 2\mu(l) + 3\mu(g) \right)},
\]

which, since $\mu^{(l)} \gg \mu^{(g)}$ and $\rho^{(l)} \gg \rho^{(g)}$, reduces to

$$V_{\text{rise}} = \frac{a^2 g \rho^{(l)}}{3 \mu^{(l)}}, \quad (25)$$

in what follows, we show that $V_{\text{rise}} \ll V_{\text{cast}}$, so that pores will simply be taken down with the casting speed.

### 3.1.2 Inclusions

Melt gets enriched during solidification due to segregation. When enrichment surpasses equilibrium value for solubility of the compound, the melt is supersaturated. Inclusions precipitate when the supersaturation is enough to overcome surface tension. Upon precipitation, concentration of the dissolved elements of the inclusion reduce according to the weight percentage of the elements in the inclusion. The concentrations decrease until the composition of the solubility curve for the particular inclusion is reached. From the composition of the equilibrium solubility, segregation has to increase the concentration of the elements to reach the nucleation supersaturation in order to precipitate another inclusion particle. Formation of TiN and Al$_2$O$_3$ is considered based on reactions [8,27]

\[
\begin{align*}
\text{Ti}(1\text{wt%}) + \text{N}(1\text{wt%}) &= \text{TiN}^{(s)}, \quad \Delta G^0 = -308799 + 114.35T, \quad (26) \\
2\text{Al}(1\text{wt%}) + 3\text{O}(1\text{wt%}) &= \text{Al}_2\text{O}_3^{(s)}, \quad \Delta G^0 = -1202000 + 386.3T, \quad (27)
\end{align*}
\]

where TiN and Al$_2$O$_3$ are stoichiometric solids (activity equal to one) and both values for $\Delta G^0$ are in joules. The equilibrium solubility for titanium nitride and aluminium oxide is calculated according to equation (14). The equilibrium solubility of MnS is given directly by [28]

$$L[\%\text{Mn}][\%\text{S}] = -8027/T + 4.745. \quad (28)$$

Nucleation supersaturation is calculated as [29]

$$RT \ln \left( \frac{SS_{\text{solubility}}}{EQ_{\text{solubility}}} \right) = \sqrt{\frac{16 \pi \gamma^3 V^2_m}{3 \cdot 60k_B T}}, \quad (29)$$

where $V_m$ is molar volume of the stoichiometric solids and $k_B$ is the Boltzmann constant ($1.3806 \times 10^{-23}$ m$^2$kg$s^{-2}K^{-1}$). The surface tension coefficient, $\gamma$, is calculated according to [4]

$$\gamma = 10^{-3} \left\{ 1840 - 0.4(T - 1823) - 0.056T \ln \left( 1 + 0.68e^{28798 - 8.5647cS} \right) \right\}. \quad (30)$$

For inclusions, we can use (24), with $\mu^{(g)} \gg \mu^{(l)}$, to obtain

$$V_{\text{rise}} = \frac{2a^2 g (\rho^{(l)} - \rho^{(i)})}{9 \mu^{(l)}}$$

where $\rho^{(i)}$ denotes the density of the inclusions. The maximum value for $V_{\text{rise}}$ for inclusions can be as high as 0.001 ms$^{-1}$.
3.2 Sub-model 3

The location of a bubble will be given by

\[
\frac{dy_b}{dt} = V_d, \tag{31}
\]
\[
\frac{dz_b}{dt} = -V_{cast}, \tag{32}
\]

where \( t \) is the time measured from the instant of precipitation. For a bubble precipitating at \((y_0, z_0)\) at \( t = 0 \), we have

\[
y_b(0) = y_0, \tag{33}
\]
\[
z_b(0) = z_0. \tag{34}
\]

\( V_d \) has to be recomputed for every \((y_b, z_b)\) that the bubble finds itself at whilst it is still in the mush. The problem for \( V_d \), involves the temperature gradient and concentration gradient. Although it is perhaps more intuitive to introduce \( t \), it is actually not entirely necessary, since we can combine (31) and (32) as

\[
\frac{dy_b}{dz_b} = -\frac{V_d}{V_{cast}}, \tag{35}
\]

where \( V_d = V_d(y_b, z_b) \); hence, (35) is a first-order ordinary differential equation, having the initial condition

\[
y_b(z_0) = y_0. \tag{36}
\]

4 Results and discussion

4.1 Temperature and solid fraction

The temperature field was computed using the finite-element software Comsol Multiphysics. Linear triangular elements were used for equation (1) on an unstructured mesh having around 3367208 elements, corresponding to around 1686865 degrees of freedom. Meshes that were finer and coarser than this were also tried, without any discernible difference in the results. The convergence criterion used was

\[
\left( \frac{1}{N_{dof}} \sum_{i=1}^{N_{dof}} |E_i|^2 \right)^{1/2} < \varepsilon, \tag{37}
\]

where \( N_{dof} \) is the number of degrees of freedom, \( E_i \) is the estimated error in the latest approximation to the \( i \)th component of the true solution vector and \( \varepsilon = 10^{-6} \).

Results for the temperature fields are shown in Figs. 3-5. The bloom is completely solidified after 8.1 m, as shown in Fig. 3. The mushy zone increases in width from the top of the strand to the bottom. The thickness of the mush
\( a = 10^{-5} - 10^{-4} \text{ m} \)
\( c_p^{(g)} = 1000 \text{ J kg}^{-1} \text{K}^{-1} \)
\( c_p^{(l)} = 500 \text{ J kg}^{-1} \text{K}^{-1} \)
\( c_p^{(s)} = 900 \text{ J kg}^{-1} \text{K}^{-1} \)
\( D = 10^{-6} - 10^{-7} \text{ m}^2 \text{s}^{-1} \)
\( k^{(g)} = 0.1 \text{ W m}^{-1} \text{K}^{-1} \)
\( k^{(l)} = 30 \text{ W m}^{-1} \text{K}^{-1} \)
\( k^{(s)} = 19 \text{ W m}^{-1} \text{K}^{-1} \)

\( L = 9 \text{ m} \)
\( T_{\text{cast}} = 1770 \text{ K} \)
\( T_{\text{liq}} = 1670 \text{ K} \)
\( T_{\text{sol}} = 1600 \text{ K} \)
\( V_{\text{cast}} = 0.01 \text{ m s}^{-1} \)
\( W = 0.13 \text{ m} \)
\( \Delta H_f = 270000 \text{ J kg}^{-1} \)
\( \mu^{(g)} = 10^{-5} \text{ kg m}^{-1} \text{s}^{-1} \)
\( \mu^{(l)} = 0.007 \text{ kg m}^{-1} \text{s}^{-1} \)
\( \rho^{(g)} = 1 \text{ kg m}^{-3} \)
\( \rho^{(l)} = 7000 \text{ kg m}^{-3} \)

Table 2: Model parameters

Figure 3: Fraction solid (\( \chi \))
Figure 4: Temperature gradients along length

Figure 5: Temperature gradients along width
increases both along the length and the width. Inside the mush, the temperature decreases as the solid fraction increases from 0 to 1.

Temperature gradients are larger in the lateral direction (width of the bloom) compared to the longitudinal direction (length of the bloom), as was discussed in Section 3.1.1. Fig. 4 shows the temperature gradients in longitudinal direction along the length of the strand, 0.065 m from the cooled surface. The temperature gradient increases almost uniformly from top to bottom. At 0.065 m from the cooling surface, 2.2 m at the top is liquid, there is the mush between roughly 2.2 m and 4.7 m and the rest is solid. The temperature gradient increases linearly in the liquid from top downwards. There is a visible change in the linearity of the temperature gradient’s behaviour from the beginning of the mush at around 2.2 m to the bottom of the strand in Fig. 4. Fig. 5 shows temperature gradients along the width at one third of the length of the strand from the top. The temperature gradient in the lateral direction is greater than the temperature gradient in the longitudinal direction along the width. At one third of the length from the top of the strand, solid extends from the cooled surface to around 0.043 m; there is mush between 0.043 m and 0.08 m and liquid between 0.08 m and 0.13 m. Temperature gradients decrease uniformly from the surface to the middle of the bloom. There is a visible change in the temperature gradient behaviour at around 0.08 m, which coincides with the liquidus line. The temperature gradient in the lateral direction is greater than that in longitudinal direction, except for 2 mm or less from the middle of the bloom. The middle of the bloom represents a symmetry line for the temperature field; hence, the temperature gradient in lateral direction becomes small at distances closer to the middle.

Figure 6: $\chi_{\text{crit}}$ (dashed line)
4.2 Bubble formation

Analysis of bubble formation show that bubbles could form in the mush all along the width of the bloom, as shown in Fig. 6. Bubbles form for solid fractions between 0.55 and 0.94. Atmospheric and metallostatic pressure work against bubble formation, according to equation (11). The atmospheric pressure is constant. The metallostatic pressure increases from top to bottom along the length of the strand. Hence, the partial pressures of the gas components need to be larger for bubbles to form at the bottom of the strand rather than the top. In Fig. 6, bubbles form at a solid fraction of around 0.55 close to the surface of the bloom, corresponding to the top of the strand, and at a solid fraction of around 0.94 closer to the middle of the bloom, corresponding to bottom of the strand.

4.3 Inclusion formation

Analysis of inclusion formation shows that multiple inclusion particles can form along the dendrite from 0 to 100% solid according to the mechanism discussed in Section 3.1.1 (Fig. 7). Figure for formation of TiN is not presented because of the similarity with Fig. 7. Equilibrium and supersaturated solubilities are numerically calculated for the mush region in a temperature interval from 1600 K to 1670 K. The precipitation of the particles are based on the mass percentage of the elements included in the inclusion component according to the stoichiometric ratios. Seven particles of Al$_2$O$_3$ can precipitate in the region where the solid fraction is greater than 0.92. Two particles of TiN can precipitate in the region 0.91 to 1 solid fraction. Maximum size of Al$_2$O$_3$ and TiN particles respectively are $1.8 \times 10^{-4}$ cm and $2.2 \times 10^{-4}$ cm. Particle sizes are calculated based on a material balance, details of which are given in Appendix D.

Fig. 8 shows inclusions precipitated in the mush at different solid fractions. Pressure is assumed not to affect particle formation; hence, particles are formed at constant solid fractions from top to the bottom of the strand.

Fig. 9 shows inclusions and bubbles forming in the mush. Bubbles move according to equation (35). It can be seen that bubble motion in horizontal direction is dominant compared to bubble motion in vertical direction. Temperature gradient of surface tension changes sign in the interdendritic melt but bubble motion is constantly towards the solid from where bubbles nucleate inside the mesh to where bubbles incorporate in the solid. At each point where bubbles, denoted by circles in Fig. 9 pass an inclusion, denoted by dashed lines, inclusions get incorporated in/on the bubble. The bubble moves with the inclusion attached. Inclusions do not have an effect on the velocity of the bubble. Bubbles stop moving and get incorporated to the solid when bubble diameter is same as distance between dendrite arms. Bubble incorporation into solid happens at a solid fraction of around 0.99. Bubbles are considered not to deform and change shape; hence, a spherical bubble can only move in a space bigger than its own diameter.
Figure 7: Precipitation of $\text{Al}_2\text{O}_3$

Figure 8: Precipitation of inclusions
5 Conclusions

The calculations show that bubbles and inclusions can form in the mush area of a continuously cast bloom. In continuous casting, bubbles inside the mush would move towards the solid under the influence of soluto-thermocapillary forces. A bubble can come into contact with several inclusions from the place that it forms to the point that it is incorporated into the solid. Since inclusions can become absorbed by the surface of the bubble, the lateral motion of the bubble in the mush could explain the formation of clusters of inclusions in steel as was presented in Fig. 1.

Acknowledgements

The authors would like to thank Hugo Carlssons stiftelse and Axel Ax:son Johnson fund for supporting this project.

Appendix A: thermocapillary drift

We re-derive the formulae for the velocity of the bubble given in Young et al. [23] and Kuznetsov et al. [30], and verify that diffusion dominates convection when parameters for the casting of steel are used; in fact, it turns out that equation (9) in [23] and equation (7) in [30] do not agree with each other. The steady-state axisymmetric governing equations for conservation of mass, momentum
Figure 10: Schematic of geometry for a drifting gas bubble

and heat in spherical polar \((r, \theta, \phi)\) coordinates, as shown in Fig. 10, and in the frame of reference in which the bubble is fixed at the origin are, for \(j = g, l,\)

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 u_r^{(j)} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( u_\theta^{(j)} \sin \theta \right) = 0, \tag{A1}
\]

\[
0 = -\frac{\partial p^{(j)}}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \tau_{rr}^{(j)} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \tau_{r\theta}^{(j)} \sin \theta \right) - \frac{\left( \tau_{\theta\theta}^{(j)} + \tau_{\phi\phi}^{(j)} \right)}{r}, \tag{A2}
\]

\[
0 = -\frac{1}{r} \frac{\partial p^{(j)}}{\partial \theta} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \tau_{r\theta}^{(j)} \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( \tau_{\theta\theta}^{(j)} \sin \theta \right) + \frac{\left( \tau_{\theta\theta}^{(j)} - \tau_{\phi\phi}^{(j)} \cot \theta \right)}{r}, \tag{A3}
\]

\[
\rho^{(j)} c_p^{(j)} \left( u_r^{(j)} \frac{\partial T^{(j)}}{\partial r} + \frac{u_\theta^{(j)}}{r} \frac{\partial T^{(j)}}{\partial \theta} \right) = \]

\[
k^{(j)} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T^{(j)}}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial T^{(j)}}{\partial \theta} \right) \right\}, \tag{A4}
\]

where \(u_r^{(j)}\) and \(u_\theta^{(j)}\) are the radial and angular velocity components, \(p^{(j)}\) is the pressure, \(c_p^{(j)}\) is the specific heat capacity of the fluid of phase \(j\) and \(k^{(j)}\) is its thermal conductivity. In equations (A2) and (A3), \(\tau_{rr}^{(j)}, \tau_{r\theta}^{(j)}, \tau_{\theta\theta}^{(j)}\) and \(\tau_{\phi\phi}^{(j)}\) denote components of the stress tensor, which are given by

\[
\tau_{rr}^{(j)} = 2\mu^{(j)} \frac{\partial u_r^{(j)}}{\partial r}, \quad \tau_{\theta\theta}^{(j)} = \frac{2\mu^{(j)}}{r} \left( \frac{\partial u_\theta^{(j)}}{\partial \theta} + u_r^{(j)} \right), \tag{A5}
\]
\[ \tau^{(j)}_{\phi\phi} = \frac{2\mu^{(j)}}{r} \left( u^{(j)}_r + u^{(j)}_\theta \cot \theta \right), \quad \tau^{(j)}_{r\theta} = \mu^{(j)} \left( r \frac{\partial}{\partial r} \left( \frac{u^{(j)}_\theta}{r} \right) + \frac{1}{r} \frac{\partial u^{(j)}_r}{\partial \theta} \right). \]

(A6)

The boundary conditions are as follows. At \( r = a \),

\[ u^{(a)}_r = u^{(l)}_r = 0, \]

\[ u^{(a)}_\theta = u^{(l)}_\theta, \]

\[ \mu^{(a)} \left( r \frac{\partial}{\partial r} \left( \frac{u^{(a)}_\theta}{r} \right) + \frac{1}{r} \frac{\partial u^{(a)}_r}{\partial \theta} \right) - \mu^{(l)} \left( r \frac{\partial}{\partial r} \left( \frac{u^{(l)}_\theta}{r} \right) + \frac{1}{r} \frac{\partial u^{(l)}_r}{\partial \theta} \right) = \frac{1}{r} \frac{\partial \gamma}{\partial \theta}, \]

(A9)

\[ p^{(a)} - 2\mu^{(a)} \frac{\partial u^{(a)}_r}{\partial r} - p^{(l)} + 2\mu^{(l)} \frac{\partial u^{(l)}_r}{\partial r} = \frac{2\gamma}{r}, \]

(A10)

\[ T^{(a)} = T^{(l)}, \]

\[ k^{(a)} \frac{\partial T^{(a)}}{\partial r} = k^{(l)} \frac{\partial T^{(l)}}{\partial r}, \]

(A12)

where \( \gamma \) is the surface tension. As \( r \to \infty \), we have

\[ u^{(l)}_r \to -V \cos \theta, \quad u^{(l)}_\theta \to V \sin \theta, \quad T^{(l)} \to T^0 + T_1 r \cos \theta, \]

(A13)

where \( V \) is the thermocapillary drift speed. If \( \gamma = \gamma (T) \), we can linearize about \( T = T^0 \) so that

\[ \gamma = \gamma^0 + \gamma_T (T - T^0), \]

(A14)

where \( \gamma^0 = \gamma (T^0) \), and \( \gamma_T := (d\gamma/dT)_{T=T^0} \) is a constant.

Nondimensionalizing with

\[ R = \frac{r}{a}, \quad U^{(j)}_R = \frac{u^{(j)}_r}{V}, \quad U^{(j)}_\theta = \frac{u^{(j)}_\theta}{V}, \quad P^{(j)} = \frac{p^{(j)}}{\mu^{(j)} V/a}, \quad \Theta^{(j)} = \frac{T^{(j)} - T_0}{a T_1}, \]

(A15)

equations (A1)-(A4) become, on dropping the tildes and using the forms given in equations (A5) and (A6) for the stress components in equations (A2) and (A3),

\[ \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 U^{(j)}_R \right) + \frac{1}{R \sin \theta} \frac{\partial}{\partial \theta} \left( \frac{U^{(j)}_\theta \sin \theta}{R} \right) = 0, \]

(A16)

\[ 0 = -\frac{\partial P^{(j)}}{\partial R} + 2 \frac{\partial}{\partial R} \left( R^2 \frac{\partial U^{(j)}_R}{\partial R} \right) + \frac{1}{R \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \left( R \frac{\partial}{\partial R} \left( \frac{U^{(j)}_\theta}{R} \right) + \frac{1}{R} \frac{\partial U^{(j)}_R}{\partial \theta} \right) \right) - 2 \frac{R}{R^2} \left\{ 2U^{(j)}_R + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( U^{(j)}_\theta \sin \theta \right) \right\}, \]

(A17)
\begin{align}
+ \frac{2}{R \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \left( \frac{1}{R} \frac{\partial U^{(j)}_\theta}{\partial \theta} + \frac{U^{(j)}_R}{R} \right) \right) \\
+ \frac{1}{R} \left\{ \frac{\partial}{\partial R} \left( \frac{U^{(j)}_\theta}{R} \right) + \frac{1}{R} \frac{\partial U^{(j)}_R}{\partial \theta} - \frac{2 \cot \theta}{R} \left( U^{(j)}_R + U^{(j)}_\theta \cot \theta \right) \right\},
\end{align}
\tag{A18}

\begin{align}
Pe^{(j)} \left( \frac{U^{(j)}_R}{R} \frac{\partial U^{(j)}(j)}{\partial R} + \frac{U^{(j)}_\theta}{R} \frac{\partial U^{(j)}(j)}{\partial \theta} \right) = & \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial \Theta^{(j)}(j)}{\partial R} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta^{(j)}(j)}{\partial \theta} \right), \\
\end{align}
\tag{A19}

where
\[ Pe^{(l)} = Pe, \quad Pe^{(g)} = \alpha Pe, \]
\tag{A20}

with \( Pe \) denoting the Péclet number and being given by
\[ Pe = \frac{Va}{\alpha l}. \]

As for the boundary conditions, we have: at \( R = 1 \),
\begin{align}
U^{(g)}_R &= 0, \quad U^{(l)}_R = 0, \\
U^{(g)}_\theta &= U^{(l)}_\theta, \\
\mu \left( \frac{\partial U^{(g)}_\theta}{\partial R} - U^{(g)}_\theta \right) - \left( \frac{\partial U^{(l)}_\theta}{\partial R} - U^{(l)}_\theta \right) &= C_1 \frac{\partial \Theta}{\partial \theta}, \\
\mu \left( P^{(g)} - 2 \frac{\partial U^{(g)}_R}{\partial R} \right) - \left( P^{(l)} - 2 \frac{\partial U^{(l)}_R}{\partial R} \right) &= 2 \left( C_0 + C_1 \Theta \right),
\end{align}
\tag{A21, A22, A23, A24}

\begin{align}
\Theta^{(g)} &= \Theta^{(l)}, \\
k \frac{\partial \Theta^{(g)}}{\partial R} &= \frac{\partial \Theta^{(l)}}{\partial R},
\end{align}
\tag{A25, A26}

where
\[ \mu = \mu^{(g)}/\mu^{(l)}, \quad k = k^{(g)}/k^{(l)}, \quad C_0 = \frac{\gamma^0}{V \mu^{(l)}}, \quad C_1 = \frac{\alpha \gamma T_1}{V \mu^{(l)}}. \]
\tag{A27}

As \( R \to \infty \), we have
\begin{align}
U^{(l)}_R &\to -\cos \theta, \quad U^{(l)}_\theta \to \sin \theta, \quad \Theta^{(l)} \to R \cos \theta.
\end{align}
\tag{A28}

Introducing streamfunctions \( \psi^{(j)} \) such that
\begin{align}
U^{(j)}_R = -\frac{1}{R^2 \sin \theta} \frac{\partial \psi^{(j)}}{\partial \theta}, \quad U^{(j)}_\theta = \frac{1}{R \sin \theta} \frac{\partial \psi^{(j)}}{\partial R},
\end{align}
\tag{A29}

it is known that these will satisfy
\begin{align}
\left( \frac{\partial^2}{\partial R^2} + \frac{\sin \theta}{R^2} \frac{\partial}{\partial \theta} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right) \right)^2 \psi^{(j)} = 0,
\end{align}
\tag{A30}
which comes algebraic manipulation of equations (A17), (A18) and (A29); the general solutions will be

$$\psi^{(j)} = \left( A^{(j)} R^4 + B^{(j)} R^2 + C^{(j)} R + \frac{D^{(j)}}{R} \right) \sin^2 \theta, \quad (A31)$$

where $A^{(j)}, B^{(j)}, C^{(j)}, D^{(j)}$ are all constants to be determined. Thus,

$$U^{(j)}_R = -\frac{2}{R^2} \left( A^{(j)} R^4 + B^{(j)} R^2 + C^{(j)} R + \frac{D^{(j)}}{R} \right) \cos \theta, \quad (A32)$$

$$U^{(j)}_\theta = \frac{1}{R} \left( 4A^{(j)} R^3 + 2B^{(j)} R + C^{(j)} - \frac{D^{(j)}}{R^2} \right) \sin \theta. \quad (A33)$$

Also, if $Pe \ll 1$, equation (A19) reduces to

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial \Theta^{(j)}}{\partial R} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Theta^{(j)}}{\partial \theta} \right) = 0; \quad (A34)$$

from our computations, we find that, for the mushy region, $3 \times 10^{-5} \leq |Pe| \leq 0.2$, indicating that this simplification is valid. The relevant solution to equation (A34) is

$$\Theta^{(j)} = \left( E^{(j)} R + \frac{F^{(j)}}{R^2} \right) \cos \theta, \quad (A35)$$

with $E^{(j)}$ and $F^{(j)}$ also constants to be determined.

First, we note that equation (A28c) requires that $E^{(l)} = 1$, whereas the fact that $\Theta^{(g)}$ is finite at $R = 0$ requires that $F^{(g)} = 0$; equations (A25) and (A26) then lead to

$$F^{(l)} = \frac{1 - k}{2 + k}, \quad E^{(g)} = \frac{3}{2 + k}. \quad (A36)$$

Note from Table 2, that $k \ll 1$, giving $F^{(l)} \approx 1/2, E^{(g)} \approx 3/2$, so that

$$\Theta^{(g)} = \frac{3}{2} R \cos \theta, \quad \Theta^{(l)} = \left( R + \frac{1}{2R^2} \right) \cos \theta. \quad (A37)$$

Next, we note that equations (A28a) and (A28b) require $A^{(l)} = 0$, $B^{(l)} = 1/2$, whereas the fact that $U^{(g)}_R$ and $U^{(g)}_\theta$ are finite at $R = 0$ requires that $C^{(g)} = 0, D^{(g)} = 0$. We will be left with four constants to be determined - $C^{(l)}, D^{(l)}, A^{(g)}, B^{(g)}$ - with four equations: (A21a), (A21b) and (A22) and (A23). Since $\mu \ll 1$, these give

$$A^{(g)} = \frac{1}{4} - \frac{C_1}{4}, \quad B^{(g)} = -\frac{1}{4} + \frac{C_1}{4}, \quad C^{(l)} = -\frac{1}{2} - \frac{C_1}{4}, \quad D^{(l)} = \frac{C_1}{4}. \quad (A38)$$

At this point, we have

$$U^{(g)}_R = -2A^{(g)}(R^2 - 1) \cos \theta, \quad U^{(g)}_\theta = 2A^{(g)}(2R^2 - 1) \sin \theta. \quad (A39)$$
\[ U_R^{(l)} = \left( 1 - \frac{(2D^{(l)} + 1)}{R} + \frac{2D^{(l)}}{R^3} \right) \cos \theta, \quad (A40) \]

\[ U_\theta^{(l)} = \left( 1 - \frac{(2D^{(l)} + 1)}{2R} - \frac{D^{(l)}}{R^3} \right) \sin \theta; \quad (A41) \]

\[ P^{(g)} = -20 \mu^{(g)} R \cos \theta + P^{(g)}_\infty, \quad P^{(l)} = \left( \frac{2D^{(l)} + 1}{R^2} \right) \cos \theta + P^{(l)}_\infty \quad (A42) \]

and so

\[ \frac{\partial U_R^{(g)}}{\partial R} = -4 \mu^{(g)} R \cos \theta, \quad \frac{\partial U_R^{(l)}}{\partial R} = -\left( \frac{2D^{(l)} + 1}{R^2} - \frac{8D^{(l)}}{R^4} \right) \cos \theta, \]

\[ \frac{\partial U_\theta^{(g)}}{\partial R} = 8 \mu^{(g)} R \sin \theta, \quad \frac{\partial U_\theta^{(l)}}{\partial R} = \left( \frac{1}{R^2} \left( \frac{1}{2} + D^{(l)} \right) + \frac{3D^{(l)}}{R^4} \right) \sin \theta. \]

We still need to determine \( C_1 \). There should be no net force parallel to the flow [31], implying that

\[ \int_0^\pi \left( \sigma_{R\theta}^{(l)} \sin 2 \theta - \sigma_{RR}^{(l)} \sin \theta \cos \theta \right) \left. \right|_{R=1} \sin \theta \, d\theta = 0. \quad (A43) \]

Now,

\[ \tau_{RR}^{(l)} = 2 \frac{\partial U_R^{(l)}}{\partial R}, \quad \tau_{R\theta}^{(l)} = R \left( \frac{U_\theta^{(l)}}{R} + \frac{1}{R} \frac{\partial U_R^{(l)}}{\partial \theta} \right), \]

so that

\[ \left. \left( \tau_{RR}^{(l)} \right) \right|_{R=1} = -2 \left( 1 - 6D^{(l)} \right) \cos \theta, \quad \left. \left( \tau_{R\theta}^{(l)} \right) \right|_{R=1} = 6D^{(l)} \sin \theta; \]

also,

\[ \left. \left( P^{(l)} \right) \right|_{R=1} = \left( 2D^{(l)} + 1 \right) \cos \theta + P^{(l)}_\infty. \]

Performing all the integrals in equation (A43), we find \( C^{(l)} = 0 \), giving \( C_1 = -2 \), and hence

\[ V = -\frac{\gamma T a T_1}{2 \mu^{(l)}}. \quad (A44) \]

It is often overlooked, but nevertheless deserves to be noted, that the solutions obtained above made no use of the normal stress condition (A24); indeed, we find that the left-hand side of (A24) is

\[ \mu \left( P^{(g)}_\infty - 9 \cos \theta \right) - \left( P^{(l)}_\infty + 8 \cos \theta \right), \]

whereas the right-hand side is

\[ 2(C_0 - 3 \cos \theta). \]
This is explained by the fact the original equations (A1)-(A13) should be formulated so that the location of the gas-liquid interface is not known, but should be determined as part of the problem; hence the bubble would, in general, not be spherical. This issue has been considered by Levan [32], and requires us to determine how unspherical might become. In our case, where $\mu \ll 1$, we require

\[-(P_{\infty}^{(l)} + 8 \cos \theta) \approx 2(C_0 - 3 \cos \theta),\]

which implies that $P_{\infty}^{(l)} = -2C_0$; thence, the bubble will be spherical if $C_0 \gg 1$, i.e. if the $\cos \theta$ terms are negligible with the leading-order terms. Thus, we see that the spherical approximation is valid provided that $|C_0| \gg 1$.

From our computations, we find that, for the mushy region, $8.3 \times 10^4 \leq |C_0| \leq 1.8 \times 10^8$, as required.

**Appendix B: solutocapillary drift**

For solutocapillary drift, the formulation is slightly different to that in Appendix A, since the sulphur concentration is only defined for the liquid, i.e. $r \geq a$; however, the governing equations for $u_r^{(l)}, u_\theta^{(l)}, p_r^{(l)}, p_\theta^{(g)}$, $u_\theta^{(g)}, p_r^{(g)}$ remain unchanged. Consequently, (A4) is replaced by

\[
\rho^{(j)} \left( u_r^{(l)} \frac{\partial c}{\partial r} + \frac{u_\theta^{(l)}}{r} \frac{\partial c}{\partial \theta} \right) = D \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial c}{\partial \theta} \right) \right\}. \tag{B1}
\]

The boundary conditions for $c$ are

\[
\frac{\partial c}{\partial r} = 0 \quad \text{at } r = a, \tag{B2}
\]

\[
c \to c_0 + c_1 r \cos \theta \quad \text{as } r \to \infty; \tag{B3}
\]

thus, (B2) replaces (A25) and (A26). The remaining boundary conditions are as before, except that here we consider $\gamma = \gamma(c)$, and linearize about $c = c^0$ so that

\[
\gamma = \gamma^0 + \gamma_c (c - c^0), \tag{B4}
\]

where $\gamma^0 = \gamma(c^0)$, and $\gamma_c := (d\gamma/dc)_{c=c^0}$ is a constant.

Nondimensionalizing with

\[
C = \frac{c - c_0}{ac_1}, \tag{B5}
\]

equation (B1) gives, for $R > 1$,

\[
Le \left( \frac{u_r^{(l)}}{R} \frac{\partial C}{\partial R} + \frac{u_\theta^{(l)}}{R} \frac{\partial C}{\partial \theta} \right) = \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial C}{\partial R} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial C}{\partial \theta} \right), \tag{B6}
\]
subject to

\[ C \to R \cos \theta \quad \text{as } R \to \infty, \quad (B7) \]
\[ \frac{\partial C}{\partial R} = 0 \quad \text{at } R = 1, \quad (B8) \]

where \( Le \) denotes the Lewis number and is given by \( Le = aV/D \). If \( Le \ll 1 \), then we arrive at

\[ C = \left( R + \frac{1}{2R^2} \right) \cos \theta \quad (B9) \]

and

\[ V = -\frac{\gamma_{cac_1}}{2\mu^{(t)}}. \quad (B10) \]

Equation (B9) looks identical to, and equation (B10) very similar to, the second equation in (A37) and equation (A44), respectively; however, this is only a coincidence that arises because \( k \ll 1 \). From our computations, we find that, for the mushy region, \( 10^{-3} \leq |Le| \leq 10 \), meaning that \( C \) and \( V \) will not be as given by (B9) and (B10), respectively, for all of the mushy region. To resolve this would require a more sophisticated approach to the governing equations, whereby the left-hand side of (B6) is not neglected. This is beyond the scope here, but see, for example, [33–36].

Appendix C: separation of time scales

The model clearly builds on the possible separation of time and length scales. Whilst the latter is feasible, we have yet to justify the former. The velocities determined in Appendices A and B are the terminal values. Instead of (A43), we have

\[ \frac{4}{3} \pi a^3 \rho^{(g)} \frac{d^2 y_b}{dt^2} = a^2 \int_0^\pi \left( \sigma^{(t)}_{r\theta} \sin^2 \theta - \sigma^{(t)}_{rr} \sin \theta \cos \theta \right)_{r=a} d\theta, \]

and the left-hand side can be neglected if

\[ \frac{a^2 \rho^{(g)} [y_b]}{[t]^2} \ll \mu^{(t)} V. \]

Here, \([y_b]\) is a characteristic length scale for the drift motion of the bubble, and \([t]\) is a characteristic time scale for this motion; we take \([y_b] \sim W, [t] \sim L/V_{\text{cast}}\), since the bubble clearly cannot move further than half-width of the casting, and it clearly cannot move through the mush for longer than the time taken for molten steel to pass from \( z = 0 \) to \( z = L \). Then, we have

\[ \frac{a^2 \rho^{(g)} W^2 V_{\text{cast}}}{L^2} \ll \mu^{(t)} V. \]

In the least favourable case, we have

\[ \mu^{(t)} V = \frac{1}{2} a \min (\gamma_{cT}, \gamma_{dT}), \]
and thus
\[
\frac{2\alpha \rho (g) W V^2_{\text{cast}}}{L^2} \ll \min (\gamma_c c_1, \gamma_T T_1).
\]
This inequality will be satisfied, since the left-hand side is around \(10^{-14}\) kg \(\text{m}^{-1}\text{s}^{-2}\), whereas
\[
24 \text{ kg m}^{-1}\text{s}^{-2} \ll \min (\gamma_c c_1, \gamma_T T_1) \ll 1.6 \times 10^6 \text{ kg m}^{-1}\text{s}^{-2}.
\]

**Appendix D: material balance**

To calculate the size of the particles TiN and Al\(_2\)O\(_3\) based on material balance:
\[
N \times \frac{4}{3} \pi r^3 = (x_{ss} - x_{eq}) \times V_M \tag{D1}
\]
where \(N\) is the number of particles, \(r\) cm is particle radius, \(x_{ss}, x_{eq}\) mol is supersaturated and equilibrium concentration and \(V_M\) cm\(^3\)/mol is molar volume.

Supersaturated and equilibrium concentrations has been calculated as weight percentage. To change the supersaturated value to number of moles the following procedure is taken:

According to random walk in one dimension, melt in between dendrite arms is uniform in concentration at constant solid fractions. Al\(_2\)O\(_3\) and TiN precipitates at 92% solid. Thickness of the liquid at this solid fraction ranges between 5 \(\times\) \(10^{-3}\) cm to 5 \(\times\) \(10^{-4}\) cm based on DAS which changes between 90 \(\mu\)m to 600 \(\mu\)m. Number of moles at supersaturated and equilibrium concentrations can only be calculated at a certain defined volume. Hence a sphere with the thickness of the liquid is considered since random walk is instantaneous at constant solid fractions. The volume fraction of Fe, Cr and Ni in the sphere is calculated according to

\[
\text{Fe}_{\text{volume fraction}} = \frac{\text{wt. % Fe}}{\rho_{Fe}} \frac{\rho_{Fe}}{\rho_{Fe}}\tag{D2}
\]

Number of moles in the sphere is

\[
\text{Total number of moles} = \frac{V_{\text{sphere}}}{V_{M(Fe)} + V_{M(Ni)} + V_{M(Cr)}} \tag{D3}
\]

Concentration of sphere is assumed to be composed of Fe, Ni and Cr since other alloying elements exist in dilute amounts. Mole fraction Al, O, Ti and N is calculates as

\[
\text{O}_{\text{mole fraction}} = \frac{2\text{SSwt. % O}}{\rho_{Fe} \times V_{M(Fe)}} + \frac{\text{wt. % Ni}}{\rho_{Ni} \times V_{M(Ni)}} + \frac{\text{wt. % Cr}}{\rho_{Cr} \times V_{M(Cr)}} \tag{D4}
\]
Table 3: Data used for material balance calculations

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<th>wt.%</th>
<th>$\rho$ (gr/cm$^3$)</th>
<th>$V_M$ (cm$^3$/mol)</th>
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<th>EQ wt.%</th>
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<tbody>
<tr>
<td>Oxygen</td>
<td>-</td>
<td>0.001429</td>
<td>11200</td>
<td>0.026</td>
<td>-</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-</td>
<td>0.0012</td>
<td>11200</td>
<td>0.019</td>
<td>-</td>
</tr>
<tr>
<td>Aluminium</td>
<td>-</td>
<td>2.7</td>
<td>10</td>
<td>1.26</td>
<td>1.22</td>
</tr>
<tr>
<td>Titanium</td>
<td>-</td>
<td>4.5</td>
<td>10.6</td>
<td>2.65</td>
<td>2.59</td>
</tr>
<tr>
<td>Iron</td>
<td>50</td>
<td>7.8</td>
<td>7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nickel</td>
<td>30</td>
<td>8.9</td>
<td>6.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chromium</td>
<td>20</td>
<td>7.19</td>
<td>7.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>-</td>
<td>-</td>
<td>26.28</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiN</td>
<td>-</td>
<td>-</td>
<td>11.808</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

where SSwt.%O is supersaturated concentration of oxygen, $\rho_O$ is oxygen density (gr/cm$^3$), $V_O$ is oxygen molar volume (cm$^3$/mol). Number of moles for Al, O, Ti and N is calculated as

$$Oxygen \; moles = Mole \; fraction \; Oxygen \times Total \; number \; of \; moles \quad (D5)$$

Formation of Al$_2$O$_3$ is controlled by concentration of aluminium since fraction of oxygen over aluminium in the sphere is 1.09 while molar fraction of oxygen to aluminium in Al$_2$O$_3$ is 1.5. Formation of TiN is controlled by concentration of titanium since fraction of nitrogen to titanium in TiN is one while 1.2 in the sphere. The number of moles from Eq. D5 for aluminium and titanium is used in Eq. D1 as $x_{ss} - x_{eq}$. The radius of one particle of TiN which forms at 92% solid where DAS is 90 $\mu$m is $r = 2.8 \times 10^{-5}$ cm and where DAS is 600 $\mu$m is $r = 1.8 \times 10^{-4}$ cm. The radius of one particle of Al$_2$O$_3$ which forms at 92% solid where DAS is 90 $\mu$m is $r = 3.4 \times 10^{-5}$ cm and where DAS is 600 $\mu$m is $r = 2.2 \times 10^{-4}$ cm.

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