Modelling the evolution of MnS inclusions and macrosegregation during solidification using a three-phase model

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Abstract. Manganese sulphide (MnS) is one of the major non-metallic inclusion in steel which greatly impacts the properties of steels. Previous models have been developed to simulate the dynamics of MnS during solidification without considering the effects of macrosegregation formation. A comprehensive model incorporating the formation kinetics of MnS with a ternary macrosegregation model is presented to investigate the evolution of MnS inclusions and its effects on C and Mn macrosegregation. Classical nucleation theory and a diffusion-controlled growth model are applied to describe the evolution of MnS, which is fully coupled with a two-phase ternary alloy solidification model. The model considers the growth of columnar dendrite trunks, thermosolutal convection of the melt, solute transport by convection and inclusion floatation. It has been applied to a benchmark case, and reasonable results are obtained with a good agreement with the reported experimental ones. The effects of MnS behaviours on the segregation of different solute elements are discussed.

1. Introduction

Macrosegregation and non-metallic inclusions in casting ingot have been the focus of metallurgists for nearly half a century, since they cannot be alleviated during the down-stream hot processing and may severely limit the application of ingots. Non-metallic inclusion like MnS, which is a ubiquitous inclusion formed in almost every steel grade and is detrimental to the properties of steel by acting as a potential starting point for crack formation or corrosion [1]. Both numerical [2, 3] and experimental [4] researches have been carried out to study the formation mechanism of macrosegregation and the precipitation, cohesion and remove of inclusions during solidification.

Solute heterogeneity occurs as soon as solidification starts when partition coefficient brings the difference between both sides of liquid/solid interface [5]. Consequently, when solidification starts, the solute rejected from the solid phase will accumulate in the solidification front, and the relative motion of solid and melt will turn the microscope solute segregation into macroscale inhomogeneity, i.e. macrosegregation. Several inner mechanisms are believed to contribute to this pivotal relative motion between phases, namely the thermal-solutal convection [6], crystal sedimentation [7], shrinkage-induced flow [8, 9] and motions of gas bubbles or inclusions [10] that develop during solidification. Modern computational ability makes it possible to directly observe and analyse the above mechanisms individually to guide experimental study. The multi-phase macrosegregation models have been greatly improved during the last decades since the first mushy zone model was developed by Fujii et al. [11]. Wang et al. [12] established a model that considered two principal solidification characteristics namely solid-phase transport and melting in the 1990s. More solidification phenomena such as equiaxed motion [13], gas-induced flow [14] and dendrite morphology [15] were coupled into the sophisticated model.
For macrosegregation modelling, nevertheless, only a few works [16] payed attention on the
inclusions, though the oxide-based inclusions have been the focus of Cao et al. [17], who found that
more inclusions exist in or at the adjacent onset site of long-fastigiate A-segregation, one of the most
typical macrosegregation in large-scale ingot. Their simulation results also showed that the inclusions
which nucleate before solidification would disturb the solidification front and alter the local melt flow
then trigger the macrosegregation. The non-metallic inclusion generated by deoxidation reactions during
the solidification, such as MnS, has less been considered in the macrosegregation model, although
thermodynamic method [18] was widely employed to calculate the composition and evolution of such
inclusions. In addition, classic precipitation and growth theories [19] have also been studied and verified
to calculate the nucleation condition. It is quite important to establish a model that consider the
interaction between the evolution of MnS inclusion and the formation of macrosegregation.

In this study, a comprehensive model incorporating the nucleation and growth of MnS inclusion with
a ternary alloy (Fe–0.45 wt%C–1.06 wt%Mn) macrosegregation model is presented to investigate the
evolution of MnS inclusions and its effects on C and Mn macrosegregation in a benchmark case.

2. Model description and configuration

The calculated domain is a 2D 50×50 mm2 grid, half of which is shown in figure 1. The other half of
figure 1 indicates the melt (l) solidifies in the form of columnar (c) solidification and the MnS (p)
inclusions (orange spheres) participate between the dendrites considered in this model. The sketch also
gives the initial and boundary conditions in such solidification process. The whole
domain is fill with
liquid at the beginning.

Figure1. A schematic of columnar solidification model with the formation of MnS inclusion in a 2D
(50×50 mm2) domain. Thermal boundary conditions are also shown in the left half.

2.1. Eulerian volume average macrosegregation model

To elucidate the effect of inclusions on the macrosegregation of Mn and C elements, a Eulerian volume
averaged ternary alloy model is established, which is basically extended from the ternary approach
established by Wu [20]. More details about the model can be found in the previous literatures [21, 22].
A brief outline of the model is given below:

- Columnar dendrites are approximated by growing cylinders starting from the mould wall
towards the casting centre by the heat transfer and each cell in the left half of figure 1 contain
uniform volume fraction of columnar. The solidification proceeds by means of the mass transfer
from the original liquid to this columnar.
- Growth of the columnar trunk is governed by diffusion with the neglection of back diffusion.
- Enthalpy equations for all phases are solved. Due to the fact that thermal diffusion is faster than
solute diffusion, we assume that only one temperature (T) represents each volume element.
Therefore, a large inter-phase volume heat transfer coefficient between the phases is applied to
balance the temperatures among the phases.
The permeability in the columnar mush zone is modelled according to Blake-Kozeny [23]. The densities of the solid and liquid are considered constant and equal. The Boussinesq approach is employed to model thermo-solutal convection. Feeding flow due to density change in the mushy zone can is not considered.

2.2. Nucleation and evolution of MnS inclusion

MnS is normally generated from the enrichment of Mn and S in the residual liquid during solidification. Thus, the abovementioned macrosegregation model alone is beyond qualified to simulate the MnS formation process since the enriched solute in the melt can be withdrawn every time-step during the calculation, in other words, the inclusion-combined model should be fully coupled. To simplify the calculations, the physical assumptions of the model are as follows:

- Only MnS formed in the residual liquid is considered.
- MnS particles are independent with each other and the collision is neglected.
- The morphology of the particles is spherical.
- Diffusion-controlled growth is used and the equilibrium content of Mn on the surface of MnS can be taken as zero since the S concentration in the surface is high [24].

It is believed that MnS is thermodynamically stable when the real concentration product, $K$, is larger than the solubility product, $K_{eq}$, with the real concentration and solubility products be calculated by $K=c_{c}\cdot c_{Mn}$ and $\log K_{eq} = -8750/T + 4.63$, respectively. Classical nucleation theory is applied to the model once the critical thermodynamic condition is achieved. For simplicity, homogeneous nucleation is considered in the current case. The growth of the spherical particle is assumed to be controlled by diffusion of the solutes in liquid steel [24, 25].

3. Simulation results and discussions

3.1. The evolution of C and Mn macrosegregation

Such columnar solidification model has been verified in previous published work, and the macrosegregation formation mechanisms have been studied in detail [21]. The focus of the current work is on the interaction between the macrosegregation and the formation of MnS. In addition, the calculated results of MnS volume fraction in the steel matrix is compared with published data which is discussed in the following parts. In this calculated case, the melt takes around 100 s of physical time for the square domain to fully solidify. The segregation of Mn and C is evaluated by segregation index ($SI=(c_{mix}-c_0)/c_0$). $c_{mix}$ is the local solute concentration after solidification, and $c_0$ is the initial solute concentration. The solidification sequence and the evolution of C and Mn SI are shown in figure 2, which are the distribution of such properties in each volume-averaged cell in the mesh shown in figure 1. The melt velocities are also indicated in the C macrosegregation contours (upper part). The black isoline of $f_t=0.9$ indicates the solidification front. Due to the combination of the solute and thermal driving force, a counterclockwise melt flow forms in the bulk melt. With this melt flow, solute depleted zones, i.e. negative macrosegregation zone, has been formed in the upper left region of the ingot in the early stage of solidification (i.e. at 10 s). The solute originally present in the negative segregation region is brought to the centre of the domain by the counterclockwise flow, thereby forming a solute enriched zone here. Both C and Mn components have similar shape of the solute depleted and enriched zones. As for C component, the negative segregation zone remains almost unchanged as the solidification progressed, but the solute enrichment degree in the solute enriched zone gradually increases, and eventually a severe positive segregation zone is formed. For the Mn component, the area of the negative segregation zone gradually increases with the progress of solidification, which results from the consumption of Mn due to the formation of MnS in the later solidification process.
3.2. The effect of MnS formation on macrosegregation

The macrosegregation patterns of C and Mn without and with the combination of MnS formation are shown in figure 3(a) and (b). By considering the inclusion formation, the range of segregation index of C is slightly enlarged from [-0.93%~+1.35%] to [-1.12%~+1.45%]. The area of negative macrosegregation zone is reduced while the positive macrosegregation zone is obviously enlarged.

The reason for these changes is that the melt flow faster, as shown in figure 3(c), due to the formation of MnS inclusion. Under such flow change, the same changes occur in the Mn component, as shown in figure 3(b) with reduced negative segregation area and increased positive segregation area. However,
the consumption of Mn during the nucleation and growth of MnS is the dominant influence on Mn positive macrosegregation. As shown in figure 3(b), the positive macrosegregation index is significantly reduced from 0.51% to 0.44%.

3.3. The effect of S composition on MnS formation

It is believed that the S composition also plays an important role in the evolution of MnS. The distribution and volume fraction of MnS with two different S composition are displayed in figure 4. It should be noted that the image in figure 4 and the embedded image in figure 5 are both based on the 50×50 mm² calculated domain shown in figure 1. The contour in figure 4 also shows the volume fraction of MnS in each cell, so the results give the preferential location for such inclusion to precipitate under such solidification condition. The distribution of inclusion shows a central symmetry characteristic, because the cooling conditions at all boundaries are uniform as 300 W·m⁻²·K⁻¹. Both contours reveal that the MnS inclusions mainly located at a quarter of the height of the benchmark grid. With the varies of S composition from 0.0028 wt% to 0.3 wt%, the maximum volume fraction of MnS is at a range of 0.0013%–0.0022%. The CT experiment of inclusions in large scale ingot from reference [17] is used to validate the predicted volume fraction. The results from experiment show one or two order of magnitude higher than the predicted results from the perspective of volume fraction, because the experiment inspected all kinds of inclusion including the more common alumina. The consistency between simulation and experiment indicates that it is reasonable to estimate the effect of the formation of MnS on the macrosegregation as discussed above.

![Figure 4](image)

**Figure 4.** Predicted distribution and final volume fraction of MnS with initial S composition of (a) 0.028 wt% and (b) 0.3 wt%.

Another two cases with different S composition are conducted to investigate its dependency with the thermodynamic condition of MnS formation. The solidification process is barely affected by the S composition, thus at t = 70 s, for all the cases, around 86% of the melt has solidified, and the temperature and f line along the A-A line(cross central line on left half part of the benchmark) are uniform, as depicted in figure 5 with red and black lines, respectively. The other four colourful lines represent the mass transfer rate (Mlp) from liquid to MnS, which denote the one-to-one correspondence between the MnS formation start point and critical condition in each case. By increasing the S composition, both of the critical liquid fraction and the temperature to precipitate inclusion MnS are magnified.
Figure 5. Effect of S composition on the formation condition (liquid volume fraction and temperature) of MnS during solidification. The embedded image is the distribution contour of mass transfer rate form liquid to MnS phase within the square domain when $t = 70$ s.

4. Conclusion
A comprehensive model combining nucleation and growth of MnS inclusion with a ternary alloy (Fe-0.45wt%C-1.06wt%Mn) columnar solidification model has been established and applied to a benchmark case study. Reasonable results were obtained with a qualitative agreement with the reported experimental results which demonstrates that the current inclusion-combined solidification model has the ability to predict the formation of MnS inclusion and macrosegregation at a certain given alloy composition. It was revealed that the formation of MnS will increase melt flow which finally alter the distribution of both C and Mn macrosegregation. However, the inclusion-correlated solute Mn is mainly affected by the consumption itself.

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