Cross-Scale Modeling of MnS Precipitation for Steel Solidification

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Abstract: One of the advantages of numerical simulations over traditional experimental methodologies is that they can synchronize nucleation, growth and coarsening during solidification from the point of view of microstructural analysis. However, the computational cost and accuracy are bottlenecks restricting simulation approaches. Here, two cellular automaton (CA) modules with different grid dimensions are coupled to form a cross-scale model in order to simulate MnS precipitation, accompanied by the matrix growth of dendrites during the solidification of a Fe-C-Mn-S steel, where the matrix growth is computed through the CA module with large grids based on the solute conservation and the undercooling of thermal, constitutional, and curvature, and increments of solid fraction of MnS are solved in combination with the transient thermodynamic equilibrium on the locally re-meshed grids once the MnS precipitation is formed. We utilize the cross-scale mode to illustrate MnS evolution in a solidifying matrix and explain the reason why it coexists in three shapes. Further, we study the effects of the content of elements Mn and S on MnS precipitation based on two continuously cast steel objects, with the factor of concentration product fixed as a constant. A re-precipitation of MnS is observed during the solidification of a system with a high content of Mn and low content of S. Simultaneous computation using cross-scale modeling can effectively save on computational resources, and the simulation results agree well with the experimental cases, which confirm its reliable accuracy.

Keywords: MnS precipitation; cross-scale modeling; cellular automaton; steel solidification

1. Introduction

Solute enrichment, caused by the segregation of the elements Mn and S, occurring at the solid-liquid interface, leads to a reduction of Gibbs free energy, which is bound to induce MnS precipitation in solidifying steel. MnS precipitation plays an entirely different role in the performance of steel. It is seriously detrimental to intergranular cracking due to the precipitation reaction within solidifying metal acting as a strong sink of free sulfur segregation to the grain boundaries [1], thus decreasing corrosion resistance by accelerating hydrogen absorption into the matrix [2] and weakening the hot ductility because boundary sliding is enhanced at austenite grains [3]. The lower modulus and hardness of MnS inclusions compared to those of a matrix give rise to a drop in the fatigue strength of steel [4], while the machinability is amended simultaneously [5]. MnS can also refine the matrix grains by suppressing austenite growth with the pinning effect of MnS-rich precipitates [6] and facilitate acicular ferrite nucleation in the coarse-grained zone so as to promote fractions of the high-toughness phase [7,8]. Many works have been conducted from a variety of perspectives, such as thermodynamics, kinetics, solute segregation and nucleation, in order to determine MnS precipitation to better control its impact on steel performance. The formation and evolution of precipitation, as well as the morphology of MnS and the matrix on which it is
adhered, have been discussed by considering the cooling rate, dendrite strain and alloy composition with the experimental methods [9–12]. In these studies, however, it was difficult to synchronize nucleation, growth and coarsening of MnS precipitation because they could only track back based on metallographic characterization and raticination. Especially, the thermal and solutal transfers, as well as the solid–liquid transformation, were too complex to be observed.

Numerical simulation is an optional approach to explore microstructural solidification due to its advantages of flexibility, adaptability, and simplicity. Some effective models have been proposed to depict precipitation evolution for various inclusions accompanied by thermal-solutal diffusion and interaction with a solidifying matrix. Choudhary and Ghosh [13] developed a computational procedure involving segregation equations and thermodynamic equilibrium calculations using FactSage to predict inclusion compositions in different solid fractions during the cooling and solidification of steel. Xu et al. [14] used an efficient computational model to determine the equilibrium precipitations of oxides, sulfides, nitrides and carbides based on satisfying the solubility limits and quantified compositions, as well as the amounts of stable precipitates in ferrite and austenite phases at any temperature. You et al. [15] presented a thermodynamic model to compute inclusion formations for the case of medium carbon steels alloyed with Ti and Al by combining them with the ChemSage datafile. Imagumbai and Kajioka [16] estimated a dendrite radius of Type II MnS inclusions by the marginal stability and perturbations under a small undercooling rather than the diffusion growth of pure inclusions after nucleation and offered confidence in theoretically evaluating the tip radius of inclusions, in spite of a rough assessment being applied to the figure of the physical properties. These models prioritized solving the composition and amount of inclusions and ignoring a detailed awareness of morphology and distribution, thus enabling the phase field method (PFM) to be introduced to trace microstructures, solutes percentages, and precipitated phases. Wheeler, Boettinger, and McFadden [17] made a WBM-PFM model for the microstructure evolution of binary alloy solidification. Kim et al. [18] changed the WBM-PFM model to have a different definition of free energy density for the interfacial region and used it for one-dimensional steady state alloy solidification. Amirouche and Plapp [19] employed a multiphase field model to probe discontinuous precipitation reactions using the consideration of surface diffusion along grain boundaries and interfaces, as well as volume diffusion. Lu et al. [20] simulated pre-precipitation in a Ni-Al-V alloy through a microscopic phase-field dynamic model. PFM requires tremendous computational resources to deal with a large-scale solute segregation. Another powerful method is cellular automaton (CA) for the simulation of the micro-evolution of solidification with phase transformations. Rapz and Gandin [21] used a CA model to determine the dendritic grain structure by combining it with finite element (FE) analysis for temperature, and a control for growth velocity, using heat transfer and solute conservation. Sebastian et al. [22] demonstrated the dendritic growth of a multicomponent ferroalloy using a modified CA method, by coupling it with virtual front tracking (VFT) for capturing the interface cell. Zhu et al. [23] determined the driving force for the growth of both graphite and austenite phases using the local solutal equilibrium and utilized a two-dimensional CA model to show the micro-evolution of divorced eutectic solidification of spheroidal graphite iron. Chen et al. [24] further raised the computational accuracy of a three-dimensional CA model by bridging with databases of thermodynamic, kinetic and equilibrium phase diagrams. Dong and Lee [25] simulated columnar-to-equiaxed transition (CET) in directional solidification by importing the thermal gradient and growth rate into a CA model, and they suggested that solute interaction among secondary and tertiary arms was strong while the interaction at columnar tips was weak. Wang et al. [26] utilized the CA method to show that the initial seed density has a direct effect on the initial growth stage of columnar dendrites during directional solidification of a binary alloy, but little effect was found on the primary dendrite arm spacing and tip undercooling after dendrite growth reached a stable state. The CA method worked out the dendritic morphology, solutal concentration, and thermal diffusion well, but was not accurate enough to represent MnS precipitation during alloy solidification. This is because the scale of sizes for a solidifying matrix and precipitated MnS are inconsistent, but their
growth shares a common thermal–solutal environment, in which the liquid phase is transformed into the matrix and MnS simultaneously and the two transformations interact with each other. Hence, a model that covers the entire evolution with precipitation and growth of solidification in the same computational domain is needed.

Our study achieved the cross-scale simultaneous computation for solidification of Fe-C-Mn-S steel by applying two CA modules with different grid dimensions to a solidifying matrix and a precipitated MnS, respectively. One CA module with large grids was used to compute the matrix growth of dendrites by acquiring the growth velocity, based on the solute conservation, and the undercooling of thermal, constitutional, and curvature, where the thermal–solutal diffusion in grids was determined using finite difference method. Then, local domains were re-meshed immediately to a mesh of a finer size once MnS was found, and the thermal-solutal diffusion of the large grids was assigned to re-meshed grids using linear interpolation to present MnS precipitation using another CA module with small grids where the increment of solid fraction of MnS was solved by combining it with the transient thermodynamic equilibrium. Here, two CA modules with different grid dimensions were coupled to be a cross-scale model to simulate the evolution and morphology of MnS precipitation, accompanied by the matrix growth of dendrites. Cross-scale modeling broke through the scale gap between the matrix and the precipitates and saved on computational costs. Its reliability was confirmed via a comparison with the matrix growth from a modified Lipton-Glicksman-Kurz (LGK) model, and experimental analysis for MnS inclusions, respectively, because the LGK dendritic tip analytical model can accurately solve the growth characteristics of dendritic tips.

2. Model and Algorithm

2.1. Heat and Mass Transfer

Thermal-solutal diffusion, shared by solidifying matrix and precipitated MnS, was formulated using Equations (1)–(3) for each grid cell in the computational domain. Equation (1) is the uniform governing formula for heat transfer in liquid and solid phases. However, diffusivity of solutes in different phases needed to be distinguished because mass transfer in the solid was an order of magnitude less than that of the liquid. Equation (2) is the governing formula for solutal diffusion in the liquid phase in considering interactions between solutes. Equation (3) is for the solid phase of neglecting interaction.

\[
\rho c_p \frac{\delta T}{\delta t} = \lambda \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + \rho L \frac{\partial f_S}{\partial t} + q_w
\]

\[
\frac{\partial c_{L,j}}{\partial t} = \nabla \left( \sum_{j=1}^{n-1} D_{L,ij} \nabla c_{L,i} \right) + \left( c_{L,j} - c_{S,j} \right) \frac{\partial f_S}{\partial t}
\]

\[
\frac{\partial c_{S,j}}{\partial t} = \nabla \left( D_{S,j} \nabla c_{S,i} \right) + \left( c_{S,j} - c_{L,j} \right) \frac{\partial f_S}{\partial t}
\]

where \( \rho, c_p \) and \( f_S \) are density (kg \( \cdot \) m\(^{-3} \)), specific heat (J \( \cdot \) kg\(^{-1} \) \( \cdot \) K\(^{-1} \)) and the solid fraction of matrix, \( \lambda \) was thermal diffusivity (kW \( \cdot \) m\(^{-1} \) \( \cdot \) K\(^{-1} \)), \( L \) is latent heat (J \( \cdot \) kg\(^{-1} \)), \( q_w \) is heat flux on heat dissipation wall (W \( \cdot \) m\(^{-2} \)), \( c_{L,i} \) and \( c_{S,i} \) were concentration of solute element \( i \) (1, 2, \ldots, \( n-1 \)) in the liquid and solid phases (wt. %), element \( n \) denotes solvent, \( D_{S,j} \) is diffusivity of element \( i \) in solid phase (m\(^{-2} \) \( \cdot \) s\(^{-1} \)), and \( D_{L,ij} \) is the Darken diffusivity of the matrix in the liquid phase, expressed as [27,28]:

\[
D_{L,ij} = D_{L,i}^\prime - D_{L,j}^\prime
\]

\[
D_{L,ij}^\prime = \sum_{k=1}^{n} \left( \delta_{ki} - x_i \right) x_k M_k \frac{\partial \mu_k}{\partial x_j}
\]
where \( a_k, x_k \) and \( \mu_k \) are activity, mole fraction and chemical potential (J·mol\(^{-1}\)) of element \( k \) (1, 2, \ldots, \( n \)), \( \delta_{ki} \) is the Kronecker delta (\( \delta_{ki} = 1 \) if \( i = k \), otherwise \( \delta_{ki} = 0 \)), \( R \) is the gas constant (J·K\(^{-1}\)·mol\(^{-1}\)), \( M_k \) is the atomic mobility (J·m\(^2\)·mol\(^{-1}\)·s\(^{-1}\)) determined using the Einstein relation and \( D_k^* = RTM_k \). \( D_k^* \) is the diffusivity of traced element \( k \) in the liquid phase (m\(^2\)·s\(^{-1}\)).

### 2.2. Matrix Growth of Dendrites

The growth velocity of dendrites at solid-liquid interface \( I \) was acquired by solving the simultaneous equations of solute conservation for elements C, Mn, and S, which follow the law of solute partition under a local thermodynamic equilibrium.

\[
v_n(c_{Li} - c_{Si}) = [-\sum_{j=1}^{n-1} D_{Li,j} \nabla c_{Li,j} |I| + D_{Si,j} \nabla c_{Si,j} |I|] \cdot \vec{n}
\]  

(7)

where \( v_n \) is growth velocity (m·s\(^{-1}\)), \( c_{Li} \) and \( c_{Si} \) are equilibrium concentrations (wt. \%) of element \( i \) in solid-liquid interface \( I \), \( c_{Si}^* = k_i c_{Li} \), \( k_i \) is partition coefficient, and \( \vec{n} \) denotes the growth orientation of a normal vector, from solid to liquid:

\[
\vec{n} = -\frac{\frac{\partial f_S}{\partial y}}{\sqrt{\left(\frac{\partial f_S}{\partial x}\right)^2 + \left(\frac{\partial f_S}{\partial y}\right)^2}}
\]

(8)

The increment of the solid fraction for all grid cells at the solid-liquid interface was expressed as:

\[
\Delta f_S = \frac{v_n \Delta t}{L_{\Phi}}
\]

(9)

\[
L_{\Phi} = \frac{\Delta l}{\max(|\sin \theta|, |\cos \theta|)}
\]

(10)

where \( \theta \) is the angle (rad) between the growth orientation and \( x \) axis, \( \Delta l \) is the grid dimension (m), \( L_{\Phi} \) is the length of the line segment (m) along the normal direction \( \vec{n} \) going through the cell center in Figure 1.
Here, the matrix growth of the dendrites at the solid–liquid interface was driven by the undercooling of thermal, constitutional, and curvature:

\[ \Delta T = (T_l - T_{cell}) + \Delta T_c + \Delta T_r \]  
(11)

\[ \Delta T_c = \sum_{i=1}^{n-1} m_L i (c_{L,i} - c_{L,io}) \]  
(12)

where \( T_l \) is the liquidus temperature (K), \( T_{cell} \) is the temperature of the liquid cell (K), \( T_l - T_{cell} \) is the thermal undercooling, \( \Delta T_c \) is the constitutional undercooling (K), \( c_{L,io} \) and \( m_L \),\( i \) are the initial concentration (wt. %) and liquidus line slope (K wt. %) of element \( i \), and \( \Delta T_r \) is the curvature undercooling (K) expressed as [22,26]:

\[ \Delta T_r = \Gamma K_{ave} f(\theta, \Phi) \]  
(13)

\[ K_{ave} = \frac{(N + 1) - 2 (f_S + \sum_{i=1}^{N} f_{S,i})}{\Delta I(N + 1)} \]  
(14)

\[ f(\theta, \Phi) = 1 - 15 \epsilon \cos(4(\theta - \Phi)) \]  
(15)

where \( \Gamma \) is the Gibbs-Thomson coefficient (m-K), \( K_{ave} \) is the average curvature, \( f(\theta, \Phi) \) is the anisotropy of surface tension, \( \epsilon \) is the parameter for anisotropy of surface tension, \( \Phi \) is the angle (rad) of preferential growth direction with respect to the x axis, \( N = 8 \) is the number of neighbor cells used, and \( f_{S,i} \) is the solid fraction of neighbor cells.

2.3. MnS Precipitation

The formation reaction of MnS in Fe-C-Mn-S Steel is expressed as:

\[ [\text{Mn}] + [\text{S}] = (\text{MnS}) \]  
(16)

\[ \Delta G = \Delta G^0 + RT \ln \frac{a_{\text{MnS}}}{a_{[\text{Mn}]}a_{[\text{S}]}} \]  
(17)

\[ \Delta G^0 = RT \ln K \]  
(18)

\[ \log K = \frac{8817}{T} - 5.16 \]  
(19)

where \( K \) is the equilibrium constant of the reaction, \( a_{\text{MnS}} = 1 \) is the activity for pure MnS, \( a_{[\text{Mn}]} \) and \( a_{[\text{S}]} \) are the Henry activities with respect to 1 mass % standard state and were determined, as follows, using Mn as an example:

\[ a_{[\text{Mn}]} = [\%\text{Mn}] f_{[\text{Mn}]} \]  
(20)

\[ \log f_{[\text{Mn}]} = \sum_{i=1}^{n-1} e_{Mn,i}[\%i] \]  
(21)

where \([\%i]\) is the concentration (wt. %) of element \( i \), \( f_{[\text{Mn}]} \) is the activity coefficient of Mn with respect to 1 mass % standard state, \( e_{Mn,i} \) is the interaction coefficient of element \( i \) to Mn and were obtained through a thermodynamic database. The thermodynamic condition for the precipitation reaction needs to be satisfied:

\[ f_{[\text{S}]}f_{[\text{Mn}]} [\%\text{Mn}] [\%\text{S}] > E_{\text{MnS}} \]  
(22)

where \( f_{[\text{S}]} \) is activity coefficient of S with respect to 1 mass % standard state, \( E_{\text{MnS}} = a_{[\text{Mn}]} a_{[\text{S}]} \) is the solubility product of MnS, \( a_{[\text{Mn}]} \) and \( a_{[\text{S}]} \) are the equilibrium activities of Mn and S. Further, the influence of kinetic on MnS nucleation was reflected with the nucleation rate [29,30]:
\[ I_v = A \exp \left( \frac{-\Delta G_n}{k_0 T} \right) = A \exp \left( \frac{16\pi \sigma_{MnS} V_m^2}{3k_0 T \Delta G^2} \right) \]  

where \( I_v \) is the nucleation rate, \( A = 10^{33} \text{ m}^{-3}\text{·s}^{-1} \) is the frequency factor, \( \Delta G_n \) is the activation energy (J·mol\(^{-1}\)), \( V_m \) is the molar volume of MnS (L·mol\(^{-1}\)), \( \sigma_{MnS} \) is the interfacial energy (N·m\(^{-1}\)) between MnS and matrix, and \( k_0 \) is the Boltzmann constant (J·K\(^{-1}\)). The kinetic condition for MnS nucleation in matrix was defined as nucleation rate \( I_v \) and was larger than a random number between 0 and 1.

Since the size of the precipitated MnS was too small to present its morphology, if only the meshed grids for solidifying the matrix were employed during the simulation, we re-meshed local domains into \( 10 \times 10 \) liquid precipitation cells (PCs) once thermodynamic and kinetic conditions were achieved and randomly allocated MnS seeds into one PC of every meshed matrix grid to become a new interface cell of MnS. Here, chemistry equilibrium required for the growth of MnS could be attained instantaneously due to the high temperature, expressed as:

\[ f_{[S]/[Mn]}([\text{Mn}] - \Delta x) ([\text{S}] - \Delta x \frac{H_S}{H_{\text{Mn}}}) = E_{\text{MnS}} \]  

\[ \Delta f_{S,MnS} = \frac{H_{MnS\rho_{Fe}}}{100H_{Fe}\rho_{MnS}} \Delta x \]  

where \( H_{\text{Mn}} \) and \( H_{\text{S}} \) are the relative atomic mass of Mn and S, \( H_{\text{MnS}} \) is the relative molecular mass of MnS, \( \Delta x \) is the reaction amount of Mn (wt. %), \( \Delta f_{S,MnS} \) is the increment of solid fraction of MnS, \( \rho_{\text{Fe}} \) and \( \rho_{\text{MnS}} \) are the densities of Fe and MnS (kg·m\(^{-3}\)). Temperature, \([\text{Mn}]\) and \([\text{S}]\) of PCs can be computed via linear interpolation using corresponding values of neighbor matrix grids in the liquid phase, as shown in Figure 2a,b. The solid fractions of PCs increased gradually to 1, making them a complete solid cell, and then their surrounding PCs were renewed as interface cells of MnS to repeat MnS evolution, accompanied by matrix growth until thermodynamic equilibrium was restored.

![Figure 2](image-url)  

**Figure 2.** Grid meshing illustration for CA (cellular automaton) model: (a) meshed grids for matrix growth and (b) re-meshed PCs (precipitation cells) for MnS precipitation.

3. Results and Discussion

3.1. Model Verification

A CA model was applied to undercooled molten steel, with components of Fe-0.6% C-1.0% Mn-0.3% S in an adiabatic domain of \( 0.3 \times 0.3 \) mm\(^2\), in order to compute the matrix growth of equiaxed dendrites with an initial temperature 1800 K. The computational domain was meshed into \( 300 \times 300 \) grids and a dendrite nucleus was placed in the centers. Computational data used in the...
present study are listed in Tables A1 and A2 (Appendix A). Figure 3 showed solutal concentrations of trace elements C, Mn and S, and the morphology of growing dendrites. The diffusivities of the solute elements conformed to the relationship $D_C^* > D_S^* > D_{Mn}^*$, resulting in a rapid rejection of element C from dendrites into the liquid phase and the formation of a large diffusion zone. The zone areas of elements S and Mn declined in turn. Solute segregation led to an enrichment of elements at the frontier of dendrites, thus forming a radical concentration gradient centered on the dendrite nucleus due to concentration being superior to the liquid phase. The tips of the dendrites grew preferentially compared to their arms because of the axial and radial diffusion of solute elements, rather than only the radial for the arm, causing a simultaneous enhancement in concentration gradient and growth velocity. Solutal diffusion at the roots of the dendrites was hindered by the surrounding arms so that the radial coarsening growth was slowed and caused root necking and solute enrichment.

![Figure 3. Solutal concentration and morphology of growing dendrites.](image)

The LGK model is an analytic method for accurately computing the axial growth velocity of dendrites because the shape of tip is solved in strict accordance with thermal and mass transfers, as well as the critical stability of the solid–liquid interface. Thus, the reliability of the CA model can be verified by comparing the growth velocity of the tips of two models. Figure 4a shows that the velocity predicted by the LGK model was constant at a fixed undercooling of 7.0 K due to the fact that the Péclet number, depending on thermal diffusivity and tip radius, was not changed [31]. However, a maximum velocity was obtained by CA model at the beginning of nucleation because a large instantaneous concentration gradient was induced in the liquid phase by a high concentration of solidifying frontier around the dendrite nucleus. This concentration gradient was decreased with the diffusion of rejected solutes into the liquid phase until the growth velocity tended to be stable (when solutal diffusion and tip growth reached equilibrium). The relative tolerance of velocity of the two models was limited within $0.6 \times 10^{-2}$ to 0.2 from solidification times ranging from 0.15 s to 0.25 s. Figure 4b shows that the velocity predicted by the CA model at a low undercooling was higher than that of by the LGK model after solidification for 0.2 s because the LGK model can only be used to solve the shape of the tip without coarsening of the dendrite arm, while the CA model contained sufficient diffusion of solutes around the dendrite arm, so that a rapid growth of the dendrite, caused by low undercooling, was included. This result can be explained in detail by formula as: Radial arm coarsening increased the solid fraction $f_{S_j}$ near the tip and decreased the average curvature $K_{ave}$ in Equation (14); then, the curvature undercooling $\Delta T_r$ was dropped accordingly in Equation (13), causing the constitutional undercooling $\Delta T_c$ to be promoted in Equation (11), which led to an enhancement of growth velocity $v_n$ due to a larger concentration gradient $\nabla C_{Li}$ in Equation (7). Further, arm coarsening was gradually weakened as undercooling rose, resulting in the growth velocity from the CA model being lower than that of the LGK model. Comparison of the two models showed that the predicted results were consistent for both fixed and different undercoolings. The reliability of the CA model was verified using an analytical LGK model.
accompanied by the matrix growth of dendrites during the solidification in the system of Fe-0.6%C-1.0%Mn-0.3%S within a computational domain of 300 × 300 μm, as shown in Figure 5. Undercooling was induced by the boundary condition of heat flux $q_w = 0.4$ W·m$^{-2}$ on two face-to-face borders and the other two sides were adiabatic, considering a balance of heat exchange. Nuclei were allocated into the domain using the Gaussian formula [25], and those at the borders began to grow into initial columnar dendrites. Mutual competition of initial dendrites enabled some of them to grow preferentially as superior ones, and rapidly reject solutes, which caused local enrichment for other columnar dendrites, resulting in the growth of these inferior dendrites to be further restrained because of a decrease in the concentration gradient. Meanwhile, secondary dendrites were formed as surface protrusions of the growing dendrite arm, and those of adjacent arms bridged each other to solidify the matrix in Zone I (inward about 80 μm from the boundary). Superior columnar dendrites that continue to extend were coarsened due to the concentration gradient rising in the liquid phase between them, also causing accompanying secondary dendrites to develop well in Zone II of the domain. MnS precipitation depended on local undercooling, solutal concentration and dendritic morphology. For example, MnS began to precipitate at a solid fraction of $f_S = 0.69$ in Zone I, while it needed to be $f_S = 0.73$ in Zone II. Details are shown in Figures 6 and 7 by taking Parts A and B as cases, respectively.

3.2. MnS Evolution in Solidifying Matrix

Cross-scale modelling consisting of two CA modules was used to simulate MnS precipitation, accompanied by the matrix growth of dendrites during the solidification in the system of Fe-0.6%C-1.0%Mn-0.3%S within a computational domain of 300 × 300 μm, as shown in Figure 5. Undercooling was induced by the boundary condition of heat flux $q_w = 0.4$ W·m$^{-2}$ on two face-to-face borders and the other two sides were adiabatic, considering a balance of heat exchange. Nuclei were allocated into the domain using the Gaussian formula [25], and those at the borders began to grow into initial columnar dendrites. Mutual competition of initial dendrites enabled some of them to grow preferentially as superior ones, and rapidly reject solutes, which caused local enrichment for other columnar dendrites, resulting in the growth of these inferior dendrites to be further restrained because of a decrease in the concentration gradient. Meanwhile, secondary dendrites were formed as surface protrusions of the growing dendrite arm, and those of adjacent arms bridged each other to solidify the matrix in Zone I (inward about 80 μm from the boundary). Superior columnar dendrites that continue to extend were coarsened due to the concentration gradient rising in the liquid phase between them, also causing accompanying secondary dendrites to develop well in Zone II of the domain. MnS precipitation depended on local undercooling, solutal concentration and dendritic morphology. For example, MnS began to precipitate at a solid fraction of $f_S = 0.69$ in Zone I, while it needed to be $f_S = 0.73$ in Zone II. Details are shown in Figures 6 and 7 by taking Parts A and B as cases, respectively.

Figure 3. Solutal concentration and morphology of growing dendrites. 

Figure 4. Comparison of growth velocity predicted by the CA and LGK (Lipton-Glicksman-Kurz) models with velocity units of (a) mm·s$^{-1}$ and (b) m·s$^{-1}$.

Figure 5. Solidification morphology expressed by solutal concentration of elements (a) Mn and (b) S.
3.2. MnS Evolution in Solidifying Matrix

Cross-scale modelling was used to simulate MnS precipitation in a system of Fe-1.0%Mn-0.3%S-1.0%Ti and Fe-1.0%Mn-0.3%S, as shown in Figure 6a. The residual liquid phase between solidifying dendrites was difficult to be transported into the liquid phase due to the low temperature and high solutal concentration, as shown in Figure 6d,e, where the content of element Mn decreased significantly and only increased in the corresponding position of holes because it failed in the formation reaction of MnS. The predicted morphology of MnS was compared with those observed using an optical microscope and scanning electron micrograph [32] for similar compositional systems of Fe-1.0%Mn-0.3%S-1.0%Ti and Fe-1.0%Mn-0.3%S, as shown in Figure 6f,g. The simulation results agreed well with the experimental characterizations in the geometric

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**Figure 6.** MnS precipitation in Part A and its comparison with experimental observations.

**Figure 7.** MnS precipitation in Part B and its comparison with experimental observations.

Preferential precipitation of MnS at a solid fraction of 0.69 in Zone I was caused by the reduction of Gibbs freedom energy due to the low temperature and high solutal concentration, as shown in Figure 6a. The residual liquid phase between solidifying dendrites was difficult to be transported into the liquid phase and formed isolated liquid holes by the bridging of secondary dendrites. The high concentrations in the holes facilitated the nucleation of MnS but the size was confined by the limited space and solute mass. Thus, the amount of MnS increased gradually from a solid fraction of 0.73 to 0.77, and the volume was hardly changed, as shown in Figure 6b,c. Precipitated MnS tended to be saturated at solid fraction \( f_s = 0.87 \) until it was completely solidified, as shown in Figure 6d,e, where the content of element Mn decreased significantly and only increased in the corresponding position of holes because it failed in the formation reaction of MnS. The predicted morphology of MnS was compared with those observed using an optical microscope and scanning electron micrograph [32] for similar compositional systems of Fe-1.0%Mn-0.3%S-1.0%Ti and Fe-1.0%Mn-0.3%S, as shown in Figure 6f,g. The simulation results agreed well with the experimental characterizations in the geometric...
dimensions, and the inconsistency in shape was due to the fact that our meshed PCs still needed to be refined.

Solutal transport was active in Zone II and almost no liquid holes formed because the large space between the columnar dendrites caused second dendrites to no longer play an important role in the liquid phase transfer. Here, precipitated MnS usually existed in three shapes. For example, the seeds $\alpha$ and $\beta$ of MnS in Part B at solid fraction $f_s = 0.73$ were immersed freely in the liquid phase or attached to a solidified matrix containing columnar and secondary arms, respectively, as shown in Figure 7a. Seed $\alpha$ was fully in contact with the liquid phase and was likely to be fostered into an isotropic two-dimensional dendrite shape. Its arms that were close to the matrix grew slowly due to local insufficiency of solutes. However, MnS grown from seed $\beta$ was restricted by the surrounding matrix and could only develop into an irregular strip- and cluster-shape. The three MnS shapes are shown in Figure 7b at solid fraction $f_s = 0.77$, and they continued to grow, as shown in Figure 7c,d, until they turned into solids (Figure 7e). Predicted dendrite-, strip- and cluster-shaped MnS were compared with those of captured microscopic images [32] (Figure 7f,g). Simulated and observed results agree well with shape and size. Our work confirmed that MnS (three shapes) had a high possibility of coexistence, and also explained why this occurs.

We found that the changing trend in the content of elements Mn and S was opposite during solidification. Element Mn was instantaneously consumed once MnS was precipitated, in Figure 6a, while element S was still abundant, as shown in Figure 7e. This was because the partition coefficient of element S $k_S = 0.035$ was far less than that of element Mn $k_Mn = 0.785$ at the solid–liquid interface, resulting in an amount of rejected element S that was higher than the level of consumption for MnS formation. Further, the solubility product of MnS, $E_{MnS}$, was fixed at a constant temperature so that the content of element Mn was reduced; see Equation (22).

### 3.3. Effect of Content of Mn and S

Cross-scale modeling was used to predict the MnS precipitations for two continuously-cast steel objects with systems of Fe-0.6%C-0.2%Mn-0.02%S and Fe-0.6%C-0.8%Mn-0.005%S in order to clarify the effects of the content of elements Mn and S. The initial contents of Mn and S were distinctly differentiated in the two systems—high content of S for former (High-S) and high content of Mn for latter (High-Mn)—but the concentration products were fixed as a constant for comparison. MnS was precipitated at solid fractions $f_s = 0.91$ and 0.93 in two systems, respectively. They were significantly higher than that of 0.69 in the system of Fe-0.6%C-1.0%Mn-0.3%S, discussed previously. This was because the low content of Mn and S enabled them to be sufficiently enriched in the later stage of solidification in order to achieve the Gibbs free energy required for the nucleation of MnS in the residual liquid phase. Hence, MnS can only be presented as a cluster shape and fails to be formed in the dendrite and strip shapes due to the narrow space and insufficient solutes, as shown in Figure 8a,b. Further, element S played a dominant role in the concentration product of solutes because of its low partition coefficient.

Because of this, it was necessary that the Gibbs free energy be reduced and the nucleation rate of MnS was enhanced in the High-S system, making the solid fraction of MnS, when it was beginning to be precipitated, slightly lower than that of the High-Mn system. Moreover, the content of Mn was a restrictive factor in deciding the amount of precipitated MnS because it was a supplement to the rejected S during MnS growth, attributed to its high partition coefficient. We counted the precipitated MnS of all PCs in the computational domain and determined that the volume ration of MnS for the two systems were $9.73 \times 10^{-6}$ and $3.76 \times 10^{-5}$, respectively, showing a relationship of 4 times that was coincident with the initial concentration of Mn. It is noteworthy that a re-precipitation of MnS was observed during solidification in the High-Mn system. Precipitated MnS was immobilized by the solidified matrix and the residual liquid phase was also partitioned into small pools, as shown in Figure 8c. Excessive Mn had great potential to react with residual S, which was able to form a new seed $\gamma$ in these pools when the required reaction conditions for MnS formation could be satisfied.
again, as shown in Figure 8d. However, re-precipitation of MnS was observed in the High-S system because rejected Mn was rapidly consumed by the high content of S, and it was difficult to reach a sufficient concentration to reduce the Gibbs free energy in the pools. We confirmed that it was likely to have a re-precipitation of MnS for solidification of Fe-C-Mn-S steel with a high content of Mn and low content of S. The predicted morphology of MnS was compared with those of in-cast billet samples that were observed using a scanning electron micrograph and energy dispersive spectrometer [13] (Figure 8e,f). They were in good agreement in terms of shape and size, as well as site. Our model was able to simulate the precipitation and re-precipitation of MnS simultaneously. This was difficult to conduct through experimentation.

4. Conclusions

We developed a cross-scale model consisting of two CA modules with different grid dimensions in order to conduct a simultaneous computation for MnS precipitation, accompanied by the matrix growth of dendrites during the solidification of Fe-C-Mn-S steel. The reliability of a single CA model was verified by comparison with an analytical LGK model and the predicted results from the cross-scale model agreed well with those observed in the experimental cases.

1) By virtue of cross-model, we illustrated MnS evolution, accompanied by the matrix growth of dendrites during solidification, and indicated that MnS precipitation depends on local undercooling, solutal concentration, and dendritic morphology, thus coexisting in three different shapes.

2) We found that element S played a dominant role in the concentration product and caused MnS to be precipitated at a low solid fraction and the content of Mn was a restrictive factor in deciding the amount of precipitated MnS, due to its high partition coefficient.

3) A re-precipitation of MnS was observed in a system with high content of Mn and low content of S because excessive Mn had great potential to react with residual S, which was able to form new seeds when the required reaction conditions for MnS formation could be satisfied again.

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Appendix A

Computational data used in the present study are listed in Tables A1 and A2, respectively.

Table A1. Data for heat transfer and the LGK model.

| Parameter                                | Symbol | Value                        | Refs. |
|------------------------------------------|--------|------------------------------|-------|
| Density of liquid matrix                 | $\rho_S$ | 7400 (kg·m$^{-3}$)           | [33]  |
| Density of solid matrix                  | $\rho_L$ | 7020 (kg·m$^{-3}$)           | [33]  |
| Specific heat capacity of liquid matrix  | $c_S$  | 648 (J·kg$^{-1}$·K$^{-1}$)   | [33]  |
| Specific heat capacity of solid matrix   | $c_L$  | 824 (J·kg$^{-1}$·K$^{-1}$)   | [33]  |
| Latent heat of matrix                    | $L$    | 272,000 (J·kg$^{-1}$)        | [33]  |
| Conductivity                             | $\lambda$ | 33.0 (kW·m$^{-1}$·K$^{-1}$)  | [33]  |
| Anisotropy of the surface tension        | $\varepsilon$ | 0.04                         | [26]  |
| Gibbs-Thomson coefficient                | $\Gamma$ | 1.9 × 10$^{-7}$ (m·K)        | [22]  |
| Liquidus slope of Mn                     | $m_{L,Mn}$ | −4.9 (K/wt. %)               | [33]  |
| Liquidus slope of C                      | $m_{L,C}$ | −78 (K/wt. %)                | [33]  |
| Liquidus slope of S                      | $m_{L,S}$ | −38 (K/wt. %)                | [33]  |

Table A2. Coefficients of solutal interaction and diffusion.

| Symbol | Value                        | Refs. |
|--------|------------------------------|-------|
| $e_{Mn}$ | −0.048                      | [34]  |
| $e_{C}$  | −0.070                      | [34]  |
| $e_{Mn}$ | 0                            | [34]  |
| $k_{Mn}$ | 0.785                       | [13]  |
| $k_{C}$  | 0.035                       | [13]  |
| $k_{S}$  | 0.340                       | [13]  |
| $D_{Mn}$ | 4.60 × 10$^{-7}$ exp (−70,300/RT) (m$^2$·s$^{-1}$) | [35]  |
| $D_{C}$  | 7.67 × 10$^{-6}$ exp (−106,000/RT) (m$^2$·s$^{-1}$) | [35]  |
| $D_{S}$  | 4.33 × 10$^{-8}$ exp (−35,600/RT) (m$^2$·s$^{-1}$) | [35]  |
| $D_{Mn,S}$ | 7.00 × 10$^{-5}$ exp (−286,000/RT) (m$^2$·s$^{-1}$) | [35]  |
| $D_{C,S}$ | −0.048                      | [34]  |
| $D_{S,S}$ | 2.40 × 10$^{-4}$ exp (−223,400/RT) (m$^2$·s$^{-1}$) | [35]  |

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