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An improved cellular automata model for TiN inclusion precipitation

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Abstract

The mesoscopic dendrite growth model in the solidification process of molten steel is established, based on the cellular automata model. To accurately describe the TiN nucleation process, a heterogeneous nucleation model was used to describe the TiN nucleation process. The accuracy of the dendrite growth model is verified by comparing the CA model and Lipton–Glicksman–Kurz (LGK) analytical model. The growth process of TiN precipitates was simulated by dynamic mesh generation. Meanwhile, the influence of grid anisotropy on dendrite growth is greatly weakened by introducing the decentered square algorithm, and the growth of the equiaxed crystal in all directions is simulated. The results show that the calculated results of the model are in good agreement with the volume and morphology of TiN observed in the experiment. Meanwhile, it is found that the smaller TiN will dissolve at the end of solidification, and there will be a re-precipitation. The precipitation time of High-N and High-Ti alloy systems with the same concentration product is basically the same, but the final precipitation solid fraction of TiN inclusions in High-N (small Ti/N) alloy is larger. N element is the decisive factor of TiN precipitation.

1. Introduction

The formation of cells and dendrites and solute segregation during alloy solidification is one of the main factors affecting the properties of steel [1]. Due to the influence of solute segregation and temperature reduction, inclusions in steel gradually begin to precipitate, which has an effect on the properties of steel. Among them, nitrogen content has many harmful effects on the physical properties and surface properties of steel, but sometimes it also produces benefits. Generally, TiN inclusions are formed by adding titanium to steel in order to stabilize nitrogen in steel [2]. Meanwhile, the formation of TiN with different sizes has an effect on the toughness, ductility, and weldability of steel [3–11]. Therefore, it is important to find out the formation rule of TiN for improving the quality of steel. The microstructure of the cold slab can only be observed by SEM and the optical microscope, while the formation of inclusions can be observed by EPMA, but it is expensive and difficult to be widely used. With the development of computer science, researchers use some commercial software or self-programming to simulate the formation process of micro-organization and gradually become an important means to study micro-organization.

In recent years, many numerical models have been established to characterize the microstructure of billet, which can be used to solve complex transport phenomena and S/L phase transition under different boundary conditions and initial conditions. Generally, the methods of microstructural simulation include frontier tracking (FT), phase-field (PF) and cellular automaton (CA). PF method deals with a complex S/L interface by introducing the smooth transition of order parameter ϕ into the thermodynamic partial differential equation system, thus avoiding the tracing S/L interface visually [12–14]. However, the PF method needs a lot of computational resources, so it can only calculate very small areas. CA method can simulate dendrite growth at various scales, solve the problem that the PF model needs a lot of computational resources, and has high computational efficiency. Therefore, the CA method, as an alternative to simulate dendrite growth during
solidification, is rapidly emerging. Gandin and Rappaz [15, 16] proposed an algorithm to simulate dendritic grain formation during Solidification. Based on two-dimensional and three-dimensional CA models. The model takes into account the heterogeneous nucleation of dendrites, growth kinetics and the growth direction of dominant dendrites. The temperature field in the domain is calculated by the finite element method (FE). Nastac [17] proposed a numerical method based on the Eulerian drop method. A two-dimensional dendrite growth model was established by explicitly tracking the S/L interface on a rectangular grid. Dendrite growth during non-isothermal solidification was calculated, and the transition from columnar to equiaxed (CET) during solidification was predicted. Beltran-Sanchez and Stefanescu [18] solved the equation of solute and heat conservation under boundary conditions, introduced a non-constant stability parameter (varying with angle) to the virtual frontier tracking method to track the S/L interface, and eliminated the dependence of the computational grid by solving the new local curvature, solid fraction, capture rule and anisotropy of the mesh. Zhu et al [19, 20] established an improved cellular automaton model (MCA), which considered the equilibrium solidification process and metastable solidification process in a multiphase system. The effects of alloy composition and eutectic undercooling on eutectic morphology and eutectic nucleation were studied. Furthermore, combined with the momentum transport equation, the growth characteristics of typical troip dendrites with various preferential orientations are reproduced, and the effects of inlet velocity on solute redistribution and dendritic tip growth rate are studied. Wei et al [21] studied the traditional capture rules, proposed a random zigzag capture rule which can greatly reduce mesh anisotropy, improved the calculation method of interface curvature, and improved the accuracy of S/L interface curvature calculation. Zaeem et al [22] Discussed the obvious advantages of the cellular automata model and phase-field model. The research shows that the CA-FE model is more effective than the PF-FE model when the scale and complexity of the problem increase. Chen et al [23] Based on an improved cellular automaton model, the dendrite growth of Al-Si-Mg three alloy was predicted. An improved ten direction eight face neighborhood tracking algorithm was introduced to eliminate the effect of mesh dependence on dendrite growth. Zhan et al [24] established the CA-FD model, and simulated the diffusion velocity coefficients of different solutes in Al-Cu alloy. The interaction between dendrite growth and solute distribution was explained. Zhang et al [25] extended the two-dimensional CA model, which involves solidification and melting mechanism. Based on in situ observation experiments, the microstructural evolution of paste zone caused by Temperature Gradient Zone Melting (TGZM) was studied. Gu et al [26] established a three-dimensional CA model to simulate the dendritic growth process of Al-Si-Mg ternary alloys. A method for calculating solute diffusion and solid fraction during solidification of ternary alloys was proposed. The CA model of Fe-C-Mn-S quaternary alloy was established by Meng [27, 28]. The precipitation process of MnS was simulated by local mesh refinement. Körner, C et al [29] established the CA-LBM model to investigate melting and re-solidification of a randomly packed powder bed under the irradiation of a Gaussian beam during selective beam melting processes. Lian et al [30] extended the CA-FVM model, extended the CA-FVM model to predict the grain structure of an alloy, e.g. Inconel 718, fabricated by Additive manufacturing. Liu et al [31] established the PF-TLBM model to simulate the microstructure evolution of alloys during the rapid solidification.

In this paper, a cellular automata model of a multielement alloy is established, and the precipitation process of TiN inclusions between grains is simulated. The model considers the influence of solute interaction on solute diffusion, thus ensuring the accuracy of solute distribution. At the same time, the heterogeneous nucleation model is used to calculate the TiN nucleation rate, and the transient thermodynamic equilibrium is used to calculate the TiN growth. The decentered square model is introduced [32], and the single grain growth in any direction is simulated.

2. Model description

A two-dimensional CA model was established to simulate the dendrite growth process and the precipitation of TiN inclusions in Fe-C-Ti-N alloy at the end of solidification. In the 2D dendrite growth CA model, the 0.3 × 0.3 mm² simulation area is divided into 300 × 300 square grids, and the initial temperature, concentration and solid ratio of each mesh are given. The grid state is updated in real-time with solidification. When the solid fraction of the interface cell changes to 1, the surrounding liquid phase cells are captured, and their states are transformed into interface cells and continue to grow.

2.1. Nucleation model

2.1.1. Grain nucleation

Nucleation is the precondition of molten steel solidification. In this paper, a continuous nucleation model proposed by Thevoz is used to describe the heterogeneous nucleation process of alloys. It is assumed that nucleation occurs at randomly selected nucleation points on the surface of the mold and in the liquid phase. Two
heterogeneous distributions are used to describe the heterogeneous nucleation in the mold wall and liquid phase. The increase of nucleation density \(dn\) is caused by the increase of undercooling \(d(\Delta T)\) [33]:

\[
\frac{dn}{d(\Delta T)} = \frac{n_{\text{max}}}{\sqrt{2\pi \Delta T^*}} \exp \left[ -\frac{1}{2} \left( \frac{\Delta T - \Delta T^*}{\Delta T^*} \right)^2 \right]
\]

(1)

where \(\Delta T^*\) and \(\Delta T^*\) are the average and standard deviation of nucleation undercooling, \(K; n_{\text{max}}\) is the maximum nucleation density, the units at the center and wall of the model are \(m^{-2}\) and \(m^{-1}\), respectively; \(\Delta T\) is the effective nucleation undercooling, \(K\). Different parameters are used to calculate the wall and the central region of the solution.

2.1.2. TiN nucleation

The thermodynamic and dynamic conditions of TiN formation are taken into account in the calculation of TiN precipitation. The thermodynamic conditions of TiN formation in steel are calculated by the following equations [34]:

\[
[Ti] + [N] = (TiN)
\]

(2)

\[
\Delta G = RT \left( \ln \frac{a_{TiN}}{a_{[Ti]}a_{[N]}} - \ln \left( \frac{17040}{T} - 6.4 \right) \right)
\]

(3)

When TiN satisfies the following equation in steel, it satisfies the thermodynamic condition of precipitation:

\[
P_v = A \exp \left( \frac{-\Delta G_{\text{TiN}}}{k_B T} \right) = A \exp \left( \frac{-16\pi \sigma_{\text{TiN}} f(\theta)}{3k_B T (\Delta G)^2} \right)
\]

(4)

where the \(\Delta G_{\text{TiN}}\) is the activation energy of TiN nucleation, \(J \cdot \text{mol}^{-1}\); \(A\) is the constant for \(10^{39} \text{m}^{-3} \text{s}^{-1}\); and \(\sigma_{\text{TiN}}\) is the interface energy between the inclusions and the matrix, \(J\); \(k_B\) is the Boltzmann constant; \(J\); \(f(\theta) = (2 - \cos \theta + \cos^2 \theta)/4\) with \(\theta\) as the constant angle and \(\Delta G\) is the Gibbs free energy difference between the melt and the crystal [35]:

\[
\Delta G = \frac{\Delta G_{\text{v}}}{V_{\text{TiN}}}
\]

(5)

where the \(\Delta G\) can be obtained by equation (3); \(V_{\text{TiN}}\) is the molar volume of TiN, and can be obtained by the lattice constant and linear expansion coefficient of TiN:

\[
V_{\text{TiN}} = [\gamma \times [1 + \delta \times (T - 273)]]^3 \times 6.022045 \times 10^{-4}/4
\]

(6)

where \(\gamma\) is the lattice constant of TiN, \(J\); \(\delta\) is the linear expansion coefficient of TiN, \(K\).

The nucleation rate \(P_v\) will be compared with a random number between 0 and 1. If \(P_v\) is larger than this random number, TiN will nucleate in the matrix.

2.2. Transmission model

Equations (7) and (8) are used to solve heat and solute transport in the computational domain:

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

(7)

\[
\frac{\partial C_{\varphi,i}}{\partial t} = \nabla \left( \sum_{j=1}^{n} D_{\varphi,j}^{n} \nabla C_{\varphi,j} \right) + (C_{L,i} - C_{\varphi,i}) \frac{\partial f}{\partial t}
\]

(8)

where \(\rho\) is the density of matrix, \(\text{kg} \cdot \text{m}^{-3}\); \(\lambda\) is thermal diffusivity, \(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\); \(c_p\) is the specific heat, \(\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}\); \(f\) is the solid fraction of matrix; \(q_w\) is heat flux on heat dissipation wall, \(\text{W} \cdot \text{m}^{-2}\); \(L\) is latent heat; \(\text{J} \cdot \text{kg}^{-1}\); \(C_{\varphi,i}\) is the concentration of the solute elements \(i\) in phase \(\varphi\) (may take L for the liquid phase or S for the solid phase, respectively); \(w\%\); \(n\) is the number of elements. The \(n\)th element is chosen as the solvent. \(D_{\varphi,j}^{n}\) is the element of the diffusivity matrix for phase \(\varphi\). It is calculated as [36, 37].

2.2.1. Calculation of interface velocity

It is assumed that the thermodynamic equilibrium is maintained at the S/L interface and the dynamic undercooling is neglected. The undercooling at the S/L interface is calculated by the following equations:

\[
\Delta T = \Delta T_0 + (\Delta T^* - \Delta T_0) + \Gamma \bar{f}(\varphi, \theta_0)
\]

(9)

\[
\Delta T_0 = \sum_{i=1}^{n} m_{L,i}(C_{L,i} - C_{L,i}^*)
\]

(10)
where $\Delta T_1 = 1563-78[\% C] – 90[\% Ti] – 18[\% N] [38]$ is the liquidus temperature, $K; \Delta T^*$ is the temperature of interface frontier, $K; \Delta T_2$ is the constitutional undercooling, $K; C_{L,i}$ and $C_{S,i}$ are liquid phase and interfacial equilibrium concentration, respectively, and the third term on the right is the curvature undercooling; $\Gamma$ is the average Gibbs-Thomson coefficient; $\bar{K}$ is the average interface curvature, and the $f(\phi, \theta_0)$ is the anisotropy of the surface tension, then are calculated by the equations (11)-(15) [1, 17]:

$$\bar{K} = \frac{1}{\Delta x} \left( 1 - 2 \bar{f}_k + \sum_{k=1}^{N} \bar{f}_k(k) \right)$$ (11)

$$f(\phi, \theta_0) = 1 - 15\varepsilon \cos(4(\phi - \theta_0))$$ (12)

$$\varphi = \arccos \left( \frac{-f_j}{\sqrt{f_j^2 - (f_i^2)}} \right)$$ (13)

where $N = 8$ is the number of neighboring cells; $\varepsilon$ is the anisotropy coefficient; $\varphi$ is the growth angle between the normal to the interface and the $x$-axis, and $\theta_0$ is the preferential orientation with respect to the $x$-axis.

### 2.3. Growth velocity and fraction of solid evolution of the S/L interface

In this paper, the sharp interface model is used and the S/L interface is assumed to be in thermodynamic equilibrium. Meanwhile, based on the law of solute conservation at the interface, the cell at the interface is calculated:

$$v_n(C_{L,k}^* - C_{S,k}^*) = \left[ -\sum_{j=1}^{N-1} D_{i,j}^{L,L} \nabla C_{L,j}^{|L} | + \sum_{j=1}^{N-1} D_{i,j}^{S,S} \nabla C_{S,j}^{|S} | \right] \cdot \vec{n}$$ (14)

where $C_{S,i}^*$ and $C_{L,i}^*$ represent the equilibrium solute concentration of solute $i$ at the interface at solid and liquid phases respectively, wt%; $v_n$ is the interface velocity at the frontier of solidification, which is a positive value without direction; $\vec{n}$ is the interfacial growth direction [34]:

$$\vec{n} = \frac{\nabla f_{k}^*}{|\nabla f_{k}^*|} = n_i \vec{i} + n_j \vec{j}$$ (15)

In order to calculate the equilibrium concentration at the interface, it is assumed that the thermodynamic equilibrium at the interface is maintained and the law of solute distribution is satisfied:

$$C_{S,i}^* = k_i C_{L,i}^*$$ (16)

where $k_i$ is the solute equilibrium partition coefficient of element $i$ at the interface.

The interfacial velocity and equilibrium solute concentration can be calculated by combining equations (9), (14) and (16). Furthermore, the solid fraction growth of interface cells per unit time can be obtained by using the obtained interface velocity.

$$\Delta f_{S}^i = GF \cdot v_n \Delta t / L_S$$ (17)

$$f_{S}^i = f_{S}^{i-1} + \Delta f_{S}^i$$ (18)

where $\Delta f_{S}^i$ is the increase in solid fraction per unit time; $f_{S}^i$ is the solid fraction of the cell at time $t$. $L_S$ is the length of the line segment along the normal passing through the cell center. $GF$ is the modified coefficient for the growth of the interface cell [39].

### 2.4. Interfacial cell capture rules

In the traditional CA model, the process of cell capture takes place after the interface cell is completely solidified, that is, when the interface cell state changes to solid-state, it will capture the surrounding liquid adjacent cells into interface cells, once it is captured as interface cells, it will start to grow. However, the growth and capture rules of CA will make dendrites tend to grow along the axis (capture the last four neighboring cells), or along the diagonal direction (capture the eight neighboring cells), regardless of the original crystallographic orientation. This is related to the inherent configuration of the orthogonal CA grid and its growth capture rules. In this paper, an improved decentered square growth algorithm is used to eliminate the influence of grid anisotropy on the direction of dendrite growth.

Figure 1 shows the two-dimensional sketch of the decentered square growth algorithm adopted in the present model. When a certain cell meets the nucleation condition, a grain with a preferential growth angle nucleates at the center, and the cell becomes an interface cell and begins to grow in the diagonal direction of the square as shown in the black square in figure 1(a). The rate of the solidification process was set to 50KW/m$^{-3}$. Wherein, the angle between the diagonal line and the $x$-axis direction is a preferential growth angle, that is, the diagonal direction is the preferential growth direction, and the length of the semi-diagonal line in the positive...
direction changes in each time step:

$$\Delta L_\varphi = \Delta f_s L_{\varphi,\text{max}}$$

(19)

Where the $\Delta f_s$ is the change of solid phase rate in unit time. In order to calculate the change of solid phase rate accurately, the influence of the $GF$ on the change of solid phase rate was considered [39]. $L_{\varphi,\text{max}}$ is the maximum length of the square semi diagonal, calculated as follows:

$$L_{\varphi,\text{max}} = \frac{\Delta x}{\max (\cos \theta, \sin \theta)}$$

(20)

When the vertex of the square contacts the adjacent liquid phase cell, capture the cell and generate a sub-square at each vertex, whose diagonal direction is the same as the initial growth direction of the dendrite, as shown in figure 1(b). With the growth of the interface cell, the vertex of the sub-square contacts with its adjacent cell, and converts it into the interface cell. Meanwhile, its vertex forms a new secondary square, and continues to grow, as shown in figure 1(c). At this time, all the liquid phase cells in the adjacent cell of Moore around the nucleation cell are captured as interface cells. In order to avoid the non-capture of Moore’s cell, when the solid phase ratio of a cell is 1, all the liquid phase cells in Moore’s cell are captured as interface cells.

2.5. Microcosmic TiN growth model

With the solidification process going on, when a cell in the liquid phase between dendrites meets the condition of TiN nucleation, TiN begins to nucleate and grow. However, due to the large gap between the precipitation size of TiN inclusions and the growth size of the matrix, the calculation of the precipitation growth process of TiN inclusions on the grid for calculating the growth of the matrix will lead to excessive errors, so the precipitation process cannot be accurately simulated. The growth process of TiN can be accurately described after the grid is fully refined, but too fine grid will lead to the significant increase of computing cost, time cost and the reduction of computing domain. These problems limit the development of simulation of inclusions precipitation process. In order to solve this problem, the dynamic mesh refinement method was used to refine the mesh of TiN inclusions. The refined grid can accurately describe the precipitation process of TiN inclusions without increasing too much calculation. Figure 2 shows the details of local grid division: when the matrix liquid phase cell meets the thermodynamic and kinetic conditions of TiN precipitation, it is subdivided into 10$\times$10 cells, and the refined grid is named as precipitation cell (PC), and a TiN seed is randomly assigned to a PC, which is the TiN interface PC. The growth price of the interface PC is calculated based on the transient thermodynamic equilibrium calculate:

$$f_{[N]} f_{[Ti]} ([Ti] - \Delta \delta) ([N] - \Delta \delta) = \frac{M_{\text{TiN}} \rho_{\text{Fe}}}{100 M_{\text{Ti}}} \Delta \delta$$

(21)

The increment of TiN ($\Delta f_{\text{TiN}}$) is calculated as follows:

$$\Delta f_{\text{TiN}} = \frac{M_{\text{TiN}} \rho_{\text{Fe}}}{100 M_{\text{Ti}}} \Delta \delta$$

(22)

$$f_{\text{TiN}}^t = f_{\text{TiN}}^{t-1} + \Delta f_{\text{TiN}}$$

(23)

In the equation, $M_{\text{N}}$ and $M_{\text{Ti}}$ represent the relative atomic mass of N atom and Ti atom respectively; $M_{\text{TiN}}$ represents the relative molecular mass of TiN; $\Delta \delta$ represents the reaction amount, wt%; and $\Delta f_{\text{TiN}}$ represents the solid-phase growth amount of TiN. The temperature, [Ti] and [N] in TiN precipitated PC are obtained by linear difference of four neighboring matrix cells, as shown in figure 2. When the solid phase ratio of TiN bound
PC reaches 1, the PC is transformed into solid-phase PC and four adjacent liquid phase PCs are captured as interface PCs. The above calculation is repeated. Meanwhile, the solute field is updated timely according to the consumption of Ti and N solute in the liquid phase, which ensures the accuracy of solute conservation and dendrite solution.

When TiN contacts the adjacent bulk liquid cells, the adjacent matrix liquid cells are subdivided into $10 \times 10$ TiN precipitated PC and TiN growth continues. Therefore, by the method of local dynamic mesh refinement, on the one hand, it can describe the matrix dendrites and TiN precipitates under different sizes well, on the other hand, it can save the calculation memory and calculation time caused by mesh refinement, which is conducive to large-scale simulation application.

3. Model validation

3.1. Model validation

To verify the accuracy of the model, this paper compares the CA model with the LGK analytical model, and the results of the two models have the same trend and good agreement. The simulation area of $0.3 \times 0.3$ mm$^2$ is divided into 300 $\times$ 300 squares with a side length of 1 $\mu$m. A seed with a growth angle of $0^\circ$ is placed in the center of the simulation area to grow, and the boundary condition is set as the adiabatic boundary condition. The model parameters are listed in tables A1, and A2 (appendix A).

Figure 3 shows the dendrite growth at undercooling 7K and solidification time of 0.15 s. Figures 3(a)–(c) shows the solute distribution of N, C, and Ti around the dendrite, respectively. It can be seen from figure 3 that the dendrite growth degree under different solutes is the same because when calculating the dendrite growth rate according to equations (9), (14) and (16), the solid phase rate increment generated by each solute diffusion is the same. The distribution of solute around dendrites is very different, which is mainly due to the different diffusion coefficient of solute, resulting in the different diffusion degree of solute in the same time. It is not difficult to see from the figure 3 that the solute diffusion area of Ti element is the largest, followed by that of C element, and that of N element is the smallest, which is consistent with their diffusion coefficient $D_{a_{\text{Ti}}} > D_{a_{\text{C}}} > D_{a_{\text{N}}}$. Meanwhile, because the slope of N liquidus ($k_{\text{N}} = 0.48$) is larger than that of Ti ($k_{\text{Ti}} = 0.33$), the enrichment degree of N element solute in dendrite root is higher than that of Ti element solute in the same time.

Figure 4 shows the prediction results of the LGK analytical model and CA model for Fe-0.33%C-0.044%Ti-0.0145%N alloy. Figure 4(a) shows the change of dendritic tip velocity with time, from which it can be seen that the predicted velocity of the CA model is much higher than that of the LGK analytical model at the beginning of solidification. As the solidification proceeds, the tip growth rate predicted by the CA model decreases rapidly and finally tends to be stable, which is in good agreement with the analytical solution of LGK. Figures 4(b) and (c) show the variation of tip velocity and tip radius with undercooling in steady-state. With the increase of undercooling, the steady-state velocity increases and the tip radius of dendrite decreases. CA prediction model is in good agreement with LGK analytical model.
3.2. Multidirectional equiaxed crystal growth

Figure 5 shows the multi-angle growth of equiaxed crystal and the distribution of solute concentration in Fe-0.33%C-0.044%Ti-0.0145%N quaternary alloy system at 7K undercooling. It can be seen from the figure that when the growth angles are 0° and 45° respectively, the equiaxed crystal grows compactly, the four dendrite arms are completely symmetrical, and there is no secondary dendrite arm. When the growth angle is other, the secondary dendrite appears in the dendrite arm due to the influence of grid anisotropy. When the growth angle is 10°, the growth of the secondary dendrite arm is the most obvious. In the case of the left dendrite arm, when the secondary dendrite appears, the secondary dendrite arm under the dendrite is more developed than the upper one, which shows that the upper side of the dendrite arm is more affected by the grid arrangement.

Figure 3. Morphology of equiaxed crystal and distribution of solute: (a) N (b) C and (c) Ti.

Figure 4. Comparison between CA model and LGK model: (a) tip velocity of the dendrite growing in an undercooling $\Delta T = 7K$; (b) the steady-state tip radius; (c) the steady-state tip velocity.
Figure 6 is a comparison of the length of equiaxed dendrite arms with different growth angles. Due to the influence of grid arrangement, the growth length of equiaxed crystals with different growth angles is different. Among them, the closer the middle region is to the range of $0^\circ - 45^\circ$, the smaller the growth length is, while the longest is at $45^\circ$. However, the absolute deviation is between $-4.6$ and $4.4 \mu m$, and the relative deviation is between $-6.4\%$ and $6\%$, which is acceptable.

4. Model application

4.1. Columnar crystal growth

Figure 7 shows the growth of columnar crystals. Because the two opposite sides of the boundary of the simulation area are heat dissipation boundary conditions and the other two boundaries are adiabatic boundary conditions, the nucleation on the boundary only occurs on the two boundaries. At the same time, in order to
simulate TiN precipitation between columnar crystals, the controlled nucleation only occurs on the boundary. Figure 7(a) shows the growth of columnar crystal with solid-phase ratio $f_s = 0.08$. Due to the vertical direction of the cooling edge is thermal diffusion direction, and the temperature gradient is large, the dendrite grows along the cooling direction.

The distribution law of solute results in solute concentration between dendrites and at the tip of dendrites, and solute diffusion to the central region. The most serious area of solute enrichment occurs at the root of the secondary dendrite arm, which is mainly due to the solute discharged from the primary dendrite arm and the secondary dendrite arm to both sides. Meanwhile, so that the regional solute concentration between the two dendrite arms increases, while the solute in the root area of the secondary dendrite arm is difficult to diffuse, and solute gradually enriches here. The enrichment of solute at the root of secondary dendrite arm inhibits the growth of dendrite here, resulting in a `pit' at the root of secondary dendrite arm, which is called necking phenomenon, as shown in figure 7.

With the growth of dendrites, the initial solute concentration area disappears, and the secondary dendrite growth is obvious. It is worth noting that with the growth of primary dendrite arm, the relative primary dendrite

**Figure 7.** Columnar morphology and N solute distribution.
arms on the two cooling boundaries exceed the center area of the simulation area, but they do not ‘collide’, but ‘dodge’ each other, as shown in figure 7(c). This is mainly because when the arms of two dendrites are close, the solute discharged from the growth of the dendrite tip is seriously enriched, which reduces the concentration.
gradient at the front of the dendrite tip and the growth rate to a very low level. However, the growth rate of the other side of the dendrite arm did not decrease significantly because there was no dendrite arm close to it.

Figure 8 shows the concentration distribution of Ti and N solute when TiN is just separated out. Because of the low initial concentration of the two solutes in the molten solution, TiN precipitation time is later. It can be seen from the figure 8 that a large number of n-solutes are consumed in TiN precipitation, and the initial solute concentration of Ti is much higher than that of N-solute. When TiN begins to precipitate, the n-solute is consumed in a large amount, the concentration is reduced to a very low level, and TiN stops growing, so the Ti solute concentration is reduced less. Meanwhile, it is found that the initial precipitation of TiN near the cooling edge is more. This is mainly due to the dendrite growth from the cooling edge, and solute enrichment first occurs near the cooling edge. Therefore, TiN precipitation condition will be satisfied near the cooling edge.

4.2. Precipitation of TiN

Figure 9 shows the simulation results of TiN precipitation in Fe-0.33%C-0.044%Ti-0.0145% N alloy. When the solid phase ratio reaches $f_s = 0.81$, TiN begins to precipitate, resulting in a significant decrease in the surrounding solute concentration, and the precipitate is soon completed, as shown in figures 9(a) and (b). Due to the late time of TiN precipitation and the low concentration of N and Ti in the molten pool, TiN mainly precipitates in the small molten pool. Because TiN precipitation consumes a lot of Ti and N elements in a short time, the concentration of solute in the molten pool decreases to a very low level, which limits the further growth of TiN. It is worth noting that TiN dissolves at $\alpha$ in figures 9(d) and (e), which is mainly due to the large consumption of the solute concentration of Ti and N elements in the small molten pool after TiN precipitates in the small molten pool so that the solute concentration in the molten pool is not enough to support the continued growth of TiN. Meanwhile, the dendritic growth of the matrix becomes fast and TiN is surrounded quickly. With the release of latent heat during the solidification process, the Gibbs free energy generated by TiN according to equation (3) increases, so that TiN with smaller volume will undergo dissolution reaction. Figures 9(h) and (l) are the morphology of TiN when the solidification is complete, and compared with the test results [40], its sizes are in good agreement, and the subtle differences in shape are mainly caused by grid anisotropy.

Figure 10 shows the simulation results of TiN precipitation in GCr15 Bearing Steel (Fe-1.01%C-0.0078%Ti-0.0049%N) and the test comparison. It can be seen that TiN begins to precipitate when the solid phase ratio
reaches 0.89 and the surrounding Ti solute is consumed. In figure 10(b), as the solidification proceeds, the secondary dendrite and the tertiary dendrite are bridged, and the liquid phase area is divided into small melting pools to form TiN inclusions, and the TiN growth is not obvious. When a small molten pool is formed, there is an increase in the concentration of Ti solute in the molten pool (as shown in figure 10(c)). The Gibbs free energy in the molten pool decreases. TiN absorbs solute in the surrounding liquid phase and grows up to a certain extent, as shown in figure 10(c).

In figure 10(c), the secondary precipitation of TiN occurs in the small molten pool, which is mainly due to the bridging phenomenon between TiN and dendrite when TiN is wrapped by the matrix, resulting in a large number of small molten pools in the liquid phase being isolated from each other, no longer consuming Ti and N elements in the liquid phase, and the Ti/N ratio in the alloy system is small. In the early stage of TiN precipitation, there are more N elements left, and with the advance of the S/L interface of the matrix, the solute concentration in the molten pool increases gradually and space is larger. According to equation (3), the Gibbs free energy of TiN formation is reduced, thus TiN nucleation rate is increased, and TiN nucleation is promoted again in the remaining liquid phase, as shown in figure 10(c). After TiN re-precipitation, the concentration of liquid Ti and N solute decreases again due to the growing consumption of TiN. However, due to the small molten pool of liquid phase when TiN re-precipitation, the precipitated TiN can absorb little Ti and N, resulting in smaller volume, which makes TiN more dispersed on the grain boundary.

Figures 10(e) and (f) are the enlarged Figures of $\gamma$ and $\delta$ in figures 10(d), and (g) and (h) are the TiN morphology observed by Tian et al. [41] through the field emission scanning electron microscope (FE-SEM). The TiN morphology of the calculation results and the test results are close to the quadrilateral, volume, and good agreement.

### 4.3. Effect of Ti/N ratio on TiN precipitation

In the solidification process of liquid metals and alloys, solute redistributes between the liquid and solid phases, resulting in uneven composition. The segregation of solute elements results in the decrease of Gibbs free energy in the system, which is conducive to the precipitation of TiN. At a certain temperature, the solute solubility in the solid phase is often less than that in the liquid phase, so the solidification phase will discharge the excess TiN. This process is also affected by the Ti/N ratio in the alloy system.
solute in the liquid phase at the S/L interface. With the solidification process, the solute in the remaining liquid phase will gradually enrich, which leads to the solute concentration in the liquid phase at the last stage of solidification will be much higher than the initial value. Therefore, the small change of initial solute concentration will have a significant impact on the solute concentration in the final stage of solidification. In order to study the effect of Ti and N solute concentration on TiN precipitation in the alloy, the TiN precipitation of Fe-0.33%C-0.09%Ti-0.02%N and Fe-0.33%C-0.06%Ti-0.03%N alloy elements at \( q_\text{w} = 50 \text{ kW} \cdot \text{m}^{-2} \) was simulated on the premise of ensuring the same initial titanium nitrogen concentration.

Figures 11 and 12 show the precipitation of TiN in Fe-0.33%C-0.09%Ti-0.02%N alloy and Fe-0.33%C-0.06%Ti-0.03%N alloy systems, respectively. To facilitate the analysis, the two alloy systems are defined as High-Ti alloy and High-N alloy. The precipitation time of the two alloy systems is obviously earlier than that of the above alloy system when the solid phase ratio is 0.66 and 0.68, respectively. This is mainly due to the high concentration of Ti and N in the High-Ti and High-N alloy systems, the Gibbs free energy of TiN formation is low, which promotes the nucleation of TiN. Meanwhile, it is found that the precipitation time of High-Ti and the High-N alloy is close, which is mainly due to the same solubility product of nitrogen and titanium in the two alloy systems, and the distribution coefficient of the two solutes is similar \( (k_\text{Ti} = 0.33, k_\text{N} = 0.48) \). With the development of solidification behavior, the enrichment degree of N and Ti solute between dendrites is close. When TiN precipitates, the solute between dendrites is consumed rapidly. Due to the low concentration of Ti and N solute in the molten pool, and because TiN precipitates mostly at the front of the S/L interface, it is quickly wrapped by solid matrix after precipitation, which blocks the solute transport, resulting in the small volume of TiN. Although the precipitation time of the two alloy systems is close and the initial concentration product is the same, the precipitation amount of TiN in the High-N alloy is more, which is mainly due to the smaller ratio of Ti/N in High-N alloy system \( (\text{Rat High-Ti} = 4.5, \text{Rat High-N} = 2) \). With the solidification going on, due to the low content of N solute in the High Ti alloy system, the formation of TiN consumes a lot of N element in the molten pool, and the N element is reduced to a very low level, which makes TiN precipitate

Figure 12. TiN Precipitation Evolution and N Solute Distribution in High-N Alloy System.
quickly, as shown in figure 13. In the High-N alloy system, because of the small Ti/N ratio and the High content of N solute, more TiN is formed with the solidification behavior, and the volume is larger.

5. Conclusions

In order to simulate the precipitation process of TiN in steel solidification, a dendrite growth model is established based on CA method, and the dendrite growth grid of matrix is refined by dynamic local grid division method, so that the precipitation process of TiN in steel can be more accurately described, and the following conclusions are obtained:

1. The precipitation time of the High-N alloy system and High-Ti alloy system is the same, but the solid fraction of TiN precipitated from High-N (small Ti/N ratio) alloy is larger.

2. The simulation results show that TiN with small volume dissolves at the end of solidification, and TiN secondary precipitation also occurs.

3. When columnar and equiaxed grains coexist, TiN nucleates first in the columnar region, but the volume of TiN nucleated in the equiaxed region is larger. The existence of the equiaxed crystal region reduces the precipitation of TiN and makes TiN precipitate in a higher solid phase ratio.

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Conflicts of interest

The authors declare no conflict of interest.

Appendix A

Computational data used in the present study are listed in tables A1–A3, respectively.
Table A1. Solute interaction coefficient [41].

| Variable   | $\epsilon_{i j}$ Ti | $\epsilon_{C j}$ Ti | $\epsilon_{N j}$ Ti | $\epsilon_{i j}$ N | $\epsilon_{C i}$ N | $\epsilon_{N i}$ N |
|------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Value      | 0.013                | −0.165               | −1.80                | −0.53                | 0.13                 | 0                    |

Table A2. Simulation parameters during dendrite growth [42, 43].

| Parameter                                                                 | Symbol | Value                                                                 |
|---------------------------------------------------------------------------|--------|----------------------------------------------------------------------|
| Density of solid matrix                                                   | $\rho_s$ | 7400 (kg · m$^{-3}$)                                                  |
| Density of liquid matrix                                                  | $\rho_L$ | 7020 (kg · m$^{-3}$)                                                  |
| Specific heat capacity of solid matrix                                   | $c_s$  | 648 (J · kg$^{-1}$ · K$^{-1}$)                                        |
| Specific heat capacity of liquid matrix                                   | $c_L$  | 824 (J · kg$^{-1}$ · K$^{-1}$)                                        |
| Latent heat of matrix                                                    | L      | 272000 (J · kg$^{-1}$)                                                |
| Conductivity                                                              | $\lambda$ | 33.0 (kW · m$^{-1}$ · K$^{-1}$)                                      |
| Anisotropy of the surface tension                                         | $\varepsilon$ | 0.04                                                              |
| Gibbs-Thomson coefficient                                                 | $\Gamma$ | 1.9 × 10$^{-2}$ (m · K)                                               |
| Liquid slope of Ti                                                        | $m_{i T}$ | −10.24 (K/ wt%)                                                       |
| Liquid slope of C                                                         | $m_{i C}$ | −78 (K/ wt%)                                                          |
| Liquid slope of N                                                         | $m_{i N}$ | −60 (K/ wt%)                                                          |
| Solute diffusivity in the solid of Ti                                     | $D_{i j S}$ | 1.50 × 10$^{-1}$ exp (−59980/RT) (m$^2$ · s$^{-1}$)                   |
| Solute diffusivity in the solid of C                                      | $D_{C j S}$ | 7.60 × 10$^{-6}$ exp (−134600/RT) (m$^2$ · s$^{-1}$)                  |
| Solute diffusivity in the solid of N                                      | $D_{i N S}$ | 9.10 × 10$^{-1}$ exp (−40270/RT) (m$^2$ · s$^{-1}$)                   |
| Self-diffusion coefficient of C                                           | $D_{C j L}$ | 1.50 × 10$^{-3}$ exp (−59980/RT) (m$^2$ · s$^{-1}$)                   |
| Self-diffusion coefficient of Ti                                          | $D_{i j L}$ | 7.60 × 10$^{-6}$ exp (−134600/RT) (m$^2$ · s$^{-1}$)                  |
| Self-diffusion coefficient of N                                           | $D_{i N L}$ | 9.10 × 10$^{-1}$ exp (−40270/RT) (m$^2$ · s$^{-1}$)                   |
| Partition coefficient of Ti                                              | $k_{i T}$ | 0.33                                                                 |
| Partition coefficient of N                                                | $k_{i N}$ | 0.48                                                                 |
| Partition coefficient of C                                                | $k_{i C}$ | 0.34                                                                 |
| the constant angle                                                        | $\theta$ | 37(°)                                                               |

Table A3. Matrix nucleation model parameters of Fe-C-Ti-N alloys [44].

| Domain surface | Domain interior |
|----------------|-----------------|
| $n_{\text{max}, i}$/m$^{-1}$ | $\Delta T_{\text{h}, i}$/K | $\Delta T_{\text{p}, i}$/K | $n_{\text{max}, b}$/m$^{-2}$ | $\Delta T_{\text{max}, b}$/K | $\Delta T_{\text{p}, b}$/K |
| 16376          | 1.0             | 0.1                        | 10$^6$                       | 12                           | 1.5                          |

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