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Theoretical Derivation of Ice Crystal Growth in Binary Compounds Based on the KKS Multi-Field Coupled Phase-Field Model

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Abstract: In this paper, a KKS multi-field coupled phase field model for seawater ice crystal growth is established by using the phase field method. The concentration field is selected as the research object, and the governing equation of concentration field is revised based on the adsorption of micro-channel adsorption module and ion exchange resin. The Forward Euler algorithm is used to disperse the phase field and concentration field, and the ADI algorithm is used to disperse the temperature field. The calculation program is written by Visual C++ to solve the governing equations of the phase field, concentration field and temperature field.

Keywords: Phase field method; concentration field; phase field; temperature field; Visual C++

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1. INTRODUCTION

The phase field method, which is based on the Ginzburg Landau theory, provides the possibility of revealing the formation mechanism of brine pockets in theoretical way. The phase field method is developed by Langer , Kobayashi , Wheeler, Boettinger, and McFadden. By introducing other external field control equations such as temperature field, solute field, and flow field into the phase field model, it has been successful in predicting the coupling mechanism of multi physical field of multi-element metal crystallization and ice crystal growth.In2020,Yuan simulated the process of free crystallisation of single crystal nuclei, competitive crystallisation fmulti-nuclei, and oriented nuclei in a NaCl–H_2O binary solution based on the coupled model of the phase field, concentration field, and temperature field.

2. PHASE FIELD MODEL

2.1 Phase field governing equation

The free energy equation of binary mixtures based on Ginzburg-Landau free energy theory is defined as：

$$F=\int_{\Omega}[f(\phi,c,T)-\frac{\varepsilon^2}{2}|\nabla\phi|^2+\frac{\delta^2}{2}|\nabla c|^2]d\Omega$$

Where f is the chemical free energy density, ε and δ is the gradient energy coefficient related to the interface anisotropy, the phase field parameter ϕ is defined as a continuous variable between $\phi=0$ (liquid) to $\phi=1$ (solid), as well as $0<\phi<1$ (solid-liquid interfacial phase), c is the concentration， T is the temperature, Ω is the domain of integration.

The free energy density of a solid–liquid mixture is defined as:

$$f(c,\phi,T)=h(\phi)f^S(c_S)+[1-h(\phi)]f^L(c_L)+wg(\phi)$$

According to the study of $h(\phi)$ and $g(\phi)$ by Warren and Boettinger

$$h(\phi)=\phi^3(10-15\phi+6\phi^2)$$

$$wg(\phi)=w\phi^2(1-\phi)^2$$

Where c_s and c_L are equilibrium concentration of solid and liquid, respectively. $h(\phi)$ is the interpolation functions which monotonously changes from $h(0)=0$ to $h(1)=1$, w is the barrier height. $g(\phi)$ is the double-well potential associated with the phase change.

The solid and liquid enthalpies of water is determined as the function of temperature:

$$H_S(T_S)=H_S(T_m)+C_p(T_S-T_m)$$

$$H_L(T_L)=H_L(T_m)+C_p(T_L-T_m)$$

Where H_L and H_S is the enthalpies per unit volume of solid and liquid, T_S and T_L is the temperatures of solid and liquid, C_p is the specific heat.

In the process of freezing crystallization of seawater under adsorption, the salt in the solution is constantly discharged and the water is constantly crystallized. Therefore, the phase field model of pure material solidification is selected, which can be known from the phase field model of pure material solidification in the references：

$$H_t=\nabla[k(\phi)\nabla T]$$

$$\frac{\partial\phi}{\partial t}=M[\nabla(\varepsilon^2\nabla^2\phi)-f_\phi]$$

$$H=h(\phi)H_S+[1-h(\phi)]H_L$$

$$T_S(x,t)=T_L(x,t)\equiv T(x,t)$$

Where H is the enthalpies per unit volume; the subscript t is the partial derivative with respect to time; $k(\phi)$ is the thermal conductivity, M is the mobility of phase field.

By eliminating H, the phase field equation can be obtained:

$$\frac{\partial\phi}{\partial t}=M[\nabla(\varepsilon^2\nabla^2\phi)+h'(\phi)(f^L-f^S)-wg'(\phi)]$$

Where f_ϕ is the partial derivative of the free energy density with respect to the phase field parameter.

The interface region is defined as a mixture of solid and liquid with compositions different from each other, while restricted by the equal chemical potential condition based on the KKS model:

$$f_{c_S}^{S}[c_S(x,t)] = f_{c_L}^{L}[c_L(x,t)]$$

where $D(\phi)$ is the diffusivity dependent on the phase field.

f^S and f^L is the free energy density of solid and liquid.

f_{cc} was added to guarantee a constant diffusivity in both the bulk solid and liquid.

Under the condition of dilute solution approximation, the free energy density can be simplified into:

$$f_\phi = \frac{RT}{V_m} h^{'}(\phi) ln \frac{(1-c_L^e)(1-c_S)}{(1-c_S^e)(1-c_L)} - wg^{'}(\phi)$$

Where the V_m is the molar volume, R is the gas constant, and the phase field equation is defined as：

$$\frac{1}{M}\phi_t = \nabla(\varepsilon^2\nabla\phi) + \frac{RT}{V_m} h^{'}(\phi) ln \frac{(1-c_L^e)(1-c_S)}{(1-c_S^e)(1-c_L)} - wg^{'}(\phi)$$

The superscript $'$ represents the first derivative.

2.2 Concentration field equation

Restricted by the equal chemical potential condition based on the KKS mode, we can find that:

$$c = h(\phi)c_S + [1-h(\phi)]c_L$$

$$f(c,\phi) = h(\phi) f^S(c_S) + (1-h(\phi)) f^L(c_L) + wg(\phi)$$

Combined with Eqs. (13), (17) and (18), the concentration field equation can be defined as:

$$\frac{\partial c}{\partial t} = \nabla[D(\phi)\nabla c] + \nabla[D(\phi)h'(\phi)(c_L - c_S)\nabla\phi]$$

The adsorption kinetics mechanism of cation and ion exchange resin is verified by experiments (the experimental results are shown in 5.1, and the experimental results are consistent with the adsorption kinetics model in the References). The pseudo-first-order adsorption kinetics model is established as the adsorption kinetics model for the ice crystal growth process under adsorption, and the governing equation of concentration field was modified.

The Lagergren first-order adsorption rate calculation equation was simplified and derived based on the assumption of reversible adsorption to calculate the adsorption rate. Its expression is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

The boundary condition is:

$$t = 0, q_t = 0; t = \infty, q_t = q_e$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Coupling the pseudo-first-order adsorption kinetic model, the concentration field governing equation in the directional growth field model of ice crystals under adsorption is modified. The modified concentration field governing equation is as follows:

$$\frac{\partial c}{\partial t} = \nabla[D(\phi)\nabla c] + \nabla[D(\phi)h'(\phi)(c_L - c_S)\nabla\phi] - k_1 \cdot q_e \cdot e^{-k_1 t}$$

Where q_e is the adsorption capacity at equilibrium, q_t is the adsorption capacity at time *t*, K_1 is the first order adsorption rate constant.

2.3 Temperature field governing equation

Considering the release of latent heat during crystallization, the governing equation of temperature field of binary solution can be defined as:

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T + \frac{L}{2c_p} h^{'}(\phi) \frac{\partial\phi}{\partial t}$$

Where T is the temperature, L is the latent heat, D_T is the thermal diffusion coefficient. The density, specific heat and thermal conductivity of salt and water remain at a relatively stable level because the solution temperature varies within a range of several degrees during crystallization. To simplify the model, density, specific heat and thermal conductivity are assumed to be constants.

3. DIFFUSION COEFFICIENT

The diffusion coefficient of the liquid phase during the crystallization is obtained by Mean Square Displacement (MSD) of Einstein method, which is expressed as follows：

$$MSD(t) = \frac{1}{N}\left\{\sum_{i=1}^{N}\left[r_i(t) - r_i(0)\right]^2\right\}$$

Then, the diffusion coefficient of each particle is calculated by Einstein equation:

$$D = \frac{1}{6N}\lim_{t\to x}\frac{d}{dt}\left\{\sum_{i=1}^{N}\left[r_i(t) - r_i(0)\right]^2\right\}$$

Where the D is the diffusion coefficient in liquid, N is the number of particles in this system, $r_i(t)$ is the position of particle *i* at time *t*, $r_i(0)$ is the position of particle *i* at time 0.

4. INITIAL CONDITIONS AND BOUNDARY CONDITIONS

At the beginning of, it is assumed that the whole calculation area is filled with uniform subcooled brine. A rectangular initial crystal nucleus with a size of 50*800 mesh is set at the bottom of the calculation area. Its initial conditions are as follows:

When $y \le 50$, $\phi = 1$ (in solid) $c = c_0$, $T = T_M - \Delta T$

When $y \ge 50$, $\phi = 0$ (in liquid) $c = c_0$, $T = T_M - \Delta T$

On the calculation boundary, the phase state on boundaries at the next time step is always updated based on the previous time step. If the change of phase gradient at the boundary is not zero, the crystallization phenomenon will appear at the very beginning, which is incompatible with the reality. Similarly, if the concentration gradient at the boundary is not zero, the result will be the same as that of the phase field. Therefore, for the phase field and concentration field, the Zero-Neumann boundary conditions are adopted.

However, for the temperature field boundary condition, the zero-Neumann boundary condition did not consider the heat loss, so the latent heat released by crystallization is accumulated in the calculation region, which reduced the growth rate of ice crystal compared with the actual situation.

Therefore, Neumann temperature boundary conditions are：

$$\frac{\partial \phi}{\partial t} = \frac{\partial c}{\partial t} = 0$$

$$\frac{\partial T}{\partial n} = const$$

Where, *n* is the normal direction of the interface.

5. CONCLUSION

In this work, the oriented growth process of freezing crystallization in a NaCl binary system under the effect of adsorption is simulated based on the coupled model of phase field, concentration field and temperature field as well as the pseudo-first-order adsorption kinetics model. The differences of ice crystal morphology and the formation of salt cell and brine channels in the process of freezing crystallization with or without adsorption are studied from both theoretical and experimental aspects. The focus is on the inhibition the formation mechanism of salt cells and brine channels during the oriented growth of ice crystals under adsorption.

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