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Abstract

This work is devoted to the researching and simulating of crystallization processes in different mediums by cellular automata. The cellular automations for describing of micro-, macro- and nanostate crystallization processes were developed. Growth of ammonium chloride crystal in conditions of rest and turbulent mixing, glass crystallization processes, Fe- nanothread crystallization and melting in silicon dioxide nanoporous were researched and simulated.

Keywords: cellular automation, crystallization, simulation

1. Introduction

The crystallization processes need high level of technology and the strict observance of all demands for process parameters. Carrying out of sufficient investigations in this field is important for making and perfection of modern effective techniques of crystal growth. Theoretical research takes place in present work by mathematical models.
The mathematical models of crystallization process in different mediums are developed by way of cellular automation. Theory of cellular automation lies in the base of simulation. Cellular automations are mathematical models of system, which describe its evolution. The cellular automation is net, that consist of elements (cells) that change their state in the discrete points of time, conform to the law in the dependence of past element state and its closest neighbors by net [1]. The cellular automaton is an instrument for the simulation of processes and phenomenon, existent in open systems, where processes have liminal character.

2. Cellular automation for solution crystal growth model

There is simulation of ammonium chloride crystal growth from solution. We view the matter of single crystal growth evolution. Simulated field is divided to cells accordingly to the hexagonal lattice. Number of variables accords to every cell, they

are concentration, temperature and value of phase state of cell ($\Phi_{ij}^{(n)} \in \{0;1\}$, 0 - liquid cell and 1 - crystal cell). Values change at every discrete moment by defined laws in accordance of other values and states of the cell and near neighbor cells. Mathematical simulation was evolved and main definitions are diffusion law (1) and heat-exchange law (2), that reflect cell interaction.

At every step (by time) mass- and heat transfer are presented by following laws accordingly:

$$C_{ij}^{(n+1)} \to C_{ij}^{(n)} + \frac{D}{m} \cdot \left(\left\langle C_{kl}^{(n)} \right\rangle - C_{ij}^{(n)} \right) \tag{1}$$

$$T_{ij}^{(n+1)} \to T_{ij}^{(n)} + \frac{a}{p} \cdot \left(\left\langle T_{kl}^{(n)} \right\rangle - T_{ij}^{(n)} \right) \tag{2}$$

where D and a – correspondingly diffusion and thermal diffusivity coefficients; m and p – parameters, characterized by discretization of time and space; $(k,l) \in O(i,j)$ – cells of near neighborhood;

$\left\langle C_{kl}^{(n)} \right\rangle = \frac{1}{n_{lq}} \cdot \sum\limits_{k,l \in O(i,j)} C_{kl}^{(n)}$ for cells, where $\Phi_{kl}^{(n)} = 0$, and $\left\langle T_{kl}^{(n)} \right\rangle = \frac{1}{6} \cdot \sum\limits_{k,l \in O(i,j)} T_{kl}^{(n)}$ – the middle values for the near neighborhood cells; n_{lq} – number of liquid cells of near neighborhood of *(i,j)*-cell ($n_{lq} \leq 6$).

Phase change conditions are given so:

- the phase change from liquid state to solid state $\Phi_{ij}^{(n)} = 0 \to 1$ is possible, the back phase change $\Phi_{ij}^{(n)} = 1 \to 0$ is impossible;

- the cell changes phase state on condition that at least the one of neighborhood cells has already crystallized;

- the condition for the supersaturation of cell

$$\Delta_{ij}^{(n)} > \Delta^* - \lambda \cdot \left[\sum\limits_{k,l \in O(i,j)} \Phi_{kl}^{(n)} - 3 \right] \tag{3}$$

where $\Delta_{ij}^{(n)}$ – the supersaturation of *(i,j)*-cell; Δ^* – the limit supersaturation; λ – the characterizing parameter of surface bending effect.

The laws of cell interaction at the phase change are also given. The phase change is accompanied by temperature increase of itself cell (4) and concentration decrease of liquid neighborhood cells (5).

$$T_{ij}^{(n+1)} \to T_{ij}^{(n)} + dT, \tag{4}$$

$$C_{kl}^{(n+1)} \to C_{kl}^{(n)} - q \cdot \Delta_{kl}^{(n)}, \tag{5}$$

where q – coefficient, that is similarly kinetic constant of crystal growth.

Simulation of turbulent mixing is based on algorithm presented authors of works [2,3].

Pictures of NH$_4$Cl-crystal growth for conditions of rest (fig. 1a) and turbulent mixing (fig. 1b,c) were calculated by developed mathematical model. The intensity of turbulent mixing influences on NH$_4$Cl-crystal form greatly as shown in the fig. 1c.
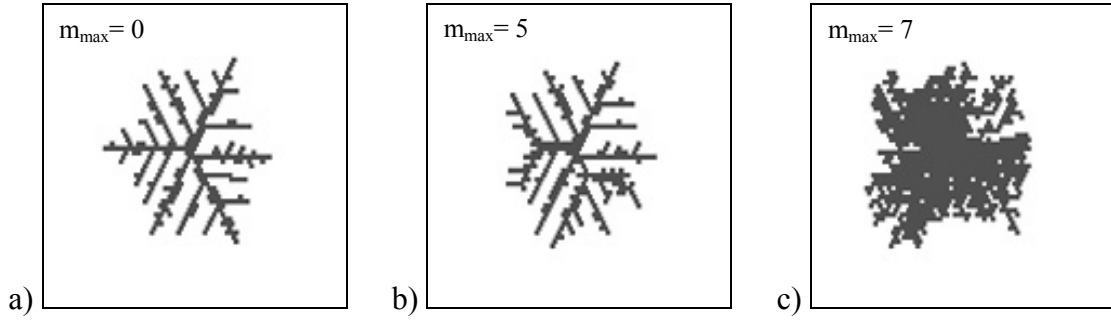
Fig. 1. The effect of mixing intensity on NH₄Cl-crystal form.

3. Cellular automation for glass crystallization model

There is simulation of glass crystallization by the example of $Li_2O \cdot SrO \cdot P_2O_5$ glass production process.

Within the bounds of this work experimental investigation was realized. Series of investigated glasses with various composition were obtained.

Experiment results for the $Li_2O \cdot SrO \cdot P_2O_5$ system:

composition 25:50:25 (in accordance to the stoichiometric composition of the crystal $LiSrPO_4$) – crystal masses;

24:48:28 – crystals with muddy glass;

23:46:31 – glass with insignificant muddy regions;

22:44:34 and 20:40:40 – absolutely clear glass.

Simulated field presents glass-mass melt at the beginning and at the end – transverse cut of glass plate. Field is divided to cells accordingly to the hexagonal lattice. At the computing there are number of variables that accords to every cell, they are concentrations of three concerned oxides $C_{1ij}^{(n)}$ (Li_2O), $C_{2ij}^{(n)}$ (SrO), $C_{3ij}^{(n)}$ (P_2O_5), temperature $T_{ij}^{(n)}$ and phase parameter $\Phi_{ij}^{(n)} \in \{0;1;2\}$, that characterizes phase state of cell: 0 – amorphous state, 1 – transitional complex, 2 – crystal cluster. Values change at every discrete moment by defined laws in accordance of other values and states of the cell and near neighbor cells.

Phase change conditions:

- complex formation $\Phi_{ij}^{(n)} = 0 \rightarrow 1$ is possible on condition that composition of calculated cell is nearly the stoichiometric composition of the crystal $LiSrPO_4$, the back phase change $\Phi_{ij}^{(n)} = 1 \rightarrow 0$ is possible too;

- crystal cluster formation $\Phi_{ij}^{(n)} = 1 \rightarrow 2$ or $\Phi_{ij}^{(n)} = 0 \rightarrow 2$ results from achievement of crystallization temperature $T_{cr} = 850°C$.

Mathematical simulation was evolved and main definitions are diffusion law (6) and heat-exchange law (7) that reflect cell interaction. At every step (by time) mass- and heat transfer are presented by following laws accordingly:

$$C_{ij}^{(n+1)} \rightarrow C_{ij}^{(n)} + \frac{1}{m}\left(\left\langle D_{kl}^{(n)} C_{kl}^{(n)}\right\rangle - D_{ij}^{(n)} C_{ij}^{(n)}\right), \tag{6}$$

$$T_{ij}^{(n+1)} \rightarrow T_{ij}^{(n)} + \frac{1}{p}\left(\left\langle a_{kl}^{(n)} T_{kl}^{(n)} \right\rangle - a_{ij}^{(n)} T_{ij}^{(n)}\right), \tag{7}$$

where D and a – correspondingly diffusion and thermal diffusivity coefficients; m and p – parameters, characterized by discretization of time and space; $(k,l) \in O(i,j)$ – cells of near neighborhood;

$$\left\langle D_{kl}^{(n)} C_{kl}^{(n)} \right\rangle = \frac{1}{6}\sum_{k,l} D_{kl}^{(n)} C_{kl}^{(n)}, \quad \left\langle a_{kl}^{(n)} T_{kl}^{(n)} \right\rangle = \frac{1}{6}\sum_{k,l} a_{kl}^{(n)} T_{kl}^{(n)} - \text{the middle values for the}$$

near neighborhood cells.

The middle value for equation (7) on the borders is calculated so:

$$\left\langle a_{kl}^{(n)} T_{kl}^{(n)} \right\rangle = \frac{1}{6}\left(2 \cdot a_b T_b + \sum_{k,l} a_{kl}^{(n)} T_{kl}^{(n)}\right), \tag{8}$$

where a_b – thermal diffusivity coefficient on the borders; T_b – temperature on the borders.
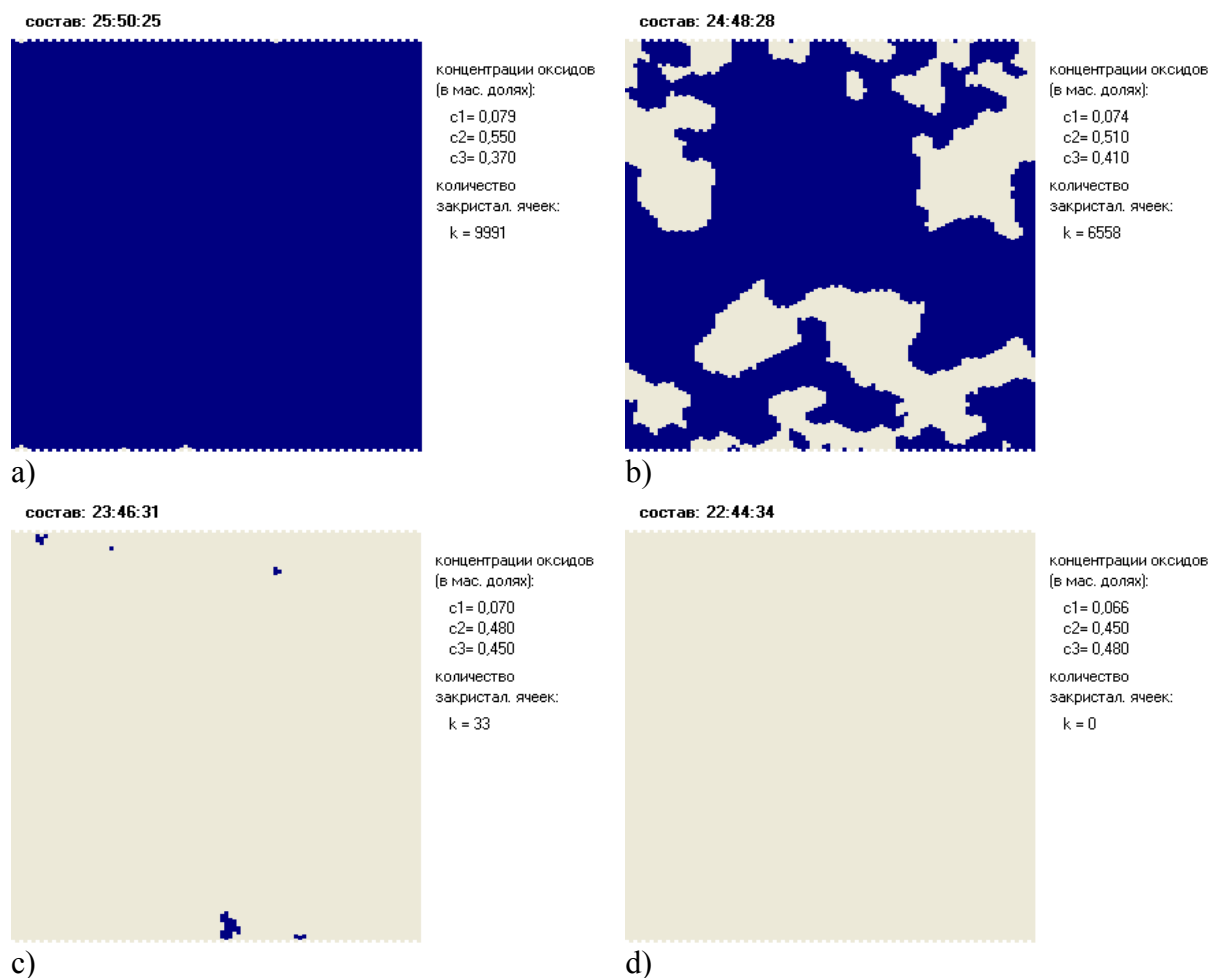

Fig. 2. Calculated $Li_2O \cdot SrO \cdot P_2O_5$ glass phase state dependence from composition.

In the work the hypotheses of exponential dependence is proposed:

$$D_{ij}^{(n)} = D_0 \cdot e^{-\frac{E}{RT_{ij}^{(n)}}}. \tag{9}$$

Pictures of $Li_2O \cdot SrO \cdot P_2O_5$ glass phase state (fig. 2) were calculated by developed mathematical model. Finding results is agreed with experimental data. Optimal composition for clear glass producing was defined.

4. Cellular automation for simulation of Fe-nanothread producing process

The simulation of nanothreads producing process is based on results of experimental work [4].

Mathematical model of iron crystallization process in mesoporous silicon dioxide matrix is developed by way of cellular automation. The network in form of hexagonal lattice was chosen for model definition. The object of simulation is pore of silicon dioxide sample.

The production processes of nanomaterials are complicated and insufficiently known because of originality and smallness of scale. Simulation requires deep and full knowledge of process, in our case it's impossible. In view of incompleteness of process information we set up hypotheses about nanomaterial production processes.

- Hypotheses about initial and boundary conditions.

a) Initial state for simulation is given set of atomic Fe-particles placed in silicon dioxide pore. Quantity of particles calculates from some experimental data. b) Initial distribution is assigned distribution with maximal concentration near by porous walls. It takes sinking of particles on porous walls into account.

- Hypotheses for formation of crystalline cluster.

Cluster is formed in the presence of the defined quantity and the location of particles in calculated cell. The quantity and the location of particles in calculated cell must be close to the quantity and the location of particles in cell of crystalline analog.

- Hypotheses about particle diffusion in porous.

A diffusion coefficient depends on temperature, in the course of simulation work the empirical dependence of the diffusion coefficient from temperature was deduced.

$$D(T) = D_0 (T-a)^b, \tag{10}$$

where D_0 – the characteristic quantity of the diffusion coefficient; T – the temperature, K; a, b – constants.

The diffusion coefficient of particles included in cluster is decreased, when cluster is formed. It suggests attraction of particles in cluster.

Cellular automation is net, which consist of cells. Cells change their state in the discrete moments in according to the law in the dependence of past element state and its closest neighbors by net.

- Correlations for crystallization.

At every step by time mass transfer are presented by following law:

a) correlations for amorphous iron phase:

$$C_{ij}^{(n+1)} \to C_{ij}^{(n)} + \frac{1}{m}\left(\left\langle D_{kl}^{(n)} C_{kl}^{(n)} \right\rangle - D_{ij}^{(n)} C_{ij}^{(n)} \frac{p}{6} \right), \tag{11}$$

where $(k,l) \in O(i,j)$ – cells of near neighborhood; $D_{ij}^{(n)}$ – the diffusion coefficient; m – parameter, characterized by discretization of time and space; $\left\langle D_{kl}^{(n)} C_{kl}^{(n)} \right\rangle$ – the middle value of multiplying of diffusion coefficient to the concentration in the near neighborhood cells,

$$\left\langle D_{kl}^{(n)} C_{kl}^{(n)} \right\rangle = \frac{1}{6} \sum_{k,l} D_{kl}^{(n)} C_{kl}^{(n)} \ ;$$

p – parameter, characterized amorphous degree of the near neighborhood cells,

$$p = \frac{\sum\limits_{k,l} D_{kl}^{(n)}}{D_{ij}^{(n)}} \ .$$

b) correlations for crystalline iron phase:

$$C_{ij}^{(n+1)} \rightarrow C_{ij}^{(n)} + \frac{D_{ij}^{(n)}}{m} \left(\left\langle C_{kl}^{(n)} \right\rangle - C_{ij}^{(n)} \right), \qquad (12)$$

where $\left\langle C_{kl}^{(n)} \right\rangle$ – the middle value of the concentration in the near neighborhood cells,

$$\left\langle C_{kl}^{(n)} \right\rangle = \frac{1}{6} \sum_{k,l} C_{kl}^{(n)} \ .$$

- Correlations for melting
a) correlations for amorphous iron phase:

$$C_{ij}^{(n+1)} \rightarrow C_{ij}^{(n)} + \frac{1}{m} \left(\left\langle D_{kl}^{(n)} C_{kl}^{(n)} \right\rangle - D_{ij}^{(n)} C_{ij}^{(n)} \frac{p}{6} \right) + q\Delta T \frac{n_{cr}}{6} \ , \qquad (13)$$

where ΔT – the difference of current temperature and melting temperature,

$$\Delta T = T_{ij}^{(n)} - T_{melt} \ ;$$

q – the coefficient of crystallization (melting), which suggests melting kinetics;
n_{cr} – the number of crystalline cells of near neighborhood of *(i,j)*-cell ($n_{cr} \le 6$).
b) correlations for crystalline iron phase:

$$C_{ij}^{(n+1)} \rightarrow C_{ij}^{(n)} + \frac{D_{ij}^{(n)}}{m} \left(\left\langle C_{kl}^{(n)} \right\rangle - C_{ij}^{(n)} \right) - q\Delta T \frac{n_{am}}{6} \ ; \qquad (14)$$

n_{am} – the number of amorphous cells of near neighborhood.
The change of temperature is described by following equation:

$$T \rightarrow T + \Delta T \ , \qquad (15)$$

where ΔT – temperature increment.
The parameters of mathematical model, such as D_0, *a*, *b*, *q*, are determined accordingly experimental data. Optimal temperature of the Fe-nanothread formation is 365ºC. The formation of the nanothread with diameter about 3 nm is observed. It is well-defined in porous center. The nanothread melts when temperature is risen. A nanothread fragmentation is observed when temperature equals 385ºC, and the nanothread solves fully when temperature is above or equal 400ºC. Therefore the optimal temperature range, that supports the nanocomposite formation, is 350÷375°C. Temperature of Fe-nanocluster melting is defined, it is equal 370°C.
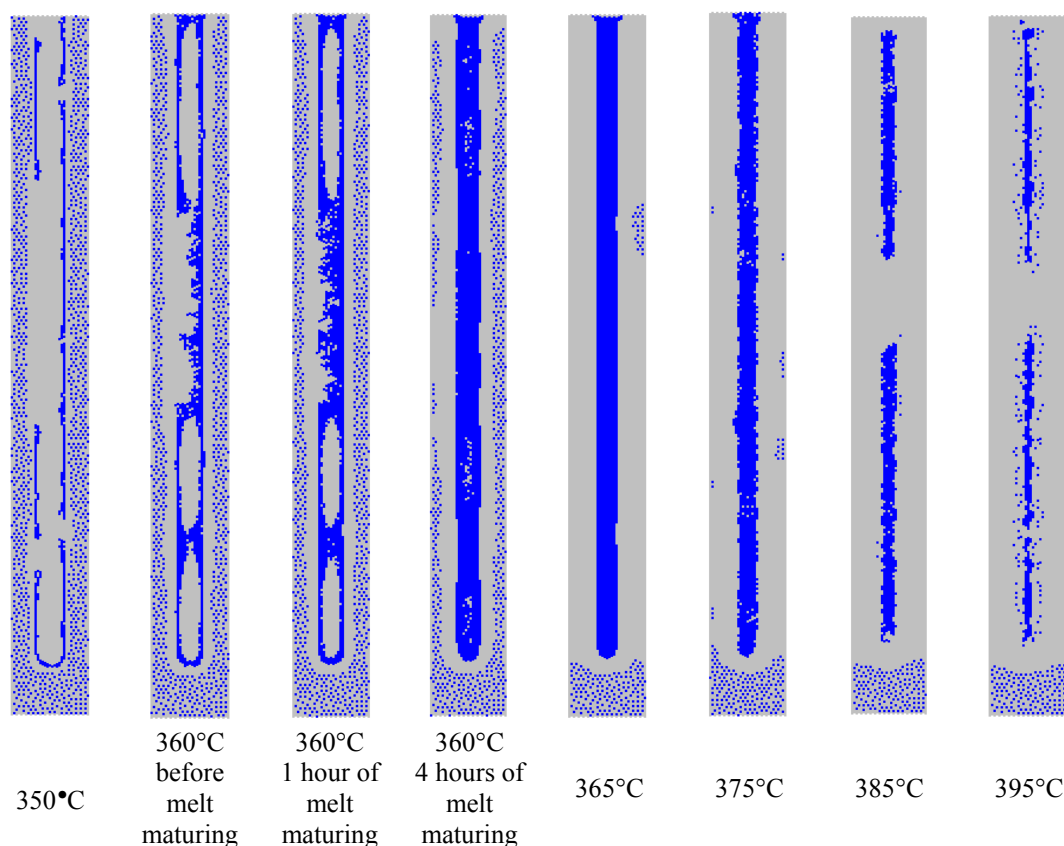
| 350°C | 360°C before melt maturing | 360°C 1 hour of melt maturing | 360°C 4 hours of melt maturing | 365°C | 375°C | 385°C | 395°C |

Fig. 3. Calculated pictures. Formation and melting of nanothread.

5. Conclusions

Mathematical models were developed in this work, which gives representation about phenomena and processes taking place during crystallization in different mediums. The cellular automata model allows monitoring the evolution of crystal formation and solid-melt interface motion.

There are investigations of physical-chemical phenomenon of crystal growth, glass crystallization and Fe-crystallization in porous of SiO_2-matrix in this work. Results are definition of optimal composition for clear glass producing, definition of optimal process parameters for producing of nanomaterials with given properties on the basis of calculated data.

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