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Influence of Microwave Radiation on Growth of Calcium Sulphate Crystal by Monte Carlo Method

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Microwaves are widely used in synthesis of biomaterials. Many experiments show that the crystal shape of biomaterials with microwave synthesis is quite different from the one with conventional method under the same crystal conditions. In this paper, we analyze the influence of microwave radiation on calcium sulphate crystal growth by Monte Carlo method and explain the reason for difference of shape. The results show microwave can deduce the surface tension and viscosity so as to influence the crystal growth and shape.

Key Words: Biomaterials, Microwave, Calcium sulphate crystal, Shape, Monte Carlo method.

INTRODUCTION

Currently, microwaves are widely used in synthesis of biomaterials. As a novel method of processing, the microwaves synthesize the biomaterials in a shorter time as well as improving the physical and mechanical properties of the final material[1-5]. Many experiments show that the crystal shape of biomaterials with microwave synthesis is quite different from the one with conventional method under the same crystal conditions[6-9]. It is reported that the shape of calcium sulphate crystal with microwave synthesis is quite different from the one with conventional method under the same crystal conditions, such as supersaturation, temperature and hydrodynamics of solution[8]. The scanning electronic microscope (SEM) of the calcium sulphate crystal are shown in Fig. 1. The obvious difference of crystal shape can be seen in Fig. 1. The calcium sulphate crystals look like sheet with water bath heating, but they look like needle with microwave heating. However, the orientation of crystal growth is agreement at the two different methods.

In this paper, the influence of microwave radiation on calcium sulphate crystal growth by Monte Carlo (MC) method is analysed and explained the reason for difference of shape. The results show microwave can deduce the surface tension and viscosity so as to influence the crystal growth and shape.

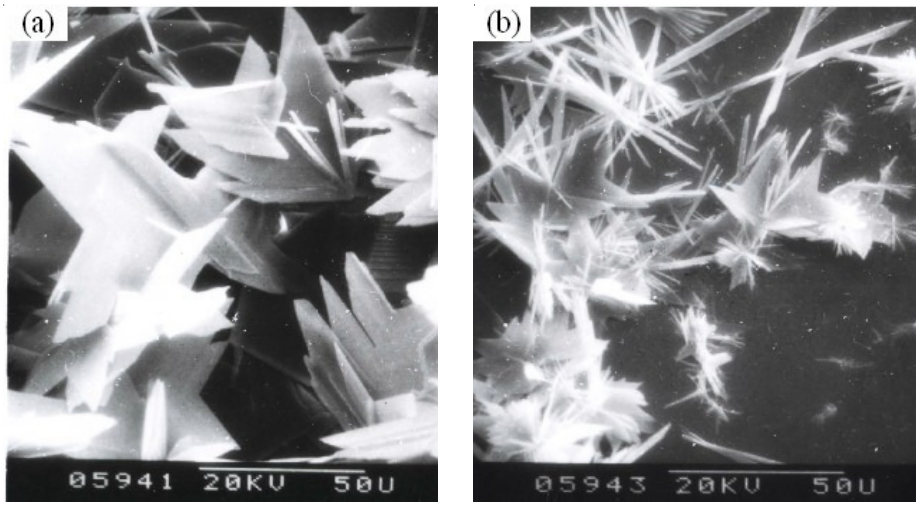

Fig. 1. SEM photos of calcium sulphate crystal (a) water bath method (b) microwave method

ANALYSIS FOR DIFFERENCE OF CRYSTAL SHAPE BY MONTE CARLO METHOD

Analysis for Nucleation theory

According to nucleation theory[10], nucleation rate per volume is described as:

$$I = \frac{D}{R_d^2} n^{-\Delta G^*/KT} \tag{1}$$

D is the diffusivity of granule, R_d is the space between granules, ΔG^* is activation energy and n is the concentration of granules. K is the Boltzmann constant, T is the temperature.

$$\Delta G^* = \frac{16\pi\sigma^3 V^2}{3[KT\ln(a/a_0)]^2} \tag{2}$$

In this formula, a/a_0 equals to supersaturating, σ is surface tension of water, approximately, we consider as the pure water. D is the diffusivity of granule, which can be written as:

$$D = KT/6\pi\eta r \tag{3}$$

η is viscosity coefficient of solution, r is radius of granule. The critical nucleus radius R^* can be expressed as follows:

$$R^* = \frac{-2\gamma}{\Delta G_V} \tag{4}$$

Here, γ is surface energy per area of nucleus, which value is equal to σ. V is the volume for nucleus. ΔG_V denotes the superfluous free energy of volume.

Liquid state water is considered as keeping the short distance order but the long distance disorder, it is quasi-crystal lattice system[11]. According to this theory, the water surface tension can be written as:

$$\sigma = \frac{0.3^2|U|}{N_A}\left(\frac{N_A\rho}{M}\right)^{2/3} \tag{5}$$

Here, |U| is the absolute value for internal energy of solution, ρ is density of liquid, N_A is Avogadro number and M is molar mass.

Meanwhile, according to Eyring viscosity theory[12], the relation of viscosity to internal energy of solution is described as:

$$\eta = C\exp\left(\frac{|U|}{KT}\right) \tag{6}$$

Here, C is the constant. From eqns. 1-4, the reduction of viscosity and surface tension will lead to the increment of nucleation rate. The reduction of surface tension will lead to the drop of the critical nucleus radius. According to eqns. 5 and 6, meanwhile, we also find that the surface tension and viscosity study are both related to the internal energy of liquid. So, we consider the change of internal energy of liquid under the microwave radiation by Monte Carlo method.

The effect of microwave on water as the addition of the alternating electric field and magnetic field was considered. Because the external magnetic and electric potential energy is smaller than others energy, they can be neglected in order to simplify the calculation while error caused by this approximation is acceptable. As water is antimagnetism material, the internal energy is approximately considered as the addition of kinetic energy, the L-J potential energy, electric dipole-electric dipole potential energy, induced electric dipole - induced electric dipole potential energy, magnetic dipole-magnetic dipole potential energy and induced magnetic dipole- induced magnetic dipole. The internal energy of water can be written as follows:

$$< u >= \frac{3}{2}N_A KT + \sum_{i=1,j=1,i\neq j}^{N}\left\{\begin{array}{l} 4\zeta\left[\left(\frac{\varsigma}{r_{ij}}\right)^{12}-\left(\frac{\varsigma}{r_{ij}}\right)^{6}\right]-\frac{1}{r_{ij}^6(4\pi\varepsilon_0)^2}\left(\frac{2\vec{\mu}_i^2\vec{\mu}_j^2}{3kT}+\alpha_i\vec{\mu}_j^2+\alpha_j\vec{\mu}_i^2\right)+ \\ \frac{\mu_0}{4\pi r_{ij}^3}\left[\vec{m}_i\cdot\vec{m}_j-3\frac{(\vec{m}_i\cdot\vec{r}_{ij})\cdot(\vec{m}_j\cdot\vec{r}_{ij})}{r_{ij}^2}\right] \end{array}\right\} \tag{7}$$

Here, ζ is energy parameter, ς is geometrical parameter. We consider the solution as pure water, ς = 0.2791 nm and ζ/K = 423.4 K[13]; μ_0 means the permeability in vacuum. ε_0 means the permittivity in vacuum.

$$\mu_j = \alpha_j\varepsilon_0\vec{E}_e \qquad \alpha_j = \alpha_i = 15.9\times10^{-31}\,m^3 \tag{8}$$

$$\vec{m} = \frac{\chi}{n}u_0\vec{B}_e \qquad \chi = -0.163\times10^{-9}\,m^3mol^{-1} \tag{9}$$

where, $\vec{E}_e$ is vector electric field, $\vec{B}_e$ is vector magnetic field.

Simulation method

Because of the limitation of memory and computing speed, a real macroscopical system can not be directly analogized. However, in order to obtain the accurate feature of the real macoscopical system, the small system is adopted, which is considered as a central cell and is enclosed by other same structural cells to form an infinite three-dimensional lattice. When a molecule passes through the central cell, it is considered that this molecule entries to the central cell in the opposite surface. All the calculation and movement are done inside the central cell. At the same time, the effect of the cells adjacent to the central cell is considered. Metropolis importance sampling[14] is used to calculate potential energy, which means that the new configuration can be acceptable only when the potential energy u_n of this configuration is less then the anterior potential energy u_0 or the value $\exp\left(-\frac{u_n - u_0}{KT}\right)$ is bigger than a random number.

In our calculation, the interaction energy can be ignore when the molecule space between longer than 0.635nm. In this way, the calculation time will be reduced and the precision can be kept in the large ensembles problem. It is reason that the energy corrected by the dispersive and dipolar action is smaller than 5 % in this situation. At the same time, trial configuration will be hold back when the molecule space in between less than 0.635 nm.

Program processing: N1 = 50000 cycle-indexes are run first to smooth out the statistical fluctuation; Then the average value of internal energy can be obtained by running N2 = 70000 cycle-indexed again, on the assumption that the maximal distance a molecule can move in one step is less than 0.014 nm. The program consists of the following modules: data-input, configuration-generation, internal energy-calculation and data-output. The electromagnetic fields inside the reaction beaker used to prepare the calcium sulphate crystal by microwave are calculated by FDTD method. The Fig. 2 shows the calculation model.

Then the breaker area is divided into ten segments. The electromagnetic fields in each segment are averaged to represent the real electromagnetic field in this segment. On the assumption that the time-harmonic electric field of each segment can be expressed as $\overline{E}_m \cos\left(\frac{2\pi}{f}t + \varphi\right)$, where f is the frequency and its value is 2.45 GHz; $\overline{E}_m$ is the mean value of the electric field amplitude; φ are the phases.

As a simplification, in each segment, φ is considered from 0 to 2 π and the time step is selected as one tenth of the microwave period. Thus ten electromagnetic field values can be obtained in each segment. Each of the ten E-field values are input in the program and accordingly five internal energy values can be obtained. The average of these ten internal energy values represents the real internal energy of the segment.

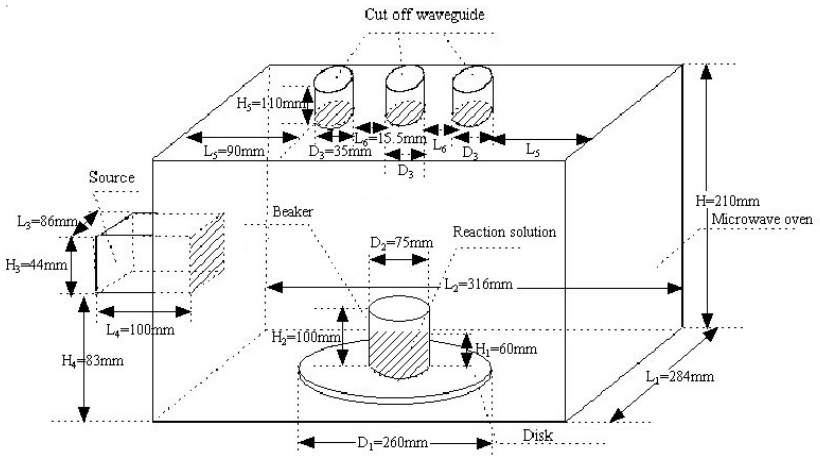

Fig. 2. The FDTD model

The process-flow chart as follows:

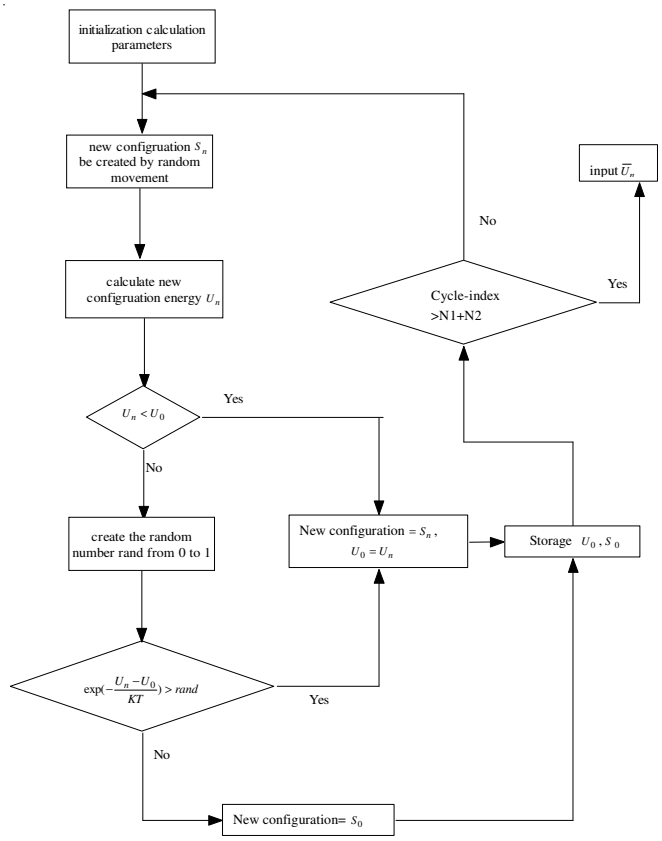

Fig. 3. Process-flow chart by Monte Carlo method

Simulation results

By calculation, we can obtain the absolute value for internal energy of each segment as Table-1

TABLE-1
THE INTERNAL ENERGY OF EACH SEGMENT

Segment No.	1	2	3	4	5	6	7	8	9	10
A	714.77	1148.16	1237.84	1423.92	1842.96	1941.48	2010.73	2130.72	2159.94	2366.22
B	2.318	2.318	2.317	2.316	2.319	2.320	2.317	2.317	2.318	2.320

$A = |\bar{E}_m|(V/m)$ $B = |U|10^4 J/mol$

*Annotate: The absolute value for internal energy is 2.321 10^4 J/mol when $|\bar{E}_m|$ equal to zero.

As we can see from Table-1, the absolute values for internal energy both are drop. So, it will lead to the drop of the critical nucleus radius and increase of nucleation rate. Then it results in the shape of crystal become smaller.

Conclusion

The shape of calcium sulphate crystal with microwave synthesis is quite different from the one with conventional synthesis under the same crystal conditions. The differences of crystal shape can be considered that the crystal growth can be influenced by microwave radiation by Monte Carlo method simulation. Microwave should be a good method for control the size of the crystal.

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