Two-scale model of hydrothermal synthesis of nanotubes

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Abstract. The hydrodynamic two-scale model of hydrothermal synthesis inorganic nanotubes is proposed. The model, which proposed at this paper is consist from two scale of parameters: micro and macro. The macro parameters are: distribution of temperature, velocity and concentrations. The distribution of concentration is binds two scales. Boundary conditions for micro-scale is concentration, which calculated from macro-scale parameters.

1. Introduction
Hydrothermal synthesis is one of the methods for synthesis nanotubes. The main characteristics of hydrothermal synthesis are distribution of velocity, temperature and concentrations. Different configuration of these characteristics determines the efficiency of synthesis. Authors have autoclave in his laboratory. This experimental setup allows investigating early step of creation nanotubes. Understanding of these processes can help create configuration of characteristics for more efficient synthesis of nanotubes. In this work a model of the formation and evolution of the ensemble nanotubes formed from particles of compounds with a layered structure is described. The nanotube source is a system consisting of crystalline nanoplates which have a layered structure having and distributed in the liquid. Crystals consist of double strained layers. Due to intercalation of the liquid occurs delamination between the layers of the outer layers. Delaminated layer is twisted in nanotube for intervals that are small in comparison with the time of diffusive growth. Internal elastic stresses in nanotube less than in the layer, which determines the energy gain nanotube rolling process.

2. Hydrodynamic model of nanotubes hydrothermal synthesis
Two-scale model of hydrothermal synthesis of nanotubes in autoclave is proposed for estimation characteristics of process. The macro-scale process includes the thermal convection of liquid, due to heating of autoclave wall, heat transfer and diffusion of chemical components dissolved in the liquid. Distribution of velocity, temperature and concentrations obtained in macro-scale model let us to describe the nano-scale processes - diffusion evolution of nanotube ensemble [1-6]. The concentrations, calculated in macro-model use in nano-model as boundary conditions on infinity. In the other hand, the summary mass flow on the nanotubes in some small volume is the mass source in diffusion equation of macro-scale model.
3. Evolution of nanotubes ensemble

Let us characterize the individual nanoplates its characteristic diameter $L_p$ and thickness $H$. Distribution of nanoplates according to the diameter and thickness of each time moment is characterized by function $f_p\left(L_p, H, t\right)$. We characterize the individual nanotube by its length $L_T$ and cross-sectional area $S$ (excluding the area of the inner hole). Distribution of nanotubes at lengths and cross-sectional area at any given time has a density $f_T\left(L_T, S, t\right)$.

Diffusive growth (dissolution) of nanoplates and nanotubes determined to transport of substances to their surfaces through the liquid phase. Density solutes $\rho$ at each time can be determined from the macroscopic model. We assume that the equilibrium concentration of solute on the solid phase density $\rho_e$ is a function of the surface energy of the strained layer. Elastic energy density in the plates exceeds the energy density of the mechanical stresses in the nanotubes. Reducing the strain and, accordingly, mechanical energy, is driving the twisting of nanotubes. Note that in this discussion we will assume that the mass transfer between the solid and liquid phase occurs in the diffusion mode, i.e. neglect kinetic effects of dissolution and precipitation of substances on the surface.

Rate of change of plate and nanotubes sizes by diffusive mass transfer is determined by the density gradient in the vicinity of the boundary, which is as a boundary value of the normal derivative of the solution corresponding to the external (for nanotubes) of the Dirichlet's problem. The calculated value of the normal derivative boundary density let us to determine the mass flow density $j$ on the boundary and the normal velocity of the interface $V$:

$$ j = -D \frac{\delta \rho}{\delta N} \sim \rho_e - \rho, \quad V = \frac{j}{\rho_m}, \quad (1) $$

where $D$ is the diffusion coefficient of the solute, $\rho_e$ is the equilibrium solute concentration on the solid surface, $\rho_m$ is the density of nanoplates and nanotubes matter. We assume that this is the equilibrium concentration of the energy density of the strained layer:

$$ \rho_e = \rho_e^0 \left(1 + \gamma \epsilon^2\right), \quad (2) $$

where $\rho_e^0$ is the equilibrium density on the surface of the unstrained layer, $\epsilon$ is the density of elastic energy of strained layer, $\gamma$ is a constant.

Elastic energy density for nanoplates is greater than the corresponding energy for nanotubes. Reducing the strain and, accordingly, the elastic energy is the driving force for twisting of the flat layer and forming of nanotube. We assume that the mass transfer between the solid and the liquid phase takes place in the diffusion regime (we do not take into account the kinetic effects on the surface of nanoplates and nanotubes).

Density of elastic energy for double layer with the thickness $\delta$ and radius of curvature $r$ may be expressed as:

$$ \epsilon = \frac{E \delta^3}{24} \left(\frac{1}{r} - \frac{1}{R_0}\right)^2, \quad (3) $$

where $R_0$ is the equilibrium radius of curvature of the layer, $E$ is the Young's modulus. Nanoplatelets energy density is
The energy density on the side surface of nanotube is

$$e_R = \frac{E\delta^3}{24R_0^2},$$

(4)

The energy density on the side surface of nanotube is

$$e_R = \frac{E\delta^3\left(\frac{1}{R} - \frac{1}{R_0}\right)}{24} \approx \frac{E\delta^3h^2}{24R_0^2},$$

(5)

where $h$ is the wall thickness of the nanotube. The average value of the elastic energy density at the end of the nanotube may be calculated as

$$\bar{e} = \frac{1}{h} \int_{R-h}^{R} e(r)dr \approx \frac{E\delta^3}{192R_0^4}.$$

(6)

We can see, that $\bar{e} < e_R << e_p$.

The evolution of the density distribution of plates and nanotubes size is described by the kinetic equations:

$$\frac{\partial f_p}{\partial t} + \frac{\partial}{\partial L_p} \left(V_{L_p} f_p\right) + \frac{\partial}{\partial H} \left(V_H f_p\right) = v \left[ f_p \left(L_p, H + a, t\right) - f_p \left(L_p, H, t\right)\right],$$

where $a$ is the thickness of the double layer, $v$ is the frequency of double layers of peeling from the plate, $\delta(x)$ is the Dirac’s delta-function, $V_Z$ is the rate of change of the parameter $Z$ due to the diffusion associated with the above-mentioned normal derivative of the density. Source the right side of equation for $f_p$ describes the occurrence of nanotubes delamination by double layers of nanoplates and subsequent twisting of nanotube. By specifying the initial distribution of the size of the plates, and assuming that the nanotubes absent at the initial moment, we obtain the temporal evolution of the size distribution of nanoplates and nanotubes. Calculations show that over time the nanotubes receive approximately the same radius $R$ with approaching to the the equilibrium radius $R_0$.

Calculation results correlated with the available experimental data on hydrothermal synthesis hydrosilicate nanotubes. Namely, there is an increase in the proportion of nanotubes having a diameter close to the equilibrium that is obtained in this model.

4. Model of macro-scale process
To describe the macro-scale hydrothermal synthesis is convenient to use the Navier-Stokes equations supplemented by the heat equation. The process which described by this system is named free convection. Those equations are allowed to evaluate distribution of temperature and velocity from initial condition.
\[
\begin{align*}
\rho \left[ \frac{\partial V}{\partial t} + (V \cdot \nabla)V \right] &= -\nabla p + \eta \nabla^2 V + \frac{1}{3} \eta \nabla (V \cdot V) + \rho g, \\
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho V) &= 0, \\
\frac{\partial T}{\partial t} + V \cdot \nabla T &= \lambda \nabla^2 T;
\end{align*}
\]

where \( V \) – velocity vector; \( p \) – pressure; \( T \) – absolute temperature of the fluid; \( \rho \) – density; \( \eta \) – dynamic viscosity; \( \lambda \) – thermal conductivity; \( c \) – specific heat; \( t \) – time; \( g \) – acceleration of free fall.

The first equation of this system at general case may be rewrite as:

\[
\frac{\partial V}{\partial t} = \eta \nabla^2 V - (V \cdot \nabla)V - \nabla p + f
\]

where \( f \) - is the body force such as gravity or buoyancy.

This equation can be split into two parts (assuming a uniform distribution of pressure):

\[
\begin{align*}
\frac{\partial V_1}{\partial t} &= \eta \nabla^2 V + f \\
\frac{\partial V_2}{\partial t} &= -(V_1 \cdot \nabla)V_2
\end{align*}
\]

The first part is diffusion and describing by eq(10). This equation can be solved by relaxation method. The second part is advection and describing by eq(11) can be solved by MacCormack method, which consist of two steps the first one is predictor and the second one is corrector.

In our case the second equation of system can be rewrite as:

\[
\nabla \cdot V = 0
\]

Using the Helmholtz decomposition this equation can be split into the following form:

\[
V = V' + \nabla \varphi
\]

where \( \varphi \) is a scalar field.

If we apply the gradient operator to both sides we obtain:

\[
\nabla \cdot V = \nabla^2 \varphi
\]

This is a Poisson equation and it can be solved by multigrid method.

The implementations of these methods allow creating a good instrument to get distribution of temperature and velocity. At fig. 1 is presented visualization of the fields of velocity vectors. The data also can be saved at a text document for following calculated. At fig. 2 is presented visualization of the isotherms for natural convection.

The future step to developing this model is an implementation of equation for concentration which will allow binding macro- and micro-scales.
5. Conclusion
At the paper described the principles of modelling hydrothermal synthesis of nanotubes by two scale model. This way of modelling can allow to estimate many important parameters for hydrothermal synthesis in practice. Also it can help to find the best parameters for synthesis nanotubes with defined configuration.

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