Diffusion controlled evolution of nanorolls ensemble

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Abstract

Present paper is devoted to the construction of the model of formation and evolution of nanorolls from compositions with layered structures and to experimental justification of the model. The dynamics of formation and diffusion growth of nanorolls in hydro-thermal medium is considered. The source of nanorolls is a system of nanoplates distributed in the fluid. Intercalation lead to separation of the upper layer which transforms to nanoroll. This transformation takes very small time in comparison with the time of the diffusion growth.

1 Introduction

Nanorolls are a wide class of nanotubes of different morphology. Its form as a nanoheterostructures [1, 2] or by rolling layers of nanocrystals [7]. Models of nanorolls formation are suggested in [6, 7, 8]. Experimental justification is also made. The models give values of rolling speed, but it is not unique parameter which determines form and size of nanotube [10, 5, 3]. The structure and evolution of nanoplates- the predecessors of nanorolls play an important role. There is also a process of morphological transformation of nanotubes due to recrystallization [12]. For different applications it is important to know not only the the morphology and composition of nanotubes, but also the distribution of nanoparticles in respect to length and diameter. Up to now there is no investigation of influence of synthesis parameters on this distribution.

2 Model description

Let $f_p(L_p, H, t)$ and $f_r(L_r, S, t)$ be the distribution density of plates and rolls, L_p, H are the diameter and width of the plate, L_r, S are the length and the area of the cross-section of the roll. The growth (solution) of the plates and rolls is determined by the mass transport at the surface. The conservation of mass takes place for densities: $\rho_s(t) + \rho_p(t) + \rho_r(t) = \rho_s(0) + \rho_p(0)$. Here

$$\rho_p = \rho_m \int f_p(L_p, H, t) L_p^2 dL_p H dH,$$

$$\rho_r = \rho_m \int f_r(L_r, S, t) L_r dL_p S dS,$$

ρ_m is the density of matter of plates and rolls, ρ_s -density of solute matter. The initial condition is $\rho_r(0) = 0$.

The speed of variation of the length and width of the plate is determined by the gradient of the density of the solute matter, which is related with the boundary value of the normal derivative of the corresponding solution of external Dirichlet problem around any nanoparticle

$$\Delta\rho = 0,$$

$$\rho|_{\partial\Omega} = \rho_e,$$

$$\rho|_{r\to\infty} = \rho_s,$$

We obtain the numerical solution of this problem. Using determined boundary value of the normal derivative of the density one can find the density of the mass flux:

$$j = -D\frac{\partial\rho}{\partial\nu} \sim \rho_e - \rho_s,$$

where D is the diffusion coefficient for the solute matter, ρ_e is the equilibrium concentration of the solute matter at the surface of the solid phase.

This question is analogous to the problem of construction of Dirichlet-to-Neuman map. The normal velocity of particle surface growth V is proportional to the mass flux:

$$V = -\frac{1}{\rho_m}j.$$

In this work we assume the nanoparticles can vary size but keep the shape. We describe the rate of particles size changing using the average normal velocity over the corresponding part of the surface. So $V_{L_p}, V_H, V_{L_r}, V_S$ are the speeds of the corresponding parameters variation due to the diffusion. For example, we use the normal velocity averaged over the edge of the nanotube for calculation of the velocity of nanotube length changing V_{L_r}. We use the normal velocity averaged over lateral surface of the nanotube for calculation of the velocity of nanotube surface changing $V_S = 2\pi R\overline{V}$ (R is the external radius of the nanotube). We assume that ρ_e is a function of the surface density of energy of the stressed layer:

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

where ρ_e^0 is the corresponding concentration for unstressed layer, γ is some constant. Density of elastic energy for nanoplates e_p is greater than the corresponding one for nanotubes. Decreasing of mechanic stress and, correspondingly, the elastic energy is the reason for rolling of flat layers and forming of nanorolls. Note that we use a basic assumption that the mass transfer from liquid to solid state is due to the diffusion only (we don't take into account the kinetic effects of solution and crystallization at the surface).

The energy density for preliminary stressed double layer of width δ' and curvature radius r can be written in the following form:

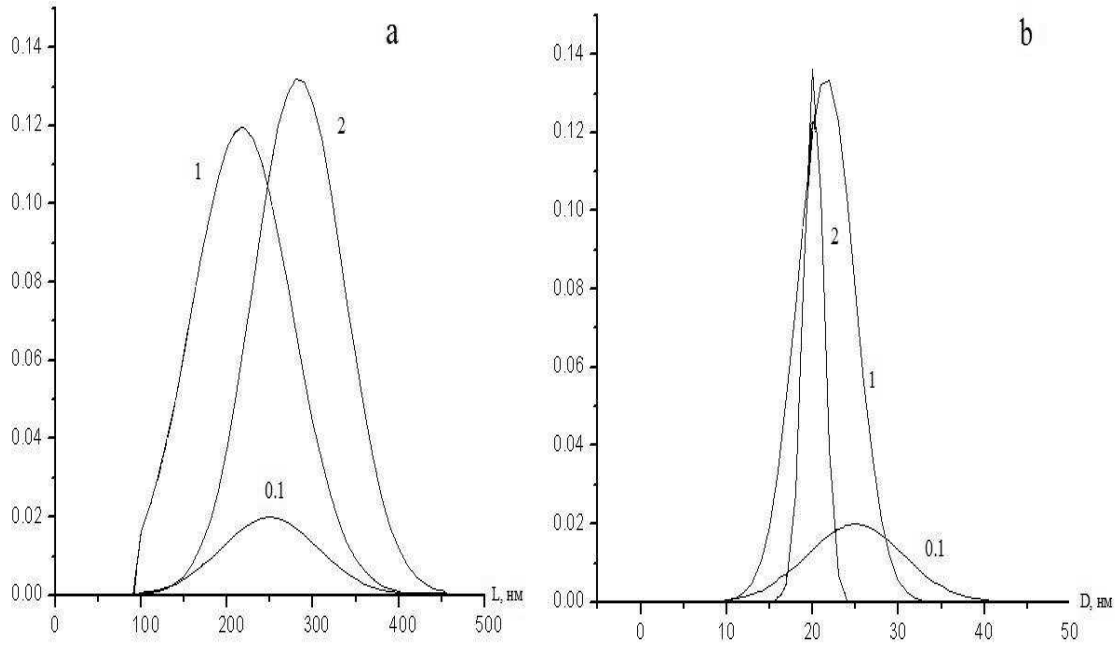$$e_r = \frac{E\delta'^3}{24}\left(\frac{1}{r} - \frac{1}{R_0}\right)^2 \tag{1}$$

Figure 1: Distribution density for nanoplates (a)and nanorolls (b) at the moments of the dimensionless time $\nu t = 0.1, \, 1, \, 2$

where R_0 is the equilibrium curvature radius of the layer, E is the Young constant. The energy density for nanoplate is obtained from (1) when $r \to \infty$:

$$e_p = \frac{E\delta'^3}{24R_0^2}. \tag{2}$$

At the surface of the nanoroll $(r = R$) the energy density is

$$e_R = \frac{E\delta'^3}{24} \left(\frac{1}{R} - \frac{1}{R_0} \right)^2 \approx \frac{E\delta'^3 h^2}{192 R_0^4}. \tag{3}$$

The mean value of the energy density for the cross section of the nanoroll is

$$\overline{e} = \frac{1}{h} \int_{R-h}^{R} e(r) dr \approx \frac{E\delta'^3 h^2}{288 R_0^4}. \tag{4}$$

One can see by comparing of (2), (3) and (4) that

$$e_R \sim \overline{e} \ll e_p$$

The evolution of the distribution density for nanoplates (nanorolls) is determined by the kinetic equations:

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

$$\frac{\partial f_r}{\partial t} + \frac{\partial}{\partial L_r} \left(V_{L_r} f_r \right) + \frac{\partial}{\partial S} \left(V_S f_r \right) = \nu \delta \left(S - a L_r \right) \int_0^\infty f_p \left(L_r, H, t \right) dH,$$

where $\delta(x)$ is the Dirac δ-function, a is the width of the double layer, ν is the frequency of the separation of double layers from a plate.

The terms in the right hand sides of the equations describe the separation of the external layers from plates and the appearance of new rolls (by rolling of these separated double layers).

Computations show that after some moment the nanoplates disappear. As for rolls, they transform to rolls of radius close to the equilibrium one (R_0) [4]. On the Fig.1 we can see the distribution density for nanoplates (a) and nanorolls (b) at the moments of the dimensionless time $\nu t = 0.1, 1, 2$.

Acknowledgements

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