

Formation and Self-arrangement of Nanocomposite Materials via Glass Anneal in Hydrogen

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The process of metal nanoparticles formation in glass during its annealing in hydrogen is studied. On the basis of phase transition theory the strict system of equations describing this process is developed and simulated. The simulation shows that the system has two qualitatively different solutions: continuous distribution of nanoparticles in bulk glass and Liesegang-like layers. The results of the numerical modeling agree well with known experimental data: both types of the distributions have been registered in experiments. The dependence of final nanoparticles distribution on system parameters (initial concentrations, diffusion coefficients) has been analysed.

Keywords: Nanoparticle, Diffusion, Hydrogen, Silver, Glass, Nucleation, Growth, Distribution, Liesegang.

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1. INTRODUCTION

Nowadays, a whole set of papers related to metal nanoparticles, its properties and producing methods is being published annually. The main interest to this topic is caused by wide possibilities for use metallic nanoparticles in various fields of science and technology [1-4], in particular, for the design of optical materials with given properties. Optical characteristics of metal nanoparticles are essentially determined by surface plasmon resonance, which causes strong electric field enhancement in the vicinity of a nanoparticle. This enhancement makes glass-nanocomposites promising materials for such applications as in nonlinear optics sensing and plasmonics. One of efficient methods to produce such composites is the anneal of the glass doped with metal ions in hydrogen atmosphere. This technique is inexpensive and allows producing nanocomposites in large scale. However, today there is no proper physical model, which could correctly describe the formation of particles in glass during in abovementioned process. There are a few papers, in which authors have analyzed process [5-6], but they didn't accounted for the dependence of nanoparticle critical radius on oversaturation and nucleation process which dramatically influence the nanocomposite parameters.

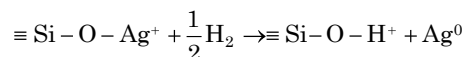
The aim of this study is to construct the correct physical model of nanoparticles formation in glass using phase transition theory, to simulate this process, and to find main dependencies of nanoparticle distribution on the process parameters (diffusion coefficients, initial concentrations of reagents, etc).

2. NANOPARTICLES FORMATION AND ANALYSIS

2.1 Nanoparticles formation

The sample is a slab of glass doped with metal ions (e.g. Ag⁺). It is being subjected to long-term (from minutes to several hours) thermal treatment (250-600

C) in hydrogen atmosphere. Hydrogen diffuses into glass, reduces silver ions via reaction [5]:



When supersaturation of neutral silver becomes critical, phase decomposition of solid solution takes place, this results in the formation and growth of metal nanoparticles. The longer treatment time, the less transparent glass becomes. The absorption of light is caused by nanoparticle surface plasmon resonance. The more processing time, the higher nanoparticle concentration and the bigger their mean radius, consequently, the absorption is stronger.

2.2 Formulation of the problem

As shown earlier [5], process of formation consists of several phases. A schematic view of phases is presented in Fig 1. First one is the placement of the glass doped with silver ions in hydrogen atmosphere at high temperature, the second phase is hydrogen diffusion into glass, third one is ionic silver reduction, and the last one is nanoparticle formation, growth and Ostwald's ripening. All phases occurs in different time scales and influence each other, that is to get correct final distribution of particles all processes should be accounted.

So, let's formulate the equations describing the whole process which involves diffusion and ion exchange in the presence of sinks and sources, nucleation, growth and repining of nanoparticles. There are six entities involved into the process: ionic and atomic silver and hydrogen, ionic sodium, which interacts with ionic silver and ionic hydrogen and influences on their diffusion, and nanoparticles.

The equation for hydrogen:

$$\frac{\partial C_{H^0}}{\partial t} = D_{H^0} \frac{\partial^2 C_{H^0}}{\partial x^2} - k_1 C_{H^0} C_{Ag^+} \quad (1)$$

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where C_{H^0} , C_{Ag^+} are the concentrations of neutral hydrogen and ionic silver, D_{H^0} is hydrogen diffusion coefficient, k_1 is the rate of reduction reaction.

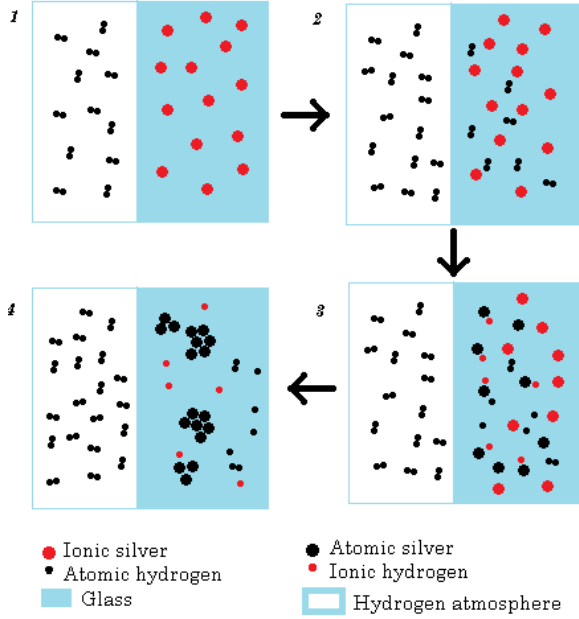


Fig. 1 – Phases of nanoparticles formation

The equation for ionic silver:

$$\frac{\partial C_{Ag^+}}{\partial t} = D_{Ag^+} \frac{\partial^2 C_{Ag^+}}{\partial x^2} - k_1 C_{H^0} C_{Ag^+} + D_{Ag^+} \frac{\partial \left(C_{Ag^+} \frac{\alpha \nabla C_i}{1 - \alpha C_i} \right)}{\partial x} \quad (2)$$

where C_i is total concentration of ionic silver and sodium, D_{Ag^+} , D_{H^+} are diffusion coefficients of ionic silver and hydrogen, respectively, $\alpha = 1 - D_{Ag^+} / D_{H^+}$. We assume that silver and sodium diffusion coefficients are

$$\frac{\partial C_{Ag^0}}{\partial t} = D_{Ag^0} \frac{\partial^2 C_{Ag^0}}{\partial x^2} + k_1 C_{H^0} C_{Ag^+} - k_2 C_{Ag^0} \ln \xi \frac{4\pi}{3\omega} R_{cr}^3 \exp\left(-\frac{k_3}{\ln^2(\xi)}\right) - \int_0^\infty 4\pi R^2 V_r N dR \quad (5)$$

where k_2 and k_3 are nucleation rate and a kind of nucleation activation parameter, respectively.

The last equation is the equation of continuity in space of sizes for particle size-distribution function N . It describes nanoparticle growth and formation [9]:

$$\frac{\partial N}{\partial t} + \frac{\partial}{\partial R} N V_r = k_2 C_{Ag^0} \ln \xi \exp\left(-\frac{k_3}{\ln^2(\xi)}\right) \delta(R - R_{cr}) \quad (6)$$

where the right part describes the nucleation of particles of critical radius R_{cr} .

We solved one-dimensional problem, and the boundary and initial conditions were chosen as follows:

$$\begin{aligned} x=0, t: C_{H^0} &= C_1; \frac{\partial C_{Ag^+}}{\partial x} = \frac{\partial C_{Ag^0}}{\partial x} = \frac{\partial C_{Na^+}}{\partial x} = \frac{\partial N}{\partial x} = 0 \\ x=\infty, t: C_{H^0} &= 0; C_{Ag^+} = (1-\eta)C_0; C_{Ag^0} = N = 0; C_{Na^+} = \eta C_0 \end{aligned}$$

equal. This simplifies the equation and allows writing it in the form (2). This equation is very similar to equation (1). As shown in [5], third term in the right part of the equation (2) is responsible for self-consistent diffusion process of hydrogen, sodium and silver ions.

The equation for ionic sodium:

$$\frac{\partial C_{Na^+}}{\partial t} = D_{Na^+} \frac{\partial^2 C_{Na^+}}{\partial x^2} + D_{Na^+} \frac{\partial \left(C_{Na^+} \frac{\alpha \nabla C_i}{1 - \alpha C_i} \right)}{\partial x}, \quad (3)$$

where C_{Na^+} is the concentration of sodium, D_{Na^+} is sodium diffusion coefficient. Sodium doesn't participate in reduction reactions, but affects the distribution of ionic silver and hydrogen since it is charged.

The equation for particle critical radius, at which it becomes stable, can be found in [7]:

$$R_{cr}(\xi) = \frac{2\gamma\omega}{k_B T \ln \xi} \quad (4)$$

where γ is the coefficient of surface tension, ω is atomic volume of silver, $\xi = C_{Ag^0} / S$ is supersaturation of the solid solution of neutral silver in glass matrix, S is the solubility of neutral silver in glass.

Equation for atomic silver is more complicated than the previous equations: it accounts for diffusion, reduction of silver, formation of nanoparticles and their growth, respectively. As it was shown in [8], nucleation rate of particles (third term of equation (5)) depends on several parameters: supersaturation, temperature, particle surface tension, and others. We consider particle growth due to diffusion flux, and, as shown in [5,9], the growth rate can be described by the formula $V_r(R) = \partial R / \partial t = D_{Ag^0} (C_{Ag^0} - S(1 + 2\gamma\omega / k_B T R)) / R$,

where R is particle radius. So, finally equation for neutral silver is:

$$x, t = 0: C_{H^0} = 0; C_{Ag^+} = (1-\eta)C_0; C_{Ag^0} = N = 0; C_{Na^+} = \eta C_0$$

where x is the distance from the glass surface, C_1 , C_0 are constants, η is the relation of silver and sodium concentrations.

Boundary conditions at $x=0$ (the surface of the glass) satisfy the condition that hydrogen concentration is constant (C_1) and there is no flux of other species through the glass surface. Penetration depth of hydrogen into glass equals to several hundred nanometers, whereas the sample thickness lays in the range of millimeters. So, the boundary conditions at the second surface of the glass describe initial glass, unaffected by diffusion processes. Initially ionic silver and ionic sodium are distributed uniformly in the volume of glass, nanoparticles and atomic silver are absent. Hydrogen is present only at the surface of the glass.

2.3 Parameters, used for modeling

Known parameters (such as diffusion coefficients, surface tension and others) were chosen according to [5] and presented in Table 1. Diffusion coefficients are still not well defined experimentally and dramatically dependent on temperature, so they have been varied with-

Table 1 – Parameters used for modeling

D_{Ag^+} nm ² /sec	D_{H^0} nm ² /sec	D_{Na^+} nm ² /sec	D_{Ag^0} nm ² /sec	$\frac{\gamma\omega}{k_B T}$, nm	C_1 nm ⁻³	C_0 nm ⁻³	k_1 nm ³ /sec	k_2 sec ⁻¹	k_3
10-10 ³	10 ²	10-10 ³	1-10 ²	0.5-5	0.5-10	0.01-0.3	10 ⁻⁵ -10 ⁻²	10 ⁻⁵ -10 ⁻¹	0.1-50

Thus we have a system of equations (1-6) describing the whole process from hydrogen diffusion to nanoparticle growth, and a set of boundary and initial conditions. The system has been solved using finite-difference method.

3. RESULTS AND DISCUSSION

Simulation has shown, that there are at least two qualitatively different solutions of the system: regular distribution of particles and Liesegang-like layers. The difference can be clearly seen in Fig. 2. Simulation has also shown that solutions do not replace one another in the course of time.

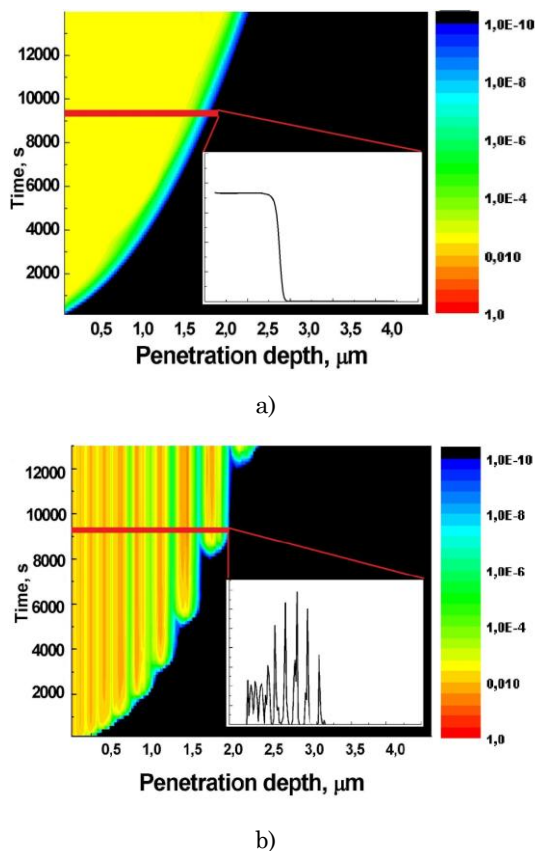


Fig. 2 – Distribution of clustered silver in regular mode (a) and in Liesegang-like mode (b). Color represents the volume fraction of neutral silver concentrated in nanoparticles. Insets demonstrate cross-section view that is the depth dependence of the volume fraction at a given time

in certain limits. Unknown parameters, like coefficients k_1, k_2, k_3 , have been varied in a wide range to understand possible distributions of particles and to provide coincidence of calculated distributions of nanoparticles and known experimental results.

Which of the modes will take place depends on several factors, for example the ratio of nucleation/growth rates, which is defined by the diffusion coefficient of neutral silver and particle surface energy. During the simulations we have found that neutral silver diffusion coefficient greatly affects nanoparticles distribution. Fig. 3 demonstrates the dependence of nanoparticles distribution on D_{Ag^0} . Transition from regular to Liesegang-like mode is well traced. While diffusion coefficient grows, the distance between Liesegang layers increases. It can be easily explained, because particles consume atomic silver faster and from farther distances.

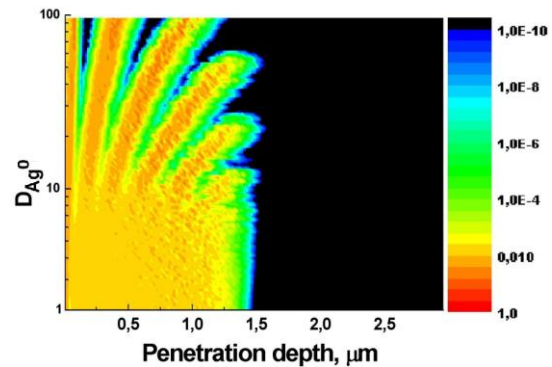


Fig. 3 – Dependence of particle distribution on silver diffusion coefficient. Color represents the volume fraction of neutral silver concentrated in nanoparticles

Particle distribution function for Liesegang-like mode is represented on Fig 4. The fine structure of each layer can be observed. For each layer, its farthest from the surface side consists of larger particles than the nearest one. It can be explained by the fact, that these particles (on far side) consume all atomic silver, located between this layer and the following one. At the same time distances between subsequent layers increase with penetration depth. This behavior is typical for Liesegang structures, and takes places because supersaturation decreases with the distance from the glass surface, and particles in each layer manage to consume silver from longer distances.

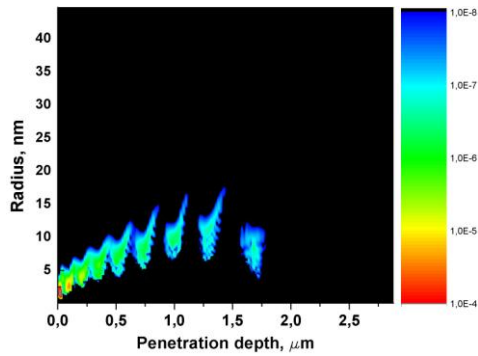


Fig. 4 – Particle distribution function after annealing process. Color represents concentration

Existence of both modes (regular and Liesegang-like) has been earlier observed in experiments [10-12]. We performed a comprehensive analysis of the influence of the system parameters on the final distribution of nanoparticles, however, the format of this article does not permit to describe them all.

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4. CONCLUSION

Annealing of metal-doped glasses in hydrogen atmosphere is a prospective technique to produce glassy nanocomposites, and the model developed allows predicting of the nanocomposite parameters depending of glass matrix properties and the mode of the anneal. Periodic structure of layers differing in their dielectric constants is of interest for applications, in particular if the character scale of such structure is comparable with the light wavelength in the media. This periodicity can be controlled via the conditions of nanocomposite formation. The model proposed provides estimating which mode of nanoparticles distribution takes place: normal mode or Liesegang-like one. The model is in a good agreement with the experimental data.

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