

Modelling the Sublimation-Desublimation Processes for Production of Ultrafine Powders

V. Golubev, A. Dosmakanbetova, and A. Brenner

Abstract—The purpose of this work is to establish the theoretical foundations for calculating and designing the sublimation-condensation processes in chemical apparatuses which are intended for production of ultrafine powders of crystalline and amorphous materials with controlled fractional composition. Theoretic analysis of the primary processes of nucleation and growth kinetics of the clusters according to the degree of super-saturation and the homogeneous or heterogeneous nature of nucleation has been carried out. The engineering design procedures of desublimation processes have been offered and tested for modification of the Claus process.

Keywords—Desublimation, controlled fraction composition, nucleation, ultrafine powders.

I. INTRODUCTION

APPLICATIONS of ultrafine materials in modern industry cover a wide range of technologies [1]. For example, we can identify the following promising directions for progress in chemical industry: producing nano-powders of oxides and dioxides of precious metals for structural, instrumental and functional bio-ceramics; creating sorbents, catalysts and molecular sieves with a given nano-structure; developing nano-powder additives to create suspensions with desired rheological characteristics.

We can distinguish the two main ways for producing nanoparticles, namely: sublimation-desublimation methods and methods of mechanical dispergation. One of the most promising methods for producing ultrafine powder materials that is being intensively developed at present is a condensation-sublimation method. The advantage of this method is in the combination of a high rate of primary nucleation stage with adjustable rate secondary aggregation, i.e. stage of growth of higher orders clusters. Although many methods have been developed today to get the ultrafine powders, it is difficult to identify relatively simple, cost-effective and environmentally friendly way to produce ultrafine powders of various substances. The main problem here is to provide both the necessary stable fractional composition of the material and the given physicochemical characteristics.

The literature review and theoretical analysis showed that the main unresolved methodological issue is the calculation of the characteristic times of various stages of the process that determine the fractional composition of the powder, whereas the main technical problem is to provide the intensive heat

transfer while maintaining control regime parameters, mainly over saturation and temperature [2], [3].

As we have noted above, the general kinetic peculiarity when arising nano-particles is a combination of a high rate of nucleation of the crystalline phase at a relatively low rate of clusters growth. The work of primary clusters formation is the main physical parameter by which the concept of the nucleation process can be formulated [4]. Although the work of cluster formation by itself does not define all the necessary data to calculate the kinetic parameters, however the value of this physical characteristic for the theory is great, since it can be used to determine the concentration of n -size clusters in the old phase which are really in stable or meta-stable equilibrium.

Our purpose here is to submit models which can be applied to engineering methods for calculating desublimation processes in chemical apparatuses for producing ultrafine powders of crystalline and amorphous materials with stabilized fractional composition.

II. ENERGY ANALYSIS OF NEW PHASE PARTICLES EMERGENCE

Creation of the state of the supersaturated old phase is a necessary condition for the first order phase transition, but it is not enough so that the necessary degree of phase transformation has occurred in the specified time.

So the super-saturation degree that is necessary to start the phase transition process, does not guarantee that the process will be realized in this unit with the required efficiency. Ability to remain the supersaturated old phase in the meta-stable state during some time is one of the most remarkable features of phase transitions. The reason for this is that the meta-stable state is separated by the energy barrier from the truly stable state. The appointed energy barrier corresponds to each specific path of the phase transition, and one would expect that the actual path of the process will meet the requirement of the lowest energy expense.

Therefore, the path of a spatially uniform change of the substance density is improbable, because it is coupled to an increase in the Gibbs energy of the system in the significant volume [2].

Another way of phase transition, which is energetically much less expensive, is the inhomogeneous variation of the density of old phase up to a density of the emerging new phase. Indeed, such change occurs locally as the density fluctuation in the spatial region occupied by the small number of molecules. Let $n^* \ll M$ be the characteristic number of molecules in the some local-scale zones with changed density.

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Then we can estimate the expectation value of the energy barrier sufficient for the phase transition as $\Delta E \approx n^* \Delta \mu$, where μ is chemical potential. Obviously, this is much less than the energy barrier for the path corresponding to the uniform density.

Numerous observations and experimental studies suggest that the first order phase transition is really accompanied by the formation of a lot of the nano-scopic germs with a density close to the density of the new phase.

These germs appear randomly in the old phase, and even at a very rapid growth of the new phase germs, the phase transition in the system of macroscopic dimensions drags out. Therefore, the following analysis will be mainly devoted to the consideration of the sequence and temporal stages of the phase transition, as these questions are the bottleneck in terms of methodology for calculating and designing chemical apparatuses for the desublimation processes.

Because a physical theory of this process is far from completion, and it does not give the engineer reliable methods of calculation, we use a heuristic approach based on known fundamental concepts and assumptions that follow from well-known experimental data. One possible way to describe is that nano-scopic new phase nuclei are considered as a group of a certain number of molecules. In this case, we can describe this group as the new phase, which is separated from the old phase by the phase boundary.

Let us consider firstly the process of homogeneous nucleation, where the clusters of a new phase are in the contact only with the old phase of the substance. Let M be the total number of molecules in a given volume before the phase transition, and n is the number of molecules forming a cluster of the new phase. Then, after the formation of the cluster, we have the old phase molecules and the new phase cluster of molecules.

Our analysis of the experimental data of different authors, and the review of theoretical models, allows us to choose the additive law for calculating the free energy of this system [2], [5].

$$G_{sys}(n) = (M - n)\mu_o + G(n) \quad (1)$$

where $G(n)$ is the Gibbs energy of n -order cluster. This approach can be easily justified at a constant temperature of the phase transition, when the chemical potentials of the old phase were held constant during the transition to a new phase.

At the same time it is not correct to rely on the additive law for calculating the Gibbs energy of the new dispersed phase, because the new free phase surface is generated during the phase transition.

Then the Gibbs energy of the system at the phase transition reads;

$$G_{sys}(n) = (M - n)\mu_o + n\mu_{n,n} - (p_n - p)V_n + \phi(V_n) \quad (2)$$

Here $\phi(V_n)$ is the total free energy of the cluster surface, p is the pressure in the bulk phase and p_n is the equilibrium pressure at the condensed phase surface.

Next, we can obtain the following relation for calculating the work of cluster formation;

$$W(n) = -(p_n - p)V_n + (\mu_{n,n} - \mu_o)n + \phi(V_n) \quad (3)$$

Now, using the definition of the chemical potentials we get the expression for the chemical potential of the new phase cluster of n - order (i.e., consisting of n molecules or monomers).

$$\mu_{n,n}(p) = \mu_n(p) + (1/n) \int_p^{p_n} V_n(P) dP \quad (4)$$

From this it follows also the relation between the additional Gibbs energy and the pressure and temperature in the system, what is important to facilitate the engineering calculations:

$$G_{ad}(n) = \phi(V_n) - (p_n - p)V_n + (1/n) \int_p^{p_n} V_n(P) dP \quad (5)$$

For condensed phase clusters we have;

$$G_{ad}(n) = \phi(V_n) + nkT(p_n - p)V_n + (\ln(p_n / p) - (1 - p / p_n)) \quad (6)$$

The total free energy of the new phase surface can be expressed by the surface tension in terms of more convenient for engineering calculations

$$\phi(V_n) = c_n \sigma_n V_n^{2/3} \quad (7)$$

where c_n is the coefficient used for accounting the non-spherical form of clusters.

More detailed studies suggest that these assumptions do not lead to principal errors [4]. According to this approach we obtain the equilibrium pressure at the cluster surface:

$$p_n = p + \frac{2c\sigma}{3} V_n^{1/3} \quad (8)$$

Then if we have the values of total free energy of the cluster surface and the equilibrium pressure, we can calculate the additional Gibbs energy by using the cluster volume or its order

$$G(V_n) = c\sigma V_n^{2/3}, \quad G(n) = a\sigma n^{2/3} \quad (9)$$

Summarizing the results of the analysis of homogeneous nucleation, we obtain relations for calculating the work of clusters formation:

$$W(n) = -n\Delta\mu + a\sigma n^{2/3}, \text{ or} \\ W(n) = -n\Delta\mu + nkT \ln(p_n/p) + \\ \frac{1}{3}c\sigma(kT/p_n)^{2/3}n^{2/3} \quad (10)$$

Fig. 1 depicts the characteristic results of calculating the work of the cluster formation, depending on its order (number of molecules in nuclei). As it can be seen from the figures the work of the cluster formation has a maximum at a certain size of the germ. This allows us to calculate the most likely order of the primary cluster-nucleate in homogeneous nucleation. Potential deviation drops significantly with increasing order of the cluster. This suggests that in the initial stage of the process, the driving force of phase transition is very high, but then in a closed system it quickly falls.

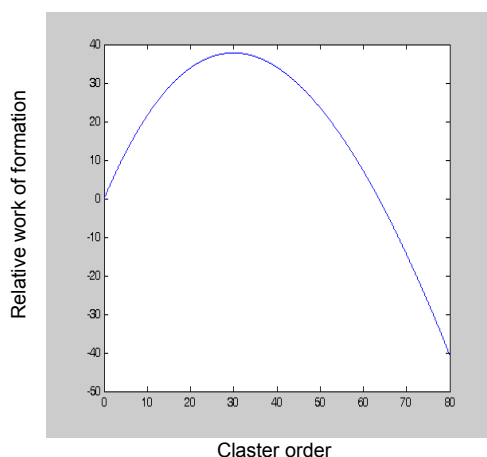


Fig. 1 Characteristic dependence of the relative work of cluster formation on its order

Further we understand the heterogeneous nucleation process as generating of new phase clusters on a cooled substrate. We think that such process organization is most relevant from an engineering point of view.

If G_s is the Gibbs free energy of the substrate on which nuclei are generated, then with accounting of total free energies of the two surfaces, namely: the surface between the cluster of new phase and the old phase and surface between the cluster of new phase and surface of the substrate, we get [5]

$$G(n) = (M - n)\mu_o + G(n) + G_s + \phi_s(n) \quad (11)$$

From the condition of mechanical equilibrium [2], we obtain the formula of Laplace type, but having more general content:

$$p_n = p + d(\phi + \phi_s)/dV_n \quad (12)$$

We can now write the expression for the additional contribution to the Gibbs energy in the form of:

$$G_{ad}(n) = \phi(V_n) - (p_n - p)V_n + \int_p^{p_n} V_n(P)dP \quad (13)$$

Further, we suppose that the total surface free energy of the substrate $\phi_{s,0}$ prior to the formation of the embryo can be written in the form [2]:

$$\phi_{s,0} = \sigma_s A_s \quad (14)$$

In accordance with the usual concept of the wetting [2], we obtain the following expressions for the non-spherical shape of the embryo.

$$\psi(\theta_w) = \frac{1}{4}(2 + \cos\theta_w)(1 - \cos\theta_w)^2 \quad (15)$$

For the work of formation of clusters in this case we obtain;

$$W(R) = \psi(\theta_w) \left[-\frac{4\pi}{3} \left(\frac{\Delta\mu}{kT} - \ln(1 + 2\sigma/pR) \right) (p + 2\sigma/R) R^3 + \frac{4\pi}{3} \sigma R^2 \right] \quad (16)$$

Fig. 2 depicts the results of calculations of the work of clusters formation under the homogeneous nucleation (curve 1) and the heterogeneous nucleation (curve 2) on a substrate.

The graphs show that the work of nuclei formation on the substrate is actually much smaller than the work of homogeneous nucleation; however it less sharply decreases with increasing the super-saturation.

This confirms the conclusion that desublimation on a cooled substrate is optimum. At the same time, here we can meet problems with the purity of the product obtained. Farjoun Y. and Neu J.C. analyzed the growth of clusters in a monomer bath with conserved total monomer density in the small super-saturation limit [3].

The description of late stage coarsening according to the classic Lifshitz-Slyozov (LS) theory [2], [4] is well known in the literature of aggregation, namely: the number of monomers in the largest clusters increases linearly in time, and the density of clusters shrinks as the smaller clusters dissolve back into monomers. But the question left open is the detail description of the aggregation start from pure monomers to clusters formation at time zero.

In the paper [3] the authors predict the cluster size distribution that emerges from the nucleation process, and its long-term limit. In this paper, the solution of the LS equations, with the long-term limit used as an effective initial condition, is tracked to late stage of coarsening.

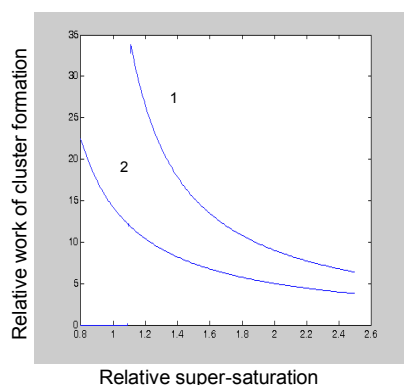


Fig. 2 Relative work of cluster formation as a function of super-saturation

In this way, we obtain a general picture of the whole aggregation process, based on classical modelling ideas due to Becker-Doring, Zeldovich, and Lifshitz-Slyozov [6]. Anyway, after the initial stage the primary nucleation process can not be considered as controlled by the fluctuation kinetics, because a sharp increase in the number of clusters in a closed system leads to a decrease of super-saturation (Fig. 3). As a result, the further growth of clusters occurs only by aggregating the existing clusters with little change in their total mass. Kinetics of this stage of the aggregation process is diffusion-limited (DLA zone).

The result of this stage is the creation of an independent on time spatially uniform distribution of clusters of the dispersed phase by sizes. Decrease in the rate of the process in the late stage creates the preconditions for realizing the kinetic control of the phase transition regime and for regulating the fractional composition of the product by the limited number of governing parameters.

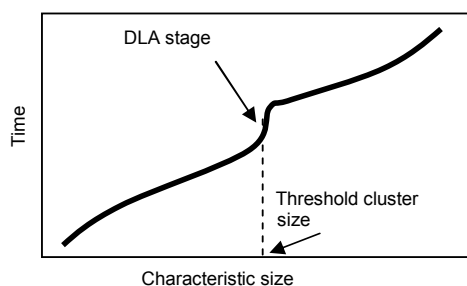


Fig. 3 Stages of nucleation process in the closed system

III. CONCLUSION

Different ways to manage the process of desublimation are known. For example, liquid or solid substances are evaporated at a controlled temperature in an atmosphere of inert gases by low pressure with subsequent condensation of the vapour on cooled surfaces. This method allows obtaining particles of sizes from two to several hundred nanometers. The desublimates obtained by this method, does not have clear particles size distribution, and the appropriate solid phase has

a loose, porous structure. Therefore, such a technical solution does not provide for the dispersion with narrow fractional composition.

The essence of our offers is that control parameters should be changed in strict sequence. In the eutectic point the system will be in the non-variant state. And the composition of the liquid phase varies over the boundary line up to the eutectic point, corresponding to the temperature of crystallization. The system changes, occurring in this zone, promote the crystal growth with different rates, and great fluctuations in chemical composition may be observed. Each particular path, along which a phase transition is going on, corresponds to a certain energy barrier.

As a result, the obtained crystals are significantly different from each other in size. With further decreasing temperature, the system is completely transformed into a crystalline state forming a mechanical mixture of crystals of various sizes. In order to provide the certain fractional composition it is important to cross the dividing line of the phase states, without going into the area of the liquid phase.

Therefore, to avoid the formation of liquid phase, it is necessary to allocate the starting point of the process in the gas phase to the right of the dew point. So, managing the process is carried out in the following sequence.

At first, the vapour pressure reduces smoothly from initial point to the critical point, corresponding to the specific component. Then, the temperature of vapour-gas mixture reduces with high rate under the constant pressure from the point allocated in vapour zone on phase diagram to the point, corresponding to the solid product in the form of ultra-dispersed powder. The process should be finished at the beginning of DLA zone.

This offer was realized for modifying the scheme of Claus process with using the desublimation condenser in the unit of sulphur containing gases final purifying [7]. The proposed offer allowed to reduce the thermal load on the scrubber, obtain portions of the sulphur in the form of fine powder in the solid state, and to increase the degree of sulphur recovery.

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