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THE REGIMES OF THE REALIZATION OF DESUBLIMATION METHOD FOR ULTRADISPERSE POWDER PRODUCTION

Abstract. The paper deals with the investigation of the method of obtaining the ultrafine powders by the desublimationprocess. In the course of the experiments, the effect of temperature, pressure, and degree of supersaturation on the process kinetics and the dispersion size distribution function was investigated.The existence of the stage of the phenomenon of multiple coagulation with a high concentration of nucleates in a supersaturated vapor-gas mixture has been experimentally confirmed. Namely, it was established that with a large initial super-saturation, when a large number of embryos (monomers) of the dispersed phase are rapidly formed per unit volume of the apparatus, the contribution of multiparticle collisions is great. The obtained data may be very important for working out the engineering method for calculating and optimizing the regimes of aggregation processes to create highly homogeneous stable nanodispersions.

Keywords:desublimation, ultradisperse, nanodispersions, method, nano-powders, super-saturation, multiparticle.

1. Introduction

Currently, the use of chemical apparatus and reactors with the formation, aggregation and sedimentation of insoluble phases in the working volume of the apparatus is becoming increasingly widespread, especially in a number of modern technological processes [1-8]. Chemical equipment and reactors in which the formation, aggregation, and sedimentation processes of insoluble phases are carried out, especially in modern thin and nano-technologies, are widely used. In many cases, the processes of chemical technology are accompanied by the formation of a new solid dispersed phase. These can be phase transitions, as in the case of crystallization or desublimation, or processes of formation of slightly soluble substances during chemical reactions [9- 12].

Applications of dispersed media, namely: emulsions, suspensions, ultrafine materials and powders in modern industry cover a wide range of technologies. In particular, the following directions can be distinguished in the chemical industry [1-8]:

- obtaining nanodispersed powders of oxides and noble metal dioxides for structural, instrumental and functional bioceramics;
- creation of sorbents, catalysts and molecular sieves with a given nanostructure;
- development of methods for producing nano-dispersed rheological additives to create suspensions with desired rheological characteristics.

Nano-objects are characterized by small size, complex internal organization, the ability to very dense packaging, strong interactions with neighboring structures; on their basis, it can be created materials with new physical and chemical properties.

The most important features of the processes associated with dispersed media is the need for highly homogeneous and stable dispersions. These indicators play an extremely important role in modern pharmacopoeia, the production of high-quality fuel materials and in many other processes.

For the preparation of nano-powders with a high homogeneity of the fractional composition, desublimation methods seem to be very promising. The production of nano-powders in the gas phase is facilitated by the relatively low surface tension at the solid-gas interface [13]. An increase in surface tension leads to compaction of the nanoparticles in the aggregate. At the same time, high temperature accelerates diffusion processes, which contributes to the growth of particles and the formation of solid bridges between particles. The main problem of the method under consideration is the separation of nanoparticles from the gas phase under conditions where the concentration of particles in the gas stream is low and the gas temperature is sufficiently high. For trapping nanoparticles, special filtering devices are used (for example, metal-ceramic filters, electric precipitators), centrifugal sedimentation of solid particles in cyclone devices and hydrocyclones, special gas centrifuges.

In this paper, the method of obtaining the ultrafine powders by the desublimationprocess has been described.

2. Experimental method

Experimental studies were conducted to verify the adequacy of the theoretical concepts previously developed in our works [13], as well as to work out ways to optimize regimes of aggregation processes in dense dispersed systems with sources of the new phase. The desublimation method of obtaining ultrafine silica powder was chosen as objects for the study. In the course of the experiments, the effect of temperature, pressure, and degree of super saturation on the process kinetics and the dispersion size distribution function was investigated.

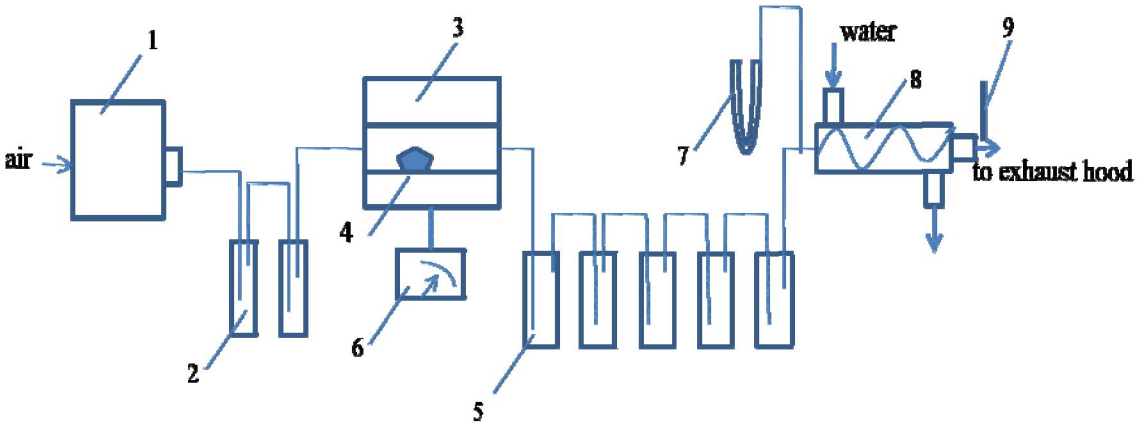
The experiment was organized on the well-known method of enriching high-silicon phosphorites [13]. The essence of this method is in the heat treatment of the raw material with ammonium fluoride followed by the conversion of silica contained in the raw material into ammonium silicofluoride. As next stage the sublimation of the obtained product was carried out.

For obtaining SiO_2, the especial reaction which at a certain temperature is carried out in the opposite direction with the rapid release of silicon dioxide was used [13]:

$$SiO_2 + 6NH_4F \Leftrightarrow (NH_4)_2SiF_6 + 4NH_3 + 2H_2O. \quad (1)$$

Earlier, in the work [13], the temperature threshold at which SiO2 emission prevails was determined . This threshold is 4500C.

A schematic diagram of the experimental setup and its photograph are presented in Figures 1 and 2.



1- compressor, 2- Drexel flasks (for drying), 3- electric furnace, 4- boat with sample,
5- Drexel flasks (for capturing solid particles), 6- temperature conroller, 7- pressure gauge, 8- heat exchanger, 9- thermometer.

Figure 1- Scheme of the experimental installation.

Figure 2- Photograph of the experimental installation

The installation is operated as follows.

A ceramic tube is inserted into the furnace 3 where the boat (tube) 4 is placed with a sample prepared in accordance with the methodological recommendations indicated below. Next, the connection is made with the help of hoses of all elements of the installation, in accordance with the circuit diagram. Then the furnace is turned on and when the set temperature is reached (400-8000C) the compressor 1 is turned on.Compressor supplies the surrounding air in the room through the system of absorption flasks 2, which prevent moisture from entering the ceramic tube.

The resulting vapors from the sublimates $(NH_4)_2SiF_6$ from the furnace 3 enter the successively installed Drexel flasks 5, where they are desublimated.

Further the remaining fumes of silicon oxide go to the heat exchanger 7, where their final desublimation takes place, and then they go to the hood. The temperature in the furnace is maintained from 400 to 8000C. In the course of the experiment, the temperature in the furnace 3 is recorded, as well as the readings of the thermometer 1 at the exit from the refrigerator, and in addition, pressure is controlled at the inlet using a manometer 6. Sampling is performed periodically at each fixed temperature in the furnace.

The finished product is collected in glass cups and sent for analysis of the chemical and dispersion composition. The crystal structure is also analyzed.

A scanning electron microscope JSM-6490LV(SEM) is used as equipment for electron microscopic studies of the dispersion composition of desublimate. The appropriate method is based on scanning the surface of the sample with an electronic probe and detecting (recognizing) the broad spectrum of radiation arising from this.

Research and determination of measurement errors is carried out by standard methods.

The procedure for sample preparation is described below.

Investigating samples are prepared, then sublimated in a furnace and subject to desublimation. It makes in the following sequence:

a) the river sand is taken in an amount of 1 kg, it is sifted in order to separate from large impurities, and then it is washed with distilled water;

b) then it is washed with hot hydrochloric acid HCl with a concentration of 15-20% for 15-20 minutes and boiled for 15 minutes. Then the sample is defended in the flooded state for 2 hours, after which the liquid is drained;

c) the resulting sludge is washed with distilled water for 30-40 minutes in order to wash out the remaining impurities and acid residues;

g) then it is dried at a temperature of 105 ° C until the moisture content is in the range of 0.5-1%. The obtained sample should be gray;

e) then 1 part (weight) of the sample is mixed with 6 weight parts of ammonium fluoride;

e) the mixture is poured into a boat, which is placed in a furnace and sublimated at the temperature of 400-6000C until the strong smell of NH_3 appears;

g) white-colored vapors that are formed intensively are captured by their desublimation on a cooled surface for 1.5-2 hours in order to estimate the temperature of sublimation and desublimation, as well as for the most complete desublimation of the vapors.

The previous operation is repeated for 3-4 times. The sampling plan is shown in Table 1.

Table 1-The sampling plan while experiments on sublimation

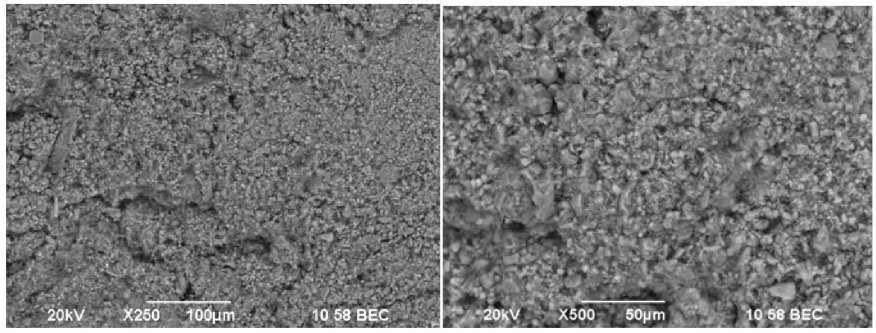
№	Vapour temperature (C)	Sampling numbers by interval, min					
		The numerator is the first sampling stage, and the denominator is the second sampling stage					
		1	2	3	4	5	
1	T1=400	5/20	10/30	15/40	20/50	30/60	
2	T2=420	5/20	10/30	15/40	20/50	30/60	
3	T3=450	5/20	10/30	15/40	20/50	30/60	
4	T4=500	10	20	30	40	60	
5	T5=510	10	20	30	40	60	
6	T6=520	10	20	30	40	60	
7	T7=550	10	20	30	40	60	
8	T8=570	10	20	30	40	60	
9	T9=600	10	20	30	40	60	
10	T10=650	10	20	30	40	60	
11	T11=700	10	20	30	40	60	

3. Results and discussion

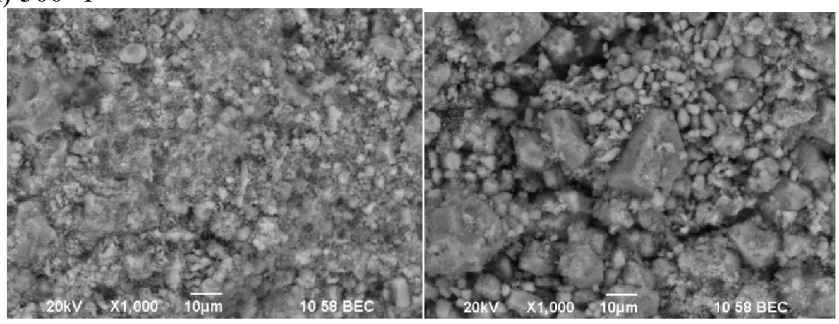
Some of the most illustrative images obtained as a result of the examination of samples using a scanning microscope are shown in Figure 3.

Inscriptions on photographs should be understood as follows. The first number is the temperature at which the sampling process is conducted, the next digit is the number of the Drexel flask in the capturing system.The obtained in the course of experiments characteristics and parameters of fractional composition of the silica dispersions, as well the microscope zoom, are automatically written in the fields of photographs.

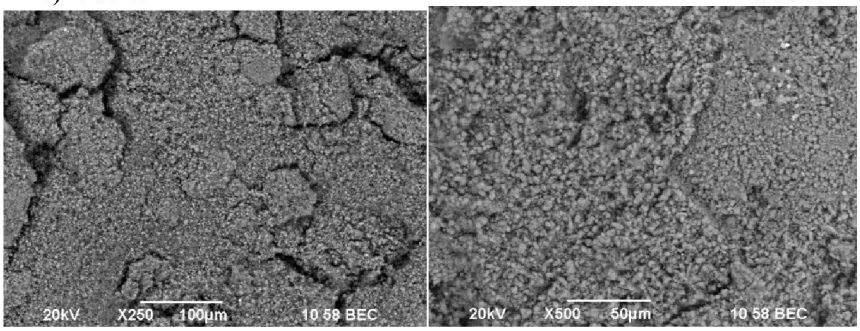
The conducted investigations convincingly show that with a large initial super-saturation, when a large number of embryos (monomers) of the dispersed phase are rapidly formed per unit volume of the apparatus, the contribution of multiparticle collisions is great [11, 14]. This is clearly seen in Figure 3, made at high magnification. Namely, large clusters of particles consist of many small embryos. Moreover, the shape of large clusters-globules is rather rounded, which is possible only with simultaneous attachment of many small particles over the entire surface of larger clusters [15].



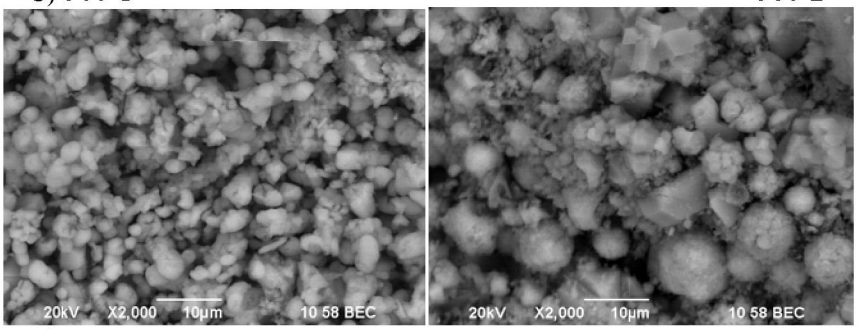
A) 300- 1



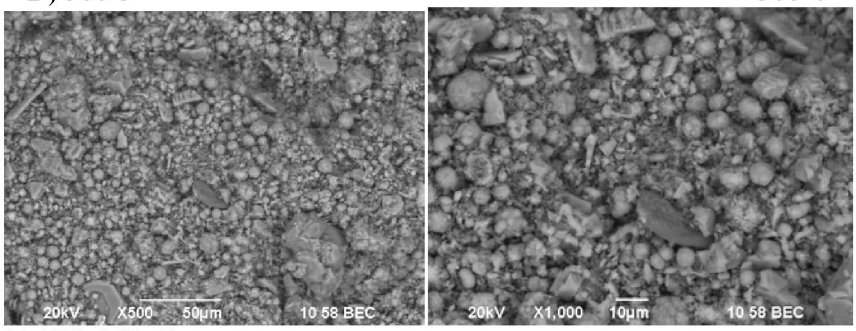
B) 300-1 300-2



C) 500-1 500-2



D) 500-3 500-4



E) 500-5 (1, 2)

Figure 3 - Images of the desublimated samples

Then there is a sharp decrease in super-saturation, and the aggregation process begins to be limited by diffusion resistance in the gas phase. This leads to a sharp decrease in the value of coagulation nuclei, the intensity of the aggregation process drops sharply, and as a result, a dispersion of a fairly homogeneous fractional composition is obtained. The fact is that the characteristic time of the process is of the order of time, which is optimal for multiparticle aggregation.

At low initial super-saturation, the aggregation process is "eroded" in time, since binary collisions prevail. Therefore, the fractional composition of the resulting dispersion is very heterogeneous.

Conclusions

The existence of the stage of the phenomenon of multiple coagulation with a high concentration of nucleates in a supersaturated vapor-gas mixture has been experimentally confirmed. The results of experimental studies are well interpreted from the theoretical considerations. It can be the basis of the engineering methodology for calculating the operational parameters of the process. Especially, this conclusion is important for the aggregation in dense disperse systems and optimization of this process in order to create highly homogeneous stable nanodispersions.

The results of experimental studies of silicon dioxide desublimations confirmed the theoretical conclusion about the presence of a stage of rapid formation of primary nucleates and a subsequent stage of slow, diffusion-controlled growth of aggregates.

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УЛЬТРАДИСПЕРЛІК ҰНТАҚ ӨНДІРУГЕ АРНАЛҒАН ДЕСУБЛИМАЦИЯ ӘДІСІНІСКЕ АСЫРУ РЕЖИМДЕРІ

Аннотация. Мақала десублимация әдісімен ультра дисперсті ұнтақтарды алу әдісін зерттеуге арналған. Эксперимент барысын датемператураның, қысымның және қанығу дәрежесінің процесс кинетикасына және дисперсияның мөлшері бойынша таралу функциясына әсері зерттелді.

Қанықпағанбу-газ қоспасында нуклеаттардың жоғары концентрациясы бар көпше коагуляция құбылысы кезеңінің болуы эксперименталды расталды. Атап айтқанда, үлкен бастапқы қанығу кезінде дисперсиялық фазаның эмбриондарының (мономерлерінің) көп саны аппарат көлемінің бірлігіне тез түзілетін кезде, көп бөлшекті қақтығыстардың үлесі үлкен.

Алынған мәліметтер біртекті фракциялық құрамы бар тұрақты нанодисперсияларды құру үшін агрегациялық процестердің режимдерін оңтайландыру және есептеудің инженерлік әдісін әзірлеу үшін өте маңызды болуы мүмкін.

Түйін сөздер: десублимация, ультрадисперсия, нанодисперсиялар, әдіс, наноұнтақтар, аса қанығу, көп бөлік.

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РЕЖИМЫ РЕАЛИЗАЦИИ МЕТОДА ДЕСУБЛИМАЦИИ ДЛЯ ПРОИЗВОДСТВА УЛЬТРАДИСПЕРНОГО ПОРОШКА

Аннотация.Статья посвящена исследованию метода получения ультрадисперсных порошков способом десублимации. В ходе экспериментов было исследовано влияние температуры, давления и степени пересыщения на кинетику процесса и функцию распределения дисперсии по размерам. Существование стадии явления множественной коагуляции с высокой концентрацией нуклеатов в пересыщенной парогазовой смеси было подтверждено экспериментально. А именно, было установлено, что при большом

начальном пересыщении, когда большое количество эмбрионов (мономеров) дисперсной фазы быстро образуется на единицу объема аппарата, вклад многочастичных столкновений велик. Полученные данные могут быть очень важны для разработки инженерного метода расчета и оптимизации режимов агрегационных процессов для создания стабильных нанодисперсий с однородным фракционным составом.

Ключевые слова:десублимация, ультрадисперсия, нанодисперсии, метод, нанопорошки, сверхнасыщение, многочастица.

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