UDC 544.77

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SPECIFICS OF THE FORMATION OF THE SPATIAL STRUCTURE OF THE SUSPENSIONS PRECIPITATES

Specifics of the formation of the spatial structure of the precipitates of basic carbonates of copper and nickel and of manganese and cobalt carbonates from their suspensions in dispersive media of various chemical nature – bidistilled water, 1,4-dioxane, isopropanol and isobutanol – are discussed. The role of the powder re-dispersion processes in the preparation of the suspensions and of the aggregation processes during sedimentation in the formation of the spatial structure of the precipitates was shown.

The spatial structure formed of the powders of the investigated carbonates is non-uniform and has sections with various particle packing density. The mean particle consistence depends on the primary particle packing density within only partially destructed aggregates (nuclei) which form during the re-dispersion of powders in liquids and on the secondary packing density of these surviving aggregates (nuclei). Coordination numbers for the primary and the secondary particle packing density in the spatial structure of the precipitates were determined from the mean particle density.

Keywords: topological structure, particle packing density, basic copper carbonate, basic nickel carbonate, manganese carbonate, cobalt carbonate

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ОСОБЛИВОСТІ ФОРМУВАННЯ ПРОСТОРОВОЇ СТРУКТУРИ СУСПЕНЗІЙНИХ ОСАДІВ

Обговорюються особливості формування просторової структури осадів основних карбонатів міді та нікелю і карбонатів марганцю та кобальту з їх суспензій в дисперсних середовищах різної хімічної природи – бідистильованій воді, 1,4-діоксані, ізопропіловому та ізобутиловому спиртах. Показано роль повторного редиспергування порошків і процесів агрегації у формуванні просторової структури осадів.

Просторова структура, сформована з порошків досліджуваних карбонатів, неоднорідна і має ділянки з різною щільністю упаковки частинок. Середній розмір часток залежить від первинної щільності упаковки частинок в частково зруйнованих агрегатах (ядрах), які утворюються у процесі повторного диспергування порошків в рідинах і вторинною щільністю укладки цих ядер під час формування осадів (ядер). Координаційні числа для первинної та вторинної щільності упаковки частинок в просторовій структурі осадів були визначені із середньої щільності частинок.

Ключові слова: топологічна структура, щільність упаковки частинок, основний карбонат міді, основний карбонат нікелю, карбонат марганцю, карбонат кобальту

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ОСОБЕНОСТИ ФОРМИРОВАНИЯ ПРОСТРАНСТВЕННОЇ СТРУКТУРЫ СУСПЕНЗИОННЫХ ОСАДКОВ

Обсуждаются особенности формирования пространственной структуры осадков основных карбонатов меди и никеля и карбонатов марганца и кобальта с их суспензий в дисперсных средах различной химической природы – бидистиллированной воде, 1,4-диоксане, изопропиловом и изобутиловом спиртах. Показана роль повторного редиспергувания порошков и процессов агрегации в формировании пространственной структуры осадков.

Пространственная структура, сформированная из порошков исследуемых карбонатов, неоднородна и имеет участки с различной плотностью упаковки частиц. Средний размер частиц зависит от первоначальной плотности упаковки частиц в частично разрушенных агрегатах (ядрах), которые образуются в процессе повторного диспергирования порошков в жидкостях и вторичной плотностью укладки этих ядер при формировании осадков (ядер). Координационные числа для первичной и вторичной плотности упаковки частиц в пространственной структуре осадков были определены из средней плотности частиц.

Ключевые слова: топологическая структура, плотность упаковки частиц, основной карбонат меди, основной карбонат никеля, карбонат марганца, карбонат кобальта

1. Introduction

The challenges of combining contradictory properties in new materials require the transition to multi-component and multi-phase physico-chemical systems. These systems put forward extraordinarily strict demands to the uniformity and compactness of the starting topological ceramic mixture that is characterized by a certain degree of interrelation of various phases and components. The metal carbonates, along with metal oxides and hydroxides, are frequently used for the synthesis of functional ceramics [1-5]. One of the important stages of the preparation of ceramics is the formation of a uniform starting topological mixture from fine particles of differing chemical nature. This spatial structure of the ceramic mixture substantially affects during the following stages the parameters of finished articles, particularly the reproducibility of the properties. The task of the formation of a uniform topological

structure of the starting ceramic batch is especially complicated when fine powders with particle size under 10 μm are used, since such disperse powders are in aggregated state in air [6]. Spontaneous aggregation of fine powders limits the possibility of achieving high uniformity of the ceramic batch and necessary quality of finished articles. The spatial structure of the powders in ceramic mixtures is also affected by their polydispersity. The dependence of the pore dimensions on the size of the particles of which the spatial structure is formed was discussed in [7]. However, future investigation of the topological structure of powders, the accumulation of new experimental results for the powders of various chemical nature and the substantiation of theoretical generalizations remain the current challenge for the modern ceramic technology.

2. Description of materials, dispersive media and experimental techniques

The following materials were used in the investigations:

- basic copper carbonate powder, $(CuOH)_2CO_3$ (Fluka), density $4.0 \cdot 10^3$ kg/m³;
- basic nickel carbonate powder, $(NiOH)_2CO_3$ (Fluka), density $3.55 \cdot 10^3$ kg/m³;
- manganese carbonate powder, $MnCO_3$ (Fluka), density $3.125 \cdot 10^3$ kg/m³;
- cobalt carbonate powder, $CoCO_3$ (Sigma-Aldrich), density $4.13 \cdot 10^3$ kg/m³.

All powders were of purum p.a. grade, were insoluble in water or organic solvents.

The following liquids were used as dispersive media:

- bidistilled water with specific conductivity 0.06 μSm/cm;
- 1,4-dioxane, $C_4H_8O_2$ (Merck), the principal component content 99.9 %;
- isopropanol, $(CH_3)_2CHOH$ (Merck), the principal component content 99,5 %;
- isobutanol, $(CH_3)_2CHCH_2OH$ (Merck), the principal component content 99,4 %.

Sedimentation volumes were determined to define the topological structure of the precipitates, from which the mean particle consistence φ_0 was calculated used formula

$$\varphi_0 = \frac{m}{V_c \cdot \rho} , \qquad (1)$$

where m is the powder mass, ρ is the density of the powder substance, V_c is the sedimentation volume of the powder precipitate from the suspensions with different dispersive media.

The mean particle radius of the powder in the investigated suspension is determined by the sedimentation analysis using a technique described in [8].

3. Results and Discussion

Spatial coagulation and non-coagulation structures of the disperse systems are distinguished. A non-coagulation structure forms under the influence of gravitational forces by the non-interacting particles (or those where the attraction forces are very weak compared to the gravitational forces). A statistical chaotic particle packing is achieved under these conditions, such as appears in gravity pouring of the powders, with mean particle consistence 0.61±0.02 [9,10]. A coagulation structure is defined as a structure formed by the interacting particles that is fixed in the site of the original contact. Thereafter, the formed aggregates do not destruct under the influence of external forces (gravitational forces, Brownian motion, mechanical mixing). The possibility of the formation of a spatial coagulation structure due to the adhesion and the incidence of contacts between the particles as a result of far-reaching surface forces is defined by the condition [11]

$$\sum_{i=1}^{K} F_i \geq m_0 \cdot g, \qquad (2)$$

where K is the number of contacts with the adjacent particles (coordination number), F_i is the adhesion force of the i-th contact, m_0 is the relative mass of the particles, g is the Earth gravity.

For the identical spherical particles of radius r and the identical adhesion force in each contact F, the condition (2) can be given as an inequality

$$K \cdot F \geq m_0 \cdot g. \qquad (3)$$

One can theoretically determine from the condition (3) a coordination number that makes possible the formation of a spatial coagulation structure

$$K \geq \frac{m_0 \cdot g}{F}. \qquad (4)$$

The inequality (4) leads to a conclusion that the coordination number in a spatial coagulation structure shows how many times the gravitational forces exceed the far-reaching surface forces (particle adhesion forces).

The mean coordination number in spatial coagulation structure formed of identical spherical particles for statistical chaotic packing varies widely between 2 and 10 [12]. The mean coordination number for polydisperse particles can be even higher.

The relative mass of the spherical particles of radius r is determined by the formula

$$m_0 = \frac{4 \cdot \pi \cdot r^3 \cdot (\rho - \rho_0)}{3} . \tag{5}$$

where ρ is the density of the powder substance, ρ_0 is the density of the dispersive medium.

The adhesion force of the singular contact of two identical spherical particles is determined from the dependence of their interaction energy on the distance between them [13]

$$F = \frac{dV_A}{dH} = \frac{r \cdot A}{12 \cdot H^2} , \tag{6}$$

where V_A is the interaction energy of particles at the distance H between them, A is the Hamaker constant.

Brownian motion does not destroy the spatial coagulation structure if the attraction energy of the particles exceeds the Brownian motion energy, i.e. if $V_A \geq 1$ kT. From this condition one can determine the boundary distance H_0 at which the particles would settle in the formation of a spatial coagulation structure

$$H_0 = \frac{r \cdot A}{12k \cdot T} . \tag{7}$$

Substituting (7) into (6) and then (5) and (6) into (4), we determine a theoretical value of a coordination number K that makes possible the formation of a spatial coagulation structure

$$K \geq \frac{\pi (\rho - \rho_0) g \cdot r^4 \cdot A}{9 (kT)^2} . \tag{8}$$

Assuming the average value of the Hamaker constant for carbonates in air as $A_{SAS} = 25$ kT [14] and $\rho \gg \rho_0$, we determine a coordination number for a possible formation of a spatial coagulation structure of the particles of investigated powders in air

$$K \geq 21.4 \rho \cdot r^4 , \tag{9}$$

where ρ is the density of the powder substance in g/cm^3, r is the particle radius in μm.

Liquid dispersive media have lower relative particle mass and the Hamaker constant compared to air. For the investigated powders and dispersive media the relative mass (and consequently, the gravitational forces) decrease 1.2-1.5 times, the Hamaker constant decreases 4.5-5 time, and cumulative average decrease is 6.4 times. Thus the coordination number for the possible formation of a spatial coagulation structure in liquid dispersive media also decreases to

$$K \geq 3.3 \cdot \rho \cdot r^4 . \tag{10}$$

The particle radii found by the sedimentation analysis of the suspensions with the solids content of 5 g/dm^3 in various dispersive media are given in Table 1. The results of the electron microscopy determination of the particle dimensions are also presented.

Table 1. **The particle radius of metal carbonates in the dispersive media of varying chemical nature**

Powder	Particle radius (μm) in liquid dispersive media				Electron microscopy particle radius (μm)
	water	1,4-dioxane	isopropanol	isobutanol	
$(CuOH)_2CO_3$	5.6	6.3	6.2	5.1	2.6
$MnCO_3$	4.2	4.4	3.6	3.1	1.6
$(NiOH)_2CO_3$	0.7	1.3	0.5	0.4	0.2
$CoCO_3$	0.4	1.2	0.4	0.2	0.1

The particle radii determined by electron microscopy are significantly lower than the particle radii in any dispersive medium. This indicates that the radii found by the sedimentation analysis

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characterize the dimensions of the aggregates of the primary particles. The radii of the particle aggregates for the powder of the same compound depend on the nature of the dispersive medium. The dimensions of these aggregates depend of re-dispersion degree and on the development of the aggregation processes in the investigated dispersive medium. The smallest particle dimensions were observed for the suspensions in isobutanol, the largest were for the suspensions in 1,4-dioxane as the dispersive medium.

The coordination numbers that theoretically allow the formation of a spatial coagulation structure are given in Table 2.

Obtained results show that only the particles of $(NiOH)_2CO_3$ and $CoCO_3$ can form a spatial coagulation structure, since the adhesion force of a singular contact between particles significantly exceed the gravitational forces (K<<1) both in air and in liquid dispersive media thus providing for the mutual particle fixation in the point of the first contact. The gravitational forces significantly exceed the adhesion force of a singular contact for the particles of $(CuOH)_2CO_3$ and $MnCO_3$ (K>>1). In cases where the adhesion force is not sufficient for the particle fixation in the point of the first contact, the gravity of the particles lead to the appearance of spatial non-coagulation structures (gravity structures).

Table 2. **Theoretically calculated coordination numbers that make possible the formation of a spatial coagulation structure for the particles of metal carbonates in air and in liquid dispersive media**

Powder	Theoretically calculated coordination numbers in liquid dispersive media:	
	air	liquid dispersive media: water, 1,4-dioxane, isopropanol, isobutanol
$(CuOH)_2CO_3$	3912	604
$MnCO_3$	438	67
$(NiOH)_2CO_3$	0.12	0.018
$CoCO_3$	0.009	0.001

The coordination number K and the particle packing density (volume filling of the precipitates) φ are connected by the correlation [12]

$$K = Q \cdot \varphi, \qquad (11)$$

where Q is a coefficient that varies from 12.6 for a non-periodic (disordered) spatial structure to 16.2 for the densest periodic (ordered) spatial structure.

The particle packing density in the sediments in air and in the investigated dispersive media is presented in Table 3.

Table 3. **The particle packing density of the powders of metal carbonates in air and in the investigated dispersive media of various chemical nature**

Powder	Particle packing density in various dispersive media				
	air	water	1,4-dioxane	isopropanol	isobutanol
$(CuOH)_2CO_3$	0.50	0.47	0.40	0.42	0.46
$MnCO_3$	0.40	0.38	0.36	0.42	0.42
$(NiOH)_2CO_3$	0.23	0.18	0.12	0.23	0.23
$CoCO_3$	0.19	0.094	0.082	0.094	0.098

For the constant dispersive medium, the decrease of the primary particle size (determined by electron microscopy) causes the decrease of the particle packing density. This agrees well with the fact that the ratio of gravitational forces to the adhesion force of a singular contact between particles decreases sharply (proportionally to r^4) with the decrease of the primary particle size. Such a decrease is illustrated by the changes of theoretically calculated coordination number (Table 3) that confirm the appearance of the conditions favourable to the formation of a coagulation structure. A similar dependence was also discovered in [9].

The far-reaching surface forces between the particles assist the aggregate formation, therefore the re-dispersion of the particles in various dispersive media does not occur fully but to certain steady aggregates the dimension of which are given in Table 2. The particle aggregation degree is better described not by the particle aggregate radius but by the number of the primary particles in them. The number of the primary particles in the aggregates *n* can be calculated by the formula

$$n = 0.617\left(\frac{r_a}{r}\right)^3, \tag{12}$$

where r_a – particle aggregate radius, r – primary particle radius, 0.617 – a coefficient of the primary particle packing density in the aggregates.

Assuming that periodic spatial structures form in the investigated systems, we can estimate a mean coordination number K_0 for the periodic particle packing from the experimentally determined particle packing density φ_0 (Table 3) and Equation (11) using formula

$$K_0 = 16.2\varphi_0. \tag{13}$$

Obtained results are presented in Table 4.

Table 4. **Coordination numbers for a periodic K_0 and disordered K_1 and K_2 spatial structures formed of the particles of metal carbonates in air and in dispersive media of various chemical nature**

Powder	Coordination numbers K_0, K_1 and K_2 in various dispersive media														
	air			water			1,4-dioxane			isopropanol			isobutanol		
	K_0	K_1	K_2	K_0	K_1	K_2	K_0	K_1	K_2	K_0	K_1	K_2	K_0	K_1	K_2
$(CuOH)_2CO_3$	8.1	10	10.3	7.68	10	9.6	6.5	10	8.2	6.8	10	8.6	7.5	10	9.4
$MnCO_3$	6.5	10	8.2	6.1	10	7.8	5.8	10	7.3	6.8	10	8.6	6.8	10	8.6
$(NiOH)_2CO_3$	3.7	10	4.7	2.9	10	3.7	1.9	10	2.5	3.7	10	4.7	3.7	10	4.7
$CoCO_3$	3.2 (6)	10	3.8 (6.6)	1.5 (6)	10	2.9 (3.2)	1.3 (6)	10	1.7 (2.8)	1.5 (6)	10	1.9 (3.2)	1.6 (6)	10	2.0 (3.3)

One can see that the mean coordination number K_0 for $(CuOH)_2CO_3$ and $MnCO_3$ in any media is less than 10, while for $(NiOH)_2CO_3$ and $CoCO_3$ particles, on occasion, the number is even less than 2. The coordination numbers below 2 are unrealistic because a spatial structure could not form were it real. The coordination number values below 10 do not correspond to the closest-packed periodic structure for which the calculations were performed. Therefore it is concluded that obtained spatial structures cannot be described by periodic formations because, clearly, sections with different (larger or smaller) particle packing density co-exist in the structures.

During the preparation of suspensions and powder re-dispersion in liquids the destruction of the particle aggregates that exist in air occurs gradually. First, the peripheral particles pull away from the aggregate as they are linked the weakest, and eventually the densest nucleus remains that retains the original structure of the particle packing. Then during the suspension sedimentation, these nuclei form the secondary structure of the particle packing. Therefore, under such conditions of the precipitate formation the mean particle packing density is determined by formula

$$\varphi_0 = \varphi_1 \cdot \varphi_2, \tag{14}$$

where φ_0 is the mean particle packing density, φ_1 is the primary particle packing density of the partially destructed aggregates (nuclei) with coordination number K_1, φ_2 is the secondary packing density of nuclei particles with coordination number K_2.

It is reasonable to assume that the partially destructed aggregates (nuclei) have the highest particle packing density of statistical-chaotic packing, i.e. $\varphi_1 = 0.617$ and $K_1 = 10$. Within this assumption, one can estimate the coordination number K_2 for the secondary particle packing density from Eqs. (11) and (13) and the mean particle packing density φ_0 (Table 3) using formula

$$K_2 = 12.6\varphi_2 = 12.6\,\varphi_0/\varphi_1 = 20.4\varphi_0 \tag{15}$$

Obtained results are presented in Table 4. The coordination numbers for the primary and the secondary particle packing density are nearly identical for the $(CuOH)_2CO_3$ particles which indicates high uniformity of the spatial structure. In these suspensions the coagulation processes do not substantially affect the formation of the spatial structure because the gravitational forces exceed the particle adhesion forces by a factor of 604 (Table 2). For the $MnCO_3$ particles, the coordination numbers for the secondary packing are somewhat lower that those for the primary packing but not significantly so. Therefore we assert sufficient uniformity of this spatial structure as well. The gravitational forces exceed the $MnCO_3$

particle adhesion forces by a factor of 67, thus the influence of the coagulation processes is minor. For the $(NiOH)_2CO_3$ particles, the coordination numbers for the secondary packing are significantly lower that those for the primary packing. This indicates the non-uniformity of the spatial coagulation structure. The least uniform is the spatial coagulation structure of the $CoCO_3$ particles because the coordination number for the secondary packing is very small; occasionally the calculated values are less than 2 which is unrealistic. Therefore it is necessary to assume for this powder that the particle packing density in the nuclei does not correspond to the highest coordination number 10, but is somewhat lower, e.g. with coordination number $K_1 = 6$. The coordination numbers for the secondary packing K_2 in this case are given in Table 4 in parentheses. These are more acceptable but still show significant non-uniformity of the spatial coagulation structure. In the $CoCO_3$ particles, the effect of the far-reaching surface forces on the formation of the coagulation structure is the greatest of the investigated powders, as the gravitational forces are 1000 times weaker than the adhesion forces.

Conclusions

The following conclusion are arrived at from the obtained results and the analysis of the spatial structure of investigated powders:

- the spatial structure formed by the powder particles of the studies carbonates is non-uniform and is characterized by sections with different (larger or smaller) particle packing density;
- the mean particle packing density in the spatial structure is defined by the primary particle packing density in the partially destructed aggregates (nuclei) that form during the re-dispersion of the powders in liquids and by the secondary packing density of these nuclei during the sedimentation process;
- the increase of the particle dispersion degree (decrease of their dimensions) favors the formation of less dense and more non-uniform spatial structures;
- among the studied dispersive media (water, 1,4-dioxane, isopropanol, isobutanol), the aggregation processes are the most intense for 1,4-dioxane; consequently, the spatial coagulation structures are the least dense.

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