Dispersion Degree and its Influence on Structure of Building Materials

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Abstract. The main basic characteristic of building materials which determines physical and technical properties of composites is structure. However, it is difficult to provide certain conditions for structure formation. For this purpose, it is possible to create space-limited environment for coagulation of submicroscopic crystals. Generally, this effect is caused by addition of high-dispersed components, usually carbon nanotubes, graphens and etc. are used. The results show that the more effective way is to use the combination of ultra- and nanofine additives and in this case nanofine additives should have specific chemical relation to the binder. Fume silica, surfactants (“Ethacryl HF”, “DC-5” including multiwall carbon nanotubes) were used for modification of building materials. In order to replace multiwall carbon nanotubes water suspension of furnace black (trade mark Palizh, Izhevsk) was added into cement matrix. When the ultrafine additive (silica fume) combines to nanofine components there is great increase of material performances. 0.5% “Ethacryl HF” and “DC-5” with 3% silica fume allow achieving compressive strength to 79.2 % and flexural strength to 94,6% accordingly (compare to test sample). To establish effect from additives and its generality gypsum binder was used. Additionally, the dispersion degrees, mineral chemistry, nature of microfine components are found to be important for modification of building materials. Nanofine additives which have chemical relation to the binder in mineral matrix also have active surfaces and on these surfaces are formed layers of new crystals. The high surface energy of nanofines reduces re-crystallization and allows creating high density and freeing from defects matrixes. Generality of this effect which include all mineral binders is proved.

1. Introduction
It is known that the optimal parameter determining the basic physical and technical properties of materials is their structure. The structure of set cement forms due to the coagulation of submicroscopic new formations, which, under space-limited conditions, form a crystalline phase with increased porosity. The pores between crystals are formed during the recrystallization of new formations in the process of supplying new submicrocrystalline phases during the hydration of binder minerals. In contrast to the formation of a dendritic structure typical for the crystallization of metals [1] that prevents recrystallization of new formations, the crystalline phase of the cement matrix due to the sufficient solubility and the possibility of migration of crystalline formations tends to reduce the surface energy due to the formation of larger crystals. In this case, cavities are formed between them.
(Figure 1a), which reduce the strength of the cement matrix. Moreover, the crystals have weak, mainly point, intergrowth contacts, which predetermine the reduced density of the structure and, therefore, do not give sufficient strength to set cement. Thus, in order to provide the increased strength, such conditions are required under which crystalline new formations would form continuous frame structures of increased density with a minimum number of defects, thereby binding the aggregates into a conglomerate.

2. Materials and Methods

The main initiator of the formation of a framework structure can be nanodispersed systems, such as carbon nanotubes [2] (Figure 2a), graphenes, nanosilica; nanostructures of natural origin, such as metakaolin (Figure 2b), chrysotile asbestos fibers (Figure 2c), biosilica and others.

3. Results and discussions

Size, shape and nature of a nano-dispersed active component determine the rate of the formation processes of the crystalline phase in setting cement. In the case of using nanoparticles, they initiate the formation process of scale-like elements of a polycrystalline structure in the system whose distribution
limit depends on the number and uniformity of distributed objects in the medium. In the presence of nano-objects in the hardening mineral matrix, a layer of new formations is formed along their active surface (Figure 3a). Due to the high surface energy of the nanostructures, this layer prevents recrystallization and creates high-density, defect-free shells that, with a sufficient number of nanostructures, join and create a solid frame combining a conglomerate of increased density and strength (Figure 3b).

![Figure 3a](image1.jpg) ![Figure 3b](image2.jpg)

**Figure 3.** A fragment of a shrinkage micro crack of a crack in set cement with carbon nanotubes coated with calcium hydro silicates (at the age of 28 days of hardening) - (a), the microstructure of set cement structured with carbon nanotubes - (b)

The effectiveness of the influence of nanoparticles on the structural modification of the cement matrix is determined by the dispersity degree of initial objects used for aqueous dispersions. In addition, an important factor is the chemical affinity of nanostructures with the components of the cement matrix. Moreover, most of known nanoobjects are inert to the components of set cement and require the functionalization of their surface for combining nanostructures with the polymineral constituent of set cement [3]. In practice, this is achieved by using surfactants, which simultaneously prevent the coagulation of nanoparticles when they are dispersed and aqueous dispersions are stored. On the one hand, the layer of surfactants provides the affinity of the added nanostructures with the components of the cement matrix, and on the other, it creates a separating layer that reduces the effect of polarization on the surface of nanostructures (Figure 4).

![Figure 4](image3.jpg)

**Figure 4.** A scheme of creating a functional layer between carbon nanotubes and components of set cement [4]

The reactivity of nanoparticles is proportional to the size of the operating surface. It must also be taken into account that a high specific activity is typical for a substance in a finely dispersed state with
a broken or deformed crystal lattice. Therefore, the most significant effect of nanostructures on the modification of set cement is their dispersion and optimum content in the hardening cement matrix.

To study the kinetics of hydration of cement in the presence of multi-walled carbon nanotubes, a study was made of total heat release and the rate of change in heat release in a thermos-type calorimeter (Figure 5). The conducted studies show that adding multi-walled carbon nanotubes increases the rate of hydration processes, which is manifested in the increased rate of heat release during the formation of crystalline hydrate new formations during the initial carcass formation (Figure 5a). In the process of formation of structured layers of the increased density on the surface of cement particles, the intensity of cement hydration decreases. The associated exothermic processes decrease when the cement matrix hardens, which can be clearly seen in the integral curves of heat release of set cement modified with carbon nanotubes (Figure 5b). It is noted that the additional treatment of dispersions with nanotubes before their adding into concrete mixture allows to accelerate the structure formation, which is reflected in the shape of heat release curves.

![Figure 5. The effect of carbon nanotubes on the rate of heat release (a) and total heat release (b) in the hydration of cement](image)

The studies conducted by P.N. Kurochka, A.V. Gavrilov [5], G.V. Nesvetaev, Ta Wang Fang [6] show the effectiveness of modifying set cement with ultrafine soot. To increase the variety of types of modifying admixtures, studies were made to replace expensive multi-walled carbon nanotubes with ultrafine soot. The results of its dispersion analysis are shown in Figure 7b. The conducted studies showed that adding soot dispersion with an average particle size of 0.16 μm into cement slurry (Figure 7b) provides a close-packed structure of the cement matrix increasing the density of matrix contact layers and fillers and improving the strength and fracture toughness of modified cement concrete.

The conducted studies show that adding a soot dispersion with an average particle size of 0.16 μm into cement slurry (Figure 7b) provides a close-packed structure of the cement matrix, increases the density of matrix contact layers and fillers, and improves the strength and fracture toughness of modified cement concrete.
Figure 6. The dispersity analysis of nanostructures in aqueous dispersions: (a) – Fulvek-100 dispersion after mechanical treatment, (b) – soot concentrate in a surfactant aqueous dispersion, (c) – multi-walled carbon nanotubes dispersion after joint mechanical and ultrasound dispersation

A dispersed soot concentrate was used as a suspension in the aqueous surfactant solution (“Pallzh” trademark, manufactured by “Novyy Dom”, Izhevsk).

The results of physical and mechanical tests of the samples modified with a soot dispersion are presented in Table 1.

Table 1. The results of determining the physical and mechanical properties of set cement modified with a suspension of ultrafine soot at the age of 14 days.

| Composition | W/C | C, % | R_bend (av), MPA | R_comp (av), MPA |
|-------------|-----|------|-----------------|-----------------|
| Check       | 0.4 | 0    | 4.75            | 28.85           |
| Soot        | 0.02| 0.02 | 4.70            | 33.30           |

Analysing the obtained data, it should be noted that the flexural strength when modifying with a dispersion of soot is at the level of the strength of the check sample, while the compression strength of these samples is higher than the strength of the check ones by 15%.

To obtain materials and products with the enhanced characteristics, such nanostructures are preferred that have affinity with the components of a mineral matrix, including cement matrix, such as micro- and nanosilica, nanocellulose, metakaolin, nanofibers from chrysotile-asbestos. It is known that the strength of the final material is strongly influenced by a joint modification of the structure by nano- and micro-dispersed admixtures [7].

The above views on the effect of complex dispersed admixtures on the structure and properties of cement concrete found their application using Ethacryl HF and DC-5 surfactants in combination with an aqueous dispersion of Fulvek-100 (its dispersity is shown in Figure 8a).

Fulvek-100 dispersion was prepared by means of mechanical dispersation in a high-speed bead disperser. The microstructure obtained as a result of the modification of set cement using microsilica is shown in Figure 8b. The microsilica added to the composition was preliminarily processed with ultrasound to destroy the aggregated particles (Figure 8a), the average particle diameter was 315 nm, with up to 12% of the ultradisperse admixture being nanosilica with an average particle diameter of 30 nm.
Figure 7. Analysis of microsilica dispersity after ultrasound dispersion for 4 min – (a), microstructure of set cement structured with micro- and nanosilica – (b)

The practical results of the modification of set cement with complex admixtures including microsilica and nanodispersed components are given in Table 2.

### Table 2. The results of strength evaluation of concrete based on Portland cement with the optimum number of dispersed complex admixtures containing nano- and microdispersed components

| №  | Composition of admixtures in tested samples | W/C | Cone slum \( p_s \) | \( \rho_{cp}' \) kg/m³ | Statistical data and strength of samples |
|----|-------------------------------------------|-----|---------------------|-----------------|------------------------------------------|
|    |                                           |     |                     |                 | \( R_{cikcp}^{7cyt} \) MPa | \( S_m^{7cyt} \) MPa | \( \Delta, \% \) | \( R_{cikcp}^{28cyt} \) MPa | \( S_m^{28cyt} \) MPa | \( \Delta, \% \) |
| 1  | Check (C)                                 | 0,43| 8                   | 2372            | 24,0           | 0,88             | -               | 36,3            | 1,73            | -               |
| 2  | C+0,5%HF+0,25%FV                         | 0,36| 14,5               | 2388            | 41,3           | 1,93             | +72,1           | 50,9            | 2,46            | +40,2           |
| 3  | C+0,5%HF+3%MK+0,25%FV                   | 0,38| 14                 | 2403            | 43,0           | 1,56             | +79,2           | 54,3            | 1,57            | +49,6           |
| 4  | C+0,5%DC-5+0,25%FV                      | 0,35| 15                 | 2425            | 44,4           | 1,78             | +85,0           | 62,2            | 1,25            | +71,3           |
| 5  | C+0,5%DC-5+3%MK+0,25%FV                 | 0,36| 13                 | 2430            | 46,7           | 2,05             | +94,6           | 67,0            | 2,36            | +84,6           |

* C – check composition, HF – amount of Ethacryl HF superplasticizer, FV - amount of Fulvek-100 modifier, DC-5 – amount of DC-5, MS- amount of microsilica

Adding multi-walled carbon nanotubes into the composition of concrete mixture increased the strength of concrete samples during all the considered periods of hardening. Thus, on the 7th day of normal hardening conditions, the strength of the samples containing Ethacryl HF and DC-5 superplasticizers in an amount of 0.5% by weight of Portland cement increased by 72.1% and 85.0%, respectively, from the check sample. In comparison with the actual strength of the samples with the required GOST strength of B25 concrete at the design age with the required strength coefficient \( k_{req}=1.32 \), the relative increase was 25.0% and 34.5% as early as the 7th day of hardening. At the design age, the relative change from the required strength was 54.2% and 88.5%, and from the check properties by 40.2% and 71.3%, respectively, for the samples containing Ethacryl HF and DC-5.
In combination with the ultrafine microsilica admixture, the produced experimental concrete compositions have more significant strength changes. Thus, on the 7th day of normal hardening conditions, the strength of the samples containing Ethacryl HF and DC-5 superplasticizers in an amount of 0.5% and MS in an amount of 3% by the weight of Portland cement increased by 79.2% and 94.6%, respectively, of the check sample. In comparison with the required GOST strength for B25 concrete at the design age with the required strength coefficient $k_{req}=1.32$, the relative increase was 30.3% and 41.5% as early as the 7th day of hardening. At the design age, the relative change from the required strength was 64.5% and 103.0%, and from the check properties by 49.6% and 84.6% respectively for the samples containing Ethacryl HF and DC-5 [8].

The conducted research studies of modification of nanodispersed admixtures in combination with ultrafine components confirm the universality of the manifested effects, which does not depend on the type of the mineral binder. The effectiveness of complex admixtures when changing the type of the binder directly depends on the nature of the microdispersed component to be combined with the nanodispersed modifier. The choice of dispersed components and their optimum ratio depend on the required characteristics of the final product, the chemical composition of the mineral matrix, and the degree of dispersion. The universality of the manifestation of this effect was confirmed by the studies based on combined dispersed admixtures, which were used to modify gypsum binders.

The research used normally hardening G-4 gypsum of an average grinding degree produced by the enterprise of Prikamskaya Gypsum Company, LTD (Perm) and meeting GOST 125-79. The complex dispersant modifiers used were multi-walled carbon nanotubes as an aqueous dispersion and metallurgical blast-furnace dust which is a technogenic product of steelmaking [9]. The analysis of the chemical composition of blast-furnace dust conducted with an X-ray fluorescence spectrometer found that the composition of the admixtures includes the following metal oxides: iron oxide (III) (Fe2O3) – 54%, magnesium oxide (MgO) – 14%, calcium oxide (CaO) – 12 %, silicon oxide (SiO2) – 6%. The impurities (1-2%) are chromium (III), aluminium, manganese and zinc oxides. The dispersion analysis of the technogenic modifier showed that the average particle size is 8-9 micrometers (Figure 1) and there are also particles of nanometre range. The specific surface area of the admixture was 3400 cm$^2$/g.

![Figure 8. The dispersity analysis of primary metallurgical blast-furnace dust](image_url)

The combined adding of carbon nanostructures and ultrafine mineral admixture proved to be an effective way of improving strength characteristics due to the changes in the morphology and the size of crystalline hydrates of calcium sulfate dehydrate.
Figure 9. The strength of gypsum matrix, metallurgical blast-furnace dust and carbon nanotubes being added together

Metallurgical blast-furnace dust and carbon nanotubes being added together, with an optimum concentration of admixtures 0.6% and 0.005%, respectively, to the gypsum composition, the compression strength of the samples increases to 15.1 MPa at the age of 28 days, which is 54.3% higher in comparison with the check sample. The obtained data also exceed the strength parameters of the gypsum matrix with admixtures added separately. Metallurgical blast-furnace dust being added, the increase in strength was 40.5% to 13.8 MPa. MWCNTs suspension dispersed in a carboxymethylcellulose medium being added, the increase was 53.0% to 14.5 MPa.

4. Conclusions
Thus, when added separately at a certain concentration (microsilica in the case of Portland cement, blast-furnace dust in the case of gypsum), the admixtures act as active centres, but because of their influence on the structure only at the micrometre level, the effect of their application is lower than the effect of being used in combination with nanodispersed components. In the case of modification with admixtures with a combined dispersity on the surface of admixture particles, crystalline hydrates form, that create a film structure of the matrix with increased density and strength in the gaps between the hydrated particles. The manifestation of this universal effect is due to the optimal selection of nanodispersed modifiers in combination with a microdispersed component and the achievement of effective dispersion corresponding to the type of the selected binder.

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