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# Structural Ceramics Modified with Technogenic Isostatic Nanographite

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# **Structural Ceramics Modified with Technogenic Isostatic Nanographite**

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**Abstract**. During the production of ceramic wall materials based on acidic and semi-acidic loams, products with low physical and technical parameters are obtained. To improve the characteristics of structural ceramics, it is suggested to modify the raw material with ultra- and nano-dispersed additives based on technogenic isostatic graphite instead of the traditionally used synthesized carbon nanosystems. The paper investigates the effect of aqueous dispersions of technogenic nanographite functionalized with surfactant additive C-3 on the properties and structure of ceramics. Infrared spectral and differential thermal analysis and computed tomography have confirmed structural modification of ceramics, occurring, when isostatic graphite being added, along with the formation of a denser and more uniform structure of the ceramic shard, which, in turn, increases the strength properties. It is noted that adding ultrafine graphite of to 0.005 % of the mass of clay gives an increase in compressive strength up to 50 %, which will increase the grade of manufactured products. The advantages of using technogenic graphite in comparison with carbon nanotubes are its low cost and preservation of properties at firing temperatures of structural ceramics.

### 1. Introduction

Graphite nanomaterials can play a multifaceted role in improving physicomechanical, physicochemical, and functional properties of composite building materials [1, 2]. Analysis of studies in the field of using dispersed technogenic isostatic graphite makes it possible to determine the following areas of influence on the structure and properties of building materials:

- modification of the structure of building materials with its subsequent compaction and improvement of mechanical properties [3];

- creating composite materials with additional functional properties, including the ability to absorb technogenic electromagnetic radiation [4, 5];

- creating composite building materials with low electrical resistance in order to obtain electrically conductive mineral-based materials [6].

Graphite nanoplates have mechanical and physical characteristics required for modifying the structure, while maintaining low cost, unlike synthesized carbon nanotubes (CNTs). In addition, they can be used not only in building materials based on mineral binders [7], but also in the production of ceramic materials since graphite can work at temperatures higher than the calcination temperature of building ceramics, while CNTs burn out at temperatures around 700 °C [8].



Figure 1. Functionalization of graphite nanoplastic by hydroxyl/carboxyl groups [2]

Proper distribution of graphite nanomaterials in the molding mass in the production of ceramics increases the efficiency of their impact on the structure and properties of the ceramic matrix. Interfacial interaction of graphite nanoplates with clay particles, in its turn, is determined by methods for modifying the surface of graphite [9]. One of the methods for functionalization of nanographite by means of the addition of hydroxyl groups (Figure 1) is described in [2].

The key conclusion of the analytical studies is the ability of graphite nanomaterials at very low dosages (0.05 % and less) to change the structure of ceramics and improve the physicomechanical characteristics of ceramic materials. On this basis, the study suggests increasing the efficiency of modification of structural ceramics by using dispersions of technogenic isostatic graphite in an aqueous medium.

## 2. Materials and methods

# 2.1. Aqueous dispersions of technogenic graphite

Technological wastes of graphite electrodes used in electroslag remelting of steel were used as an ultra-and nano-dispersed modifier. Based on these wastes of isostatic graphite, 1 % aqueous dispersions were made using two types of stabilizers: plasticizer C-3 (2.8 % by the weight of dispersion) and wetting agent Altarau S8 (0.1 % by the weight of dispersion).

The wetting agent Altarau S8, manufactured by Stahem, provides rapid wetting and dispersion of graphite particles in an aqueous medium. Plasticizer C-3 (Figure 2), related to superplasticizers based on the condensation product of naphthalenesulfonic acid and formaldehyde, also increases the stability of dispersions.

Aqueous dispersions of isostatic graphite were obtained by the method of hydrodynamic cavitation using the installation described in detail in [10]. A diagram of a cavitation disperser based on the VTG 2.2 kW vortex heat generator is shown in Figure 3.



**Figure 3.** "VTG 2.2 kW": a) – VTG 2.2 kW vortex heat generator; b) – layout view of the applied circular dispergation method [10]

The study of dehydrated dispersion films with plasticizer C-3 in images taken with a TESCAN MIRA 3 scanning electron microscope showed that the dispersion is graphite plates uniformly coated with a surfactant (Figure 4).



**Figure 4.** Graphite plates coated with superplasticizer C-3: a) – at 10.000-fold magnification, b) – at 100.000-fold magnification

The analysis of the sizes of graphite plates in aqueous dispersions by the number of particles was carried out using a Shimadzu SALD-7500 laser analyzer. The average particle size was:

- in a dispersion stabilized by the plasticizer C-3, 0.207  $\mu$ m;
- in a dispersion stabilized by the plasticizer C-3 and the wetting agent Altarau S8, 0.323 µm;
- in a dispersion stabilized by the wetting agent Altarau S8, 0.008  $\mu m.$

#### 2.2. Preparation of ceramic samples

For the manufacture of ceramic samples, a mixture was used of 70 % of brick loams and 30 % of quartz sand as a leaner. Loams are acidic since the  $Al_2O_3$  content by the mass is 13.33 %; the mineralogical composition of loams is represented by a mixture of clay minerals with a predominance of montmorillonite and illite.

Technogenic isostatic graphite was added into the mixture in the form of aqueous dispersions with water until the molding moisture for plastic molding. The concentration of graphite in the composition of ceramics varied from 0.001 to 0.05 % by the weight of loam.

Ceramic samples for testing, having a shape of cylinders with a diameter of 50 mm and a height of 50 mm, were made by plastic molding from a mixture kept for two days for averaging the moisture content by volume. The samples dried to constant weight were burned with isothermal aging for two hours at 950  $^{\circ}$ C.

#### 2.3. Methods of research

Differential-thermal analysis was performed using a TGA/DSC1 thermogravimetric analyzer produced by Mettler-Toledo. The analysis of the microstructure of the samples was carried out using an electron microscope TESCAN MIRA 3. Non-destructive testing of the structure of the ceramic material was conducted using the computed tomography method on a "GE Phoenix Vtomex M300" tomograph. The IR spectra of the samples of calcinated ceramics were obtained on a SpektrumOne FT-IR spectrometer in the frequency range of 4000-400 cm<sup>-1</sup>.

### 3. Results and discussions

The main process of obtaining ceramic materials is firing, which has a decisive influence on the formation of the structure and properties of ceramics. Differential-thermal analysis (Figure 5) of the control sample and the sample modified by isostatic technogenic graphite showed that, at low

concentrations of graphite, there are no significant changes in the ceramic firing process. Endothermic effects at temperatures of 150-300 °C are associated with the removal of adsorption water, accompanied by weight loss of the sample. The endoeffect at 580 °C is typical for the polymorphic transformation of  $\beta$ -quartz into  $\alpha$ -quartz. In the range of 750-850 °C, dehydration of clay minerals occurs, and then in the temperature range of 880 °C, the crystal lattice of these minerals is rebuilt.



Figure 6. Derivatograms of ceramic samples: a control sample in red, a sample containing 0.005 % graphite in black (dispersion stabilized with C-3)

However, it was found that the concentration of graphite and the type of stabilizer of graphite dispersion affect the density of the raw and calcined ceramic samples (Figure 6).





At the same time, the samples modified with an aqueous dispersion of graphite with C-3 surfactant used as a stabilizer have the highest density (Figure 6a).

Images of the modified sample (Figure 8), obtained by computed tomography, show that its structure and pore space are more homogeneous compared with the control sample, which has quite a lot of large defects.



**Figure 8.** The distribution of pores in ceramic samples after firing, obtained using computed tomography: a) the control sample; b) – the sample modified with 0.005 % graphite (dispersion stabilized with C-3)

When analyzing the microstructure of ceramics after firing (Figure 9), it was found that the adding 0.005 % graphite in the form of an aqueous dispersion stabilized with C-3 results in compaction of the ceramic matrix, increasing its uniformity and reducing pore sizes (Figure 9b).



**Figure 9.** The microstructure of ceramic samples after firing: a) control sample; b) - sample modified with 0.005 % graphite (dispersion stabilized with C-3)

The obtained data on the increase in the density and homogeneity of the structure of ceramics with graphite particles being added correlate with the results of mechanical tests of the strength characteristics of the samples. Figure 10 shows the dependence of the ultimate strength of ceramics under compression on the concentration of graphite and the type of stabilizer of graphite dispersion.

It has been established that the most effective additive for improving the strength characteristics of ceramics is graphite water dispersion stabilized with plasticizer C-3. The maximum increase in strength with graphite being added in an amount of 0.005 % by the weight of loam can reach 50 % (Figure 10a). The next most effective modification is graphite dispersion stabilized by the wetting agent Altarau S8, which allows to increase the strength of ceramics to 25 % at a graphite concentration of 0.005-0.01 % by the weight of loam (Figure 10c). At the same time, studies have shown that adding only stabilizers without graphite into the mixture does not give an increase in strength, and the tensile



strength of the samples under compression still corresponds with values of the tensile strength of the control samples.

**Figure 10.** Compressive strength of ceramic samples under compression (1 — after drying, 2 — after calcination): a) — with graphite dispersion stabilized with C-3; b) - with graphite dispersion stabilized by C-3 and Altarau S8; c) - with graphite dispersion stabilized by Altarau S8

At the same time, the joint stabilization of the water dispersion of graphite with the plasticizer C-3 and the wetting agent Altarau S8 does not give positive results when modifying ceramics to increase its strength (Figure 10b).



**Figure 11.** IR spectra of ceramic samples: black is the control sample, green is the sample containing 0.005% graphite (dispersion stabilized with C-3)

Analysis of the IR spectrum of the control sample (Fig. 11a) revealed an intense absorption line corresponding to the vibrations of the atoms of the silicon-oxygen tetrahedron Si-O-Si at a frequency of 1078 cm<sup>-1</sup>. The infrared spectrum of the ceramic sample with graphite (Fig. 11b) showed a bifurcation and displacement of the absorption line band of the main valence vibration of Si – O – Si towards lower frequencies (1051 cm<sup>-1</sup>), which can occur due to an increase in the distance of bonds between Si-Al–O atoms [11]. The latter circumstance allows us to speak of the formation of other crystalline compounds that affect the change in the mechanical parameters of calcinated ceramics.

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#### 4. Conclusions

It has been established that ultra- and nano-dispersed particles of graphite affect the structure of ceramics not only at the stage of molding raw material, but also during its firing, contributing to the formation of new phases, which is confirmed by IR-spectral analysis. Adding ultrafine graphite makes it possible to obtain a denser and more uniform ceramic matrix.

The change in the structure of the matrix as a result of adding ultra- and nano-dispersed graphite increases the strength of ceramics. It has been established that ceramics with graphite particles dispersed in an aqueous medium and stabilized with C-3 superplasticizer have the maximum strength characteristics in an amount of 0.005 % by the weight of loam. After drying, the compressive strength of the modified samples increases by 40 % compared with the control sample, after firing at 950 °C - by 50%. Thus, the conducted studies show the effectiveness of modifying building ceramics with aqueous dispersions of technogenic isostatic graphite stabilized by surfactants.

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