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Structural Modification of Ceramic Brick with Multi-Walled Carbon Nanotubes

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Abstract. The paper considers a method for improving physical and mechanical properties of ceramic bricks made from low-melting low-grade clay and quartz sand. The priority task is to develop a kind of batch based on widespread low-grade clay containing less than 13.5% of Al_2O_3. This provides high physical, technical and operational characteristics of brick. To improve the properties of ceramic building materials, multi-walled carbon nanotubes (MWCNTs) can be used as an effective structural modifier in an amount of 0.001-0.009% of the clay mass. Adding an aqueous dispersion of MWCNTs to the composition of ceramic batch increases the density and uniformity of the structure of ceramic matrix and influences its strength characteristics. The increase in the strength indices of ceramic has been found to occur in both cases of using freshly prepared batch and batch seasoned for a long time, up to 6 months. Nanotubes already influence the strength of the samples at the stage of air brick forming, while the compressive strength increases by 50%. After firing, the compressive strength of fired modified samples increases by 109%. Thus, using an aqueous dispersion of MWCNTs improves the structure and physical and mechanical properties of ceramic brick.

1. Introduction

At the moment, there is a shortage of quality raw materials in the field of clay masonry production. This leads to a search for new formulations of ceramic batch based on a widespread low-grade low-melting clay. This will contribute to the full use of the raw material base in the Udmurt Republic (Russia) in producing ceramic brick and other ceramic building materials. In this case, products based on this clay must meet the needs of a high-rise construction for brick grade above M150.

One of the methods for increasing physical, mechanical and operational properties of ceramic is using various modifying admixtures in the batch. These include carbon nanostructures: nanodiamonds [1]; graphenes [2,3]; nanotubes [4-8]. The effect of strengthening of ceramic matrix when using carbon nanotubes can be explained by the electrostatic interaction of clay particles in the weak acidic medium of MWCNTs suspensions at the stage of air brick forming [9,10], as well as the improved ceramic burn ability [11-13].

Strength characteristics are of primary importance for clay masonry. Therefore, the conducted research focused on obtaining their maximum values.

2. Research materials and methods

The batch composition is based on low-melting clay from Shaberdin deposit (Udmurt Republic, Russia) with the following oxides (mass percentage, %): 65.34 – 69.64 % SiO_2; 13.33 – 16.10 % ($Al_2O_3 + TiO_2$); 4.71 – 5.86 % $FeO + Fe_2O_3$; 0.01 – 0.23% SO_3. The ceramic batch used for producing the samples consisted of 70 % of clay and 30 % of quartz sand.

The modifying admixture was MWCNTs of Masterbatch CW 2-45 (Arkema, France) consisting of 55 % carboxymethyl cellulose and 45 % carbon nanotubes. For more uniform distribution of the modifier in the batch, aqueous dispersions of MWCNTs were made: dispersion 1 was prepared by mechanical homogenization; dispersion 2 was also prepared by a mechanical method and treated with ultrasound. Volume dispersion analysis conducted with Shimadzu SALD-7500 laser analyser showed that the average particle diameter in dispersion 1 was 2.53 μm, in dispersion 2 – 1.31 μm. MWCNTs were added to the batch in an amount of 0.001, 0.005 and 0.009 % from the mass of clay within three days after preparing the dispersion.

Cylindrical ceramic samples with a diameter and height of 50 mm were made by means of balling. To determine the effectiveness of nanotubes, some samples were prepared after 2 days of the batch seasoning, another part was formed after six months of the batch seasoning. The samples were fired after drying at 105 °C up to constant weight with isothermal time of two hours at a firing temperature of 950 °C.

The microstructure of the samples was analysed using electron microscopes Quanta 250 (FEI Company) and TESCAN MIRA 3. Differential thermal analysis was conducted using Mettler-Toledo thermogravimetric analyser TGA/DSC1.

3. Results and discussions

Figure 1 shows the density values of the samples after drying and firing. After drying, the density of the samples is 2070-2110 kg/m^3, after firing – 1910-1930 kg/m^3.

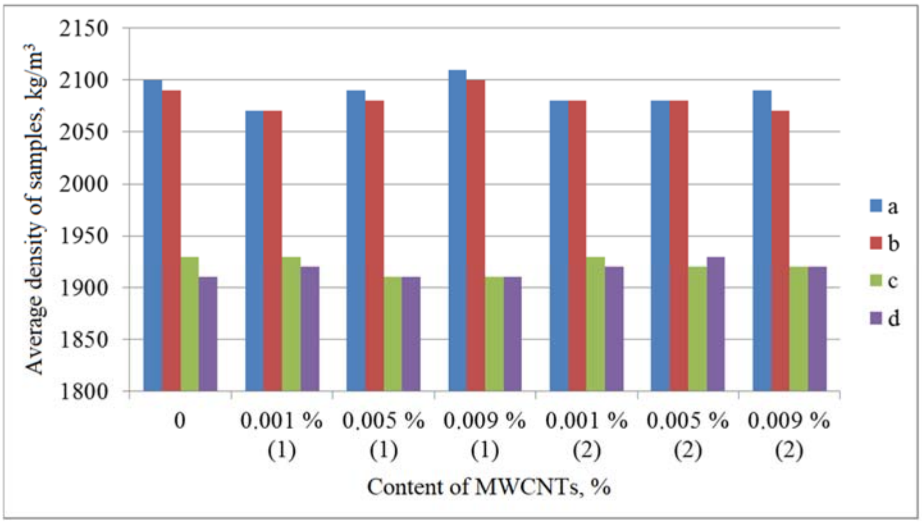

Figure 1. Average density of ceramic samples: (1) – dispersion 1; (2) – dispersion 2; a – after drying; b – after drying from the batch seasoned for 6 months; c – after firing samples (a) at 950 °C; d – after firing samples (b) at 950 °C

The values of compressive strength of the air brick and the fired samples are shown in Figure 2. The compressive strength of the sample without admixtures after drying was 4.5 MPa, after firing 9.9 MPa. The maximum strength increase for the dried air brick (up to 55 %) was recorded with a MWCNTs content of 0.009 % (dispersion 1). After firing at 950 °C, the maximum strength, twice the strength of the check sample, was recorded for the sample with 0.001 % MWNT (dispersion 2).

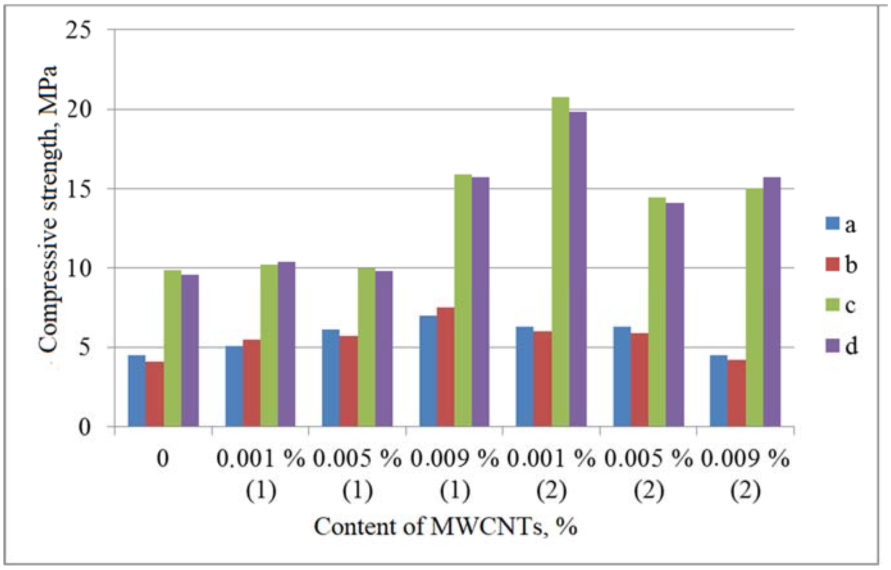

Figure 2. Compressive strength of ceramic samples: (1) – dispersion 1; (2) – dispersion 2; a – after drying; b – after drying from the batch seasoned for 6 months; c – after firing samples (a) at 950 °C; d – after firing samples (b) at 950 °C

Besides the compressive strength values, the brick grade also depends on the flexural strength. However, it is reasonable to test the cylindrical samples for splitting tensile strength that bending tensile strength is directly proportional to.

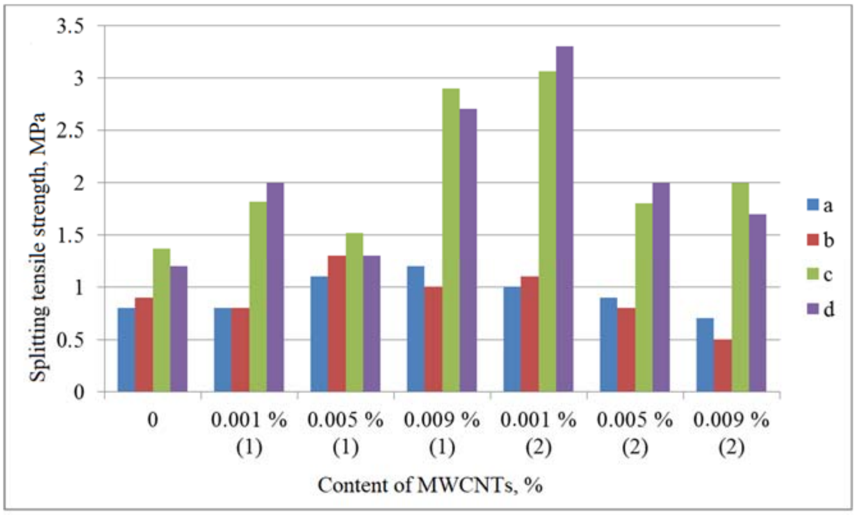

Figure 3. Splitting tensile strength: (1) – dispersion 1; (2) – dispersion 2; a – after drying; b – after drying from the batch seasoned for 6 months; c – after firing samples (a) at 950 °C; d – after firing samples (b) at 950 °C

The results of testing the ceramic samples for splitting tensile strength are shown in Figure 3. The compositions with 0.009 % MWCNTs (dispersion 1) and 0.001% MWCNTs (dispersion 2) also have the best results exceeding the strength of the check samples almost twice.

Figures 2 and 3 show that there is also strengthening of ceramic for the samples formed 6 months after the batch preparation. In addition, dispersion 2 being used, fewer nanotubes were needed to achieve the increased strength of ceramic. This can be due to better dispersion of nanoparticles processed with ultrasound.

The analysis of ceramic microstructure after drying (Figure 4) shows that, when MWCNTs in the amount of 0.009 % is added to the composition of the batch, the matrix is compacted and the pore size is reduced (Figure 4b). These data confirm the increase in the strength characteristics of the ceramic samples due to increasing the homogeneity of their structure.

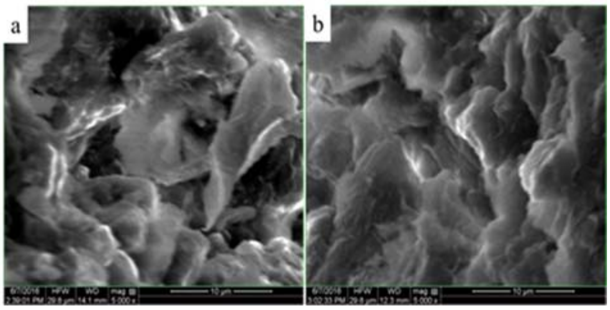

Figure 4. Microstructure of ceramic samples after drying at 105 °C: a – check sample; b – sample with 0.009 % of MWCNTs (dispersion 1)

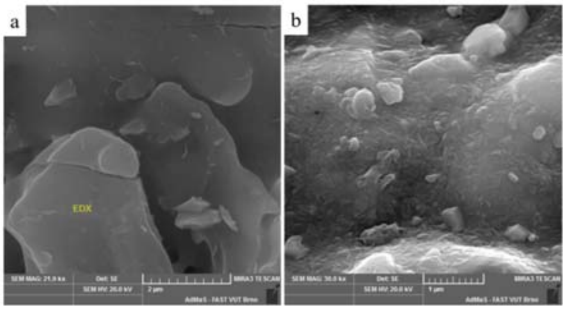

Figure 5. Microstructure of ceramic samples after firing at 950 °C: a – check sample; b – sample with 0.009 % of MWCNTs (dispersion 1)

The studies of the microstructure of the ceramic samples after firing at 950 °C revealed in the structure of the modified sample (Figure 5b) crystalline acicular formations corresponding to mullite crystals [14]. Mullite crystals contribute to micro-reinforcement of the ceramic matrix, thereby increasing its strength.

The derivatograms of the samples of the used batch show three thermal effects typical for montmorillonite clay [15]: 150-300 °C (endoeffect) – adsorption water removal; 770-800 °C (endoeffect) – dehydration of clay minerals; 950 °C (exoeffect) – beginning of crystallization of mullite. Montmorillonite is also characterized with an endothermic peak at 860 °C [16] associated with the destruction of the crystal lattice.

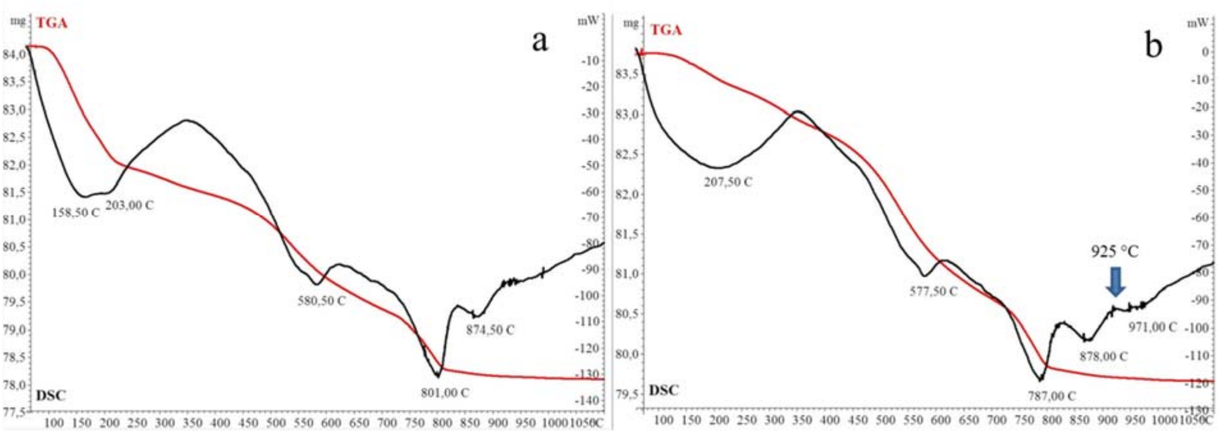

Figure 6. Derivatograms of ceramic samples: a – check sample; b – sample modified with 0.009 % of MWCNTs (dispersion 1)

The beginning of the formation of mullite in the samples with MWCNTs at 925 °C (Figure 6b) can be explained by the fact that the orderliness degree of raw material affects the amount of mullite formed. The material with a highly ordered structure provides more mullite at a lower temperature, and the reaction of its formation, which can be observed in Figure 6b, is stretched in time in comparison with compositions with disordered structure [16].

4. Conclusion

Thus, the conducted studies show the effectiveness of modifying building ceramic materials with dispersions of multi-walled carbon nanotubes. MWCNTs affect the ceramic matrix starting from the formation stage and provide a denser and more stable structure of air brick, which can reduce the amount of rejection when drying brick at a production site. The maximum strength characteristics are typical for the ceramic containing 0.001 % of nanotubes from the mass of clay, previously dispersed in an aqueous medium by means of a high-speed homogenizer and treated with ultrasound. After firing at 950 °C, the compressive strength of the modified samples increases by 109 % compared to the check sample, the splitting tensile strength increases by 123 %. At the same time, the effect of strengthening the ceramic matrix is kept even when using the batch with nanotubes 6 months after its preparation.

Acknowledgment

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