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APPLYING NANODISPERSED MODIFIERS FOR PRODUCING SHIELDING POLYFUNCTIONAL COATINGS

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Abstract. The first mineral based lacquer and paint coating have been developed based on Portland cement and soda glass, which does not require traditional silicators of zinc oxide and is also capable of absorbing man-made radiation. A significant change in the structure of silicate paint has been achieved by its modification with multi-layered carbon nanotubes. The developed composition has water resistance, good adhesion to the base, the improved durability, is capable of operating at high temperatures; the life of coating is 3 times longer in comparison with its analogues.

Keywords: silicate coating, carbon nanotubes, microstructure, liquid glass, Portland cement, screening, man-made radiation, the electro absorption.

Introduction

Currently, the coatings which are capable of absorbing electromagnetic radiation are becoming popular. There are various materials for shielding facilities from harmful radiation, including the materials with come carbonaceous substances (Barsukov 2004; Nikitina *et al.* 2005; Kozlovskiy, Sofienko 2009). The new type of carbonaceous materials includes multi-walled carbon nanotubes (MWCNTs), which are capable of absorbing electromagnetic radiation, but they also serve as a modifier of structure of silicate coatings to which they are added (Cho *et al.* 2009; Rana *et al.* 2009; Qing *et al.* 2013).

The existing analogs of similar coatings are used as a binder (synthetic resins): acrylic, phenolic, etc., which have low durability due to their low weather ability (Gulbin *et al.* 2013). A significant drawback of modern lacquer and paint materials based on polymeric binders for finishing facades of buildings and interior decoration is their low permeability, high quality requirements to the surface to be painted and low durability of the coating. Low durability is worsened by the organic components of the given paints which eventually decompose under the influence of the environmental factors.

The durability of the known silicate paints based on liquid glass and silicators is limited by the low water resistance of liquid glass, which is the main binder. A significant change in the structure of silicate paint is possible due to its modification with MWCNTs, the use of which as structuring additives for mineral matrix has not been studied enough. At the same time, the presence of carbon nanosystems in silicate coating provides the protection of buildings and structures from excessive anthropogenic radiation due to its absorption. Thus, the development of silicate paints modified with complex nanodispersed systems and showing the improved physical and technical properties, including the protection from man-made radiation, is an urgent task.

1. Experimental part

For the preparation of silicate coating liquid sodium glass was used as a binder (module 2.7...2.9, with an average density of 1.45 g/cm^3). Its drawbacks as a binder

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being taken into account, Portland cement was used as a binder to address these drawbacks. To prevent instant hardening of the system a retarder was added to temporarily neutralize the effect of Portland cement due to the formation of poorly soluble film on the surface of its particles. To improve the physical and technical characteristics of silica coating and simultaneous increase of the structure density metakaolin, fine ground limestone, microsilica (Nam *et al.* 2012), was used. In order to form the structure of finishing silicate composition and create the shielding effect (Crespo *et al.* 2014), multilayer carbon nanostructures of Graphistrenght^{TM} of Arkema company, France, were used.

For silicate composite materials with the predictable characteristics MWCNTs should be used as a binder. In recent years, the modeling of nanosystems has been mainly performed with quantum-chemical methods and programs (Kodolov, Khokhryakov 2009; Chillemi *et al.* 2001). Simulation of the interaction processes of components of silicate composition and graphene plane was made with HyperChemRelease 6 program. Assessing the possibility of interactions between molecules was conducted on the basis of changing the length of bonds in molecules as a result of the geometry optimization, which shows the interaction of the system and its stability.

The analysis of structure and properties of facade coatings was conducted with modern methods of physical and chemical research.

The microstructure research was conducted using Phenom G2 Pure, a scanning electron microscope with an increase of up to 7500 times.

To determine the mineralogical composition of the original materials and the structure of new formations in the structure of silicate coating X-ray phase analysis was conducted with a general purpose diffractometer of DRON-3.

The shielding properties of the composition were examined by the measuring unit with the generator of microwave radiation at the frequency of 1 GHz. The function and appearance of the unit are presented in Figure 1. For the experiment zigzag antenna was selected.

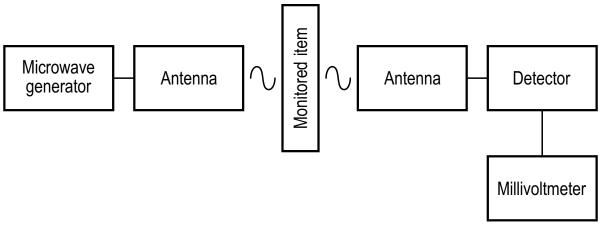

Fig. 1. Block structure of measuring unit

2. Results and discussion

Simulation of interaction processes of the components of silicate coating. Simulation of chemical reactions occurring in the prepared mixture is limited to the simulation of the initial components. The model of a silicate coating is presented with molecules of calcium phosphate, sodium orthosilicate (Korneev, Danilov 1996), calcium orthosilicate and tomermorita (Gorshkov *et al.* 1994).

The possible interactions of the initial components were considered in the framework of ZINDO/1 and PM3, the quantum-chemical approximation implemented in HyperChem v.6.03software product.

Figures 2a, b, c and d show that the carbon graphene film is active with respect to the components of the cement-silicate composition which suggests the possibility of modifying the finishing composition with MWCNTs. The significant absorptive capacity is driven by two factors: high surface area of new phases and considerable activity of the forming colloidal system (Yakovlev 2004).

The findings of this simulation suggest the conclusion of useful use of MWCNTs as a modifier for finishing compositions based on liquid sodium glass and Portland cement without the use of traditional silicators of zinc oxide. The data of the performed theoretical models gives understaning of possible chemical processes in the mixture of cement and silicate composition with carbon nanostructures. The formation of coordination compounds is confirmed with the changed microstructure. The improvement of the

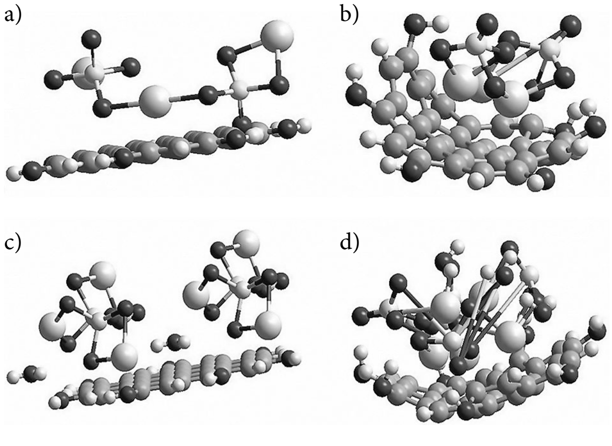

Fig. 2. Interaction of $Ca_3(PO_4)_2$ molecule and a graphene plate in the framework of quantum-chemical approximation of PM3: a – original structure; b – structure after optimization. Interaction of $Ca_2SiO_7*H_2O$ ule and a graphene plate in the framework of quantum-chemical approximation of PM3: c – original structure; d – structure after optimization

physical and mechanical properties of finishing coating is due to the changes in the morphology of crystal hydrate new formations with the increased density of the structure and additional ultrafine reinforcement of silicate composition with nanodispersed systems.

X-ray phase analysis. According to this analysis of the developed composition there is formation of crystalline phase in the coating structure in the form of silicon oxide in combination with amorphous binder matrix providing the composite material with increased water resistance (Fig. 3).

Thus the spectra show that at 100% there is more complete hydration of Portland cement minerals. The main line $d\alpha = 2.61$ Å in Figure 3b has a considerably less intensity in comparison with Figure 3a. This suggests the better hydration of Portland cement minerals which ultimately leads to the increased strength of the coating.

Microstructure study. The analysis of silicate coating microstructure shows that the composition structure changes, being modified with MWCNTs. Structure densification and the strength increase of the material is supported by the hardening connections between new formations that are formed during solidification of the composition modified with complex nanodispersed systems (Fig. 4).

Thus, adding MWCNTs to silicate composition (Fig. 5) stimulates structure formation of compositions and improves its physical and technical properties. Physical and chemical studies of the structure of silica coating show the possibility to control the morphology of crystal hydrate phases and an increase of the contact surface between them by forming structure of the increased strength and water resistance.

Study of electromagnetic properties. To study the shielding properties the samples were produced with silica glass substrate 3.2 mm thick of 150–150 mm size, on which the studied silicate coating was applied (Figs 6, 7).

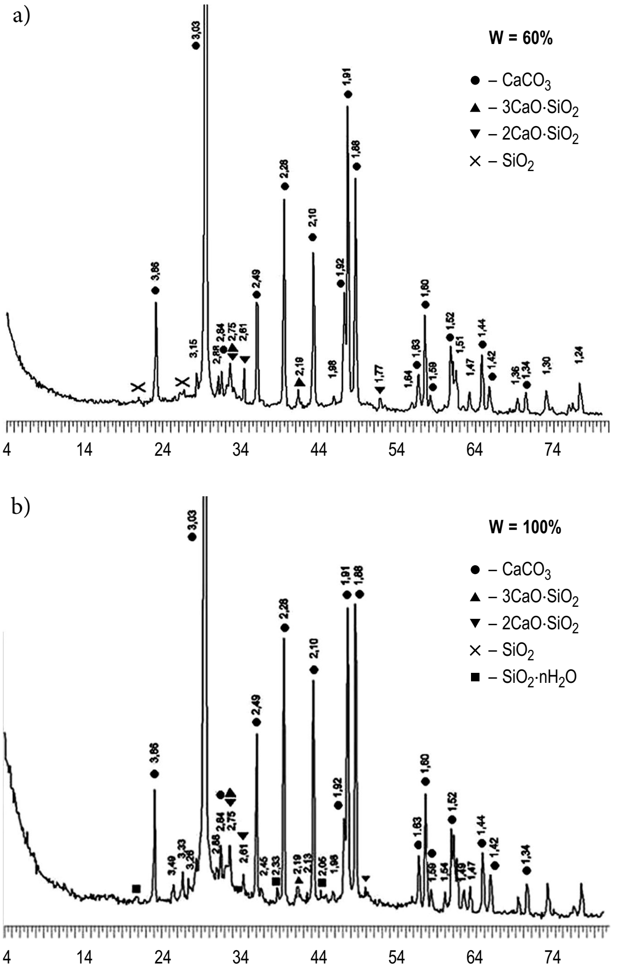

Fig. 3. X-ray diagram of silicate coating dried: a – with 60% humidity, b – with 100% humidity

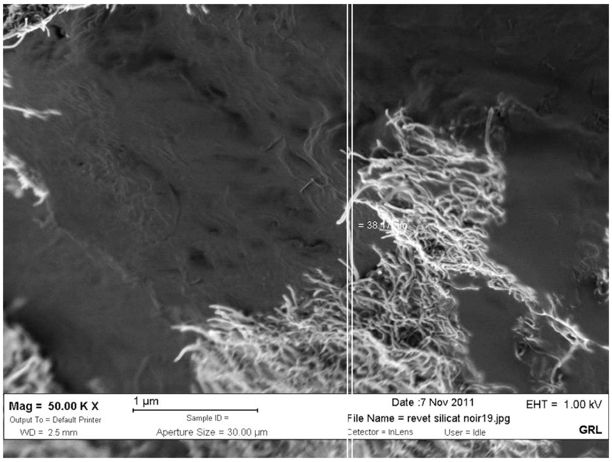

Fig. 4. Microstructure of silicate coating modified with MWCNTs

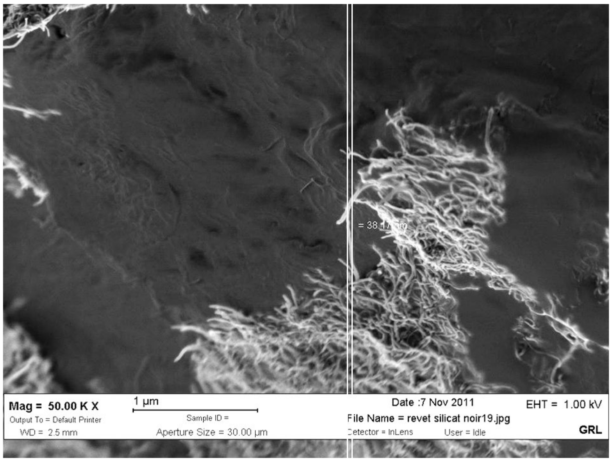

Fig. 5. Microstructure of silicate coating modified without MWCNTs

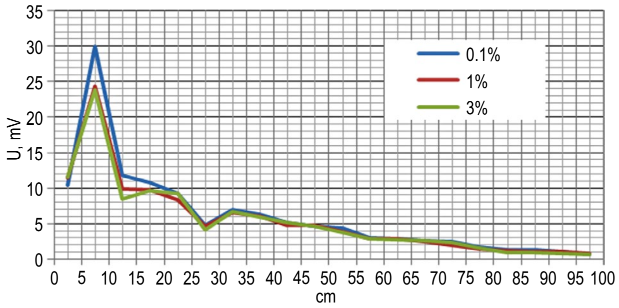

Fig. 6. EMI shielding at 1 GHz coatings with nanotubes

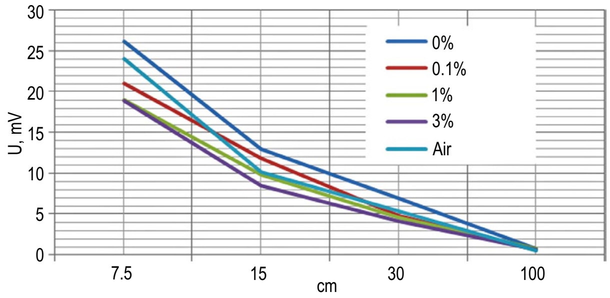

Fig. 7. EMI shielding coatings nanotubes within the wavelength

The analysis of the literature (Bonaldi *et al.* 2014) provides variation of the measured values of electrical resistance of carbon nanotubes at the indoor temperature within the range of 1.5 to 104 kOhm for individual nanotubes, from 1.5 to 14 Ohm for bundles of nanotubes and from 3 to 12 Ohm for fabric material made of nanotubes (Yeletskiy 2009).

The shielding properties of MWCNTs are provided with their good conductivity (Wanga *et al.* 2013). Moreover, their low specific gravity and the possibility of producing thin nanobased transparencies without changing the appearance of the shielded object provide the ease of their use as a protective coating.

One of the reasons of such good conductive properties is few defects that occur during the nanotube synthesis, as well as its high thermal conductivity. It is almost twice higher than the heat-conducting properties of diamond.

Adding MWCNTs to the composite material results in a smooth increase in absorptive values. Effective absorptive capacity has a typical dependence and increases with the increase of concentration of conductive filler. The research results can be useful for creating high-performance low reflective radar absorbing coatings reducing the overall level of electromagnetic radiation.

Conclusions

1. Adding carbon multiwalled nanotubes stimulates structure formation of compositions and improves their physical and technical properties; EMI shielding effect occurs.
2. The developed compositions are non-magnetic materials that do not reduce the natural magnetic field of the Earth. Combining structural and shielding properties in one structure significantly reduces the time of commissioning of such shielded facilities.
3. The shielding facade compositions are applied by traditional construction techniques.

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