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Aluminosilicate coatings with enhanced heat- and corrosion resistance

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ABSTRACT

This paper summarizes the results of development of heat- and acid resistant mineral coatings intended for protection of concrete structures and brickwork from exposure of acid media and elevated temperatures. The protective coatings are produced basing on the alkaline aluminosilicate bonds, in which the alkaline compounds are strongly bound into water insoluble hydroaluminosilicate complexes. On the contrary to the known-in-the-art mineral coatings based on cements containing slag and slag/ash, the coatings based on the alkaline aluminosilicates advantageously explore a correlation between corrosion resistance and phase composition due to the synthesis in the structure of the alkaline aluminosilicate matrix of high-silica zeolite-like phases (faujasite, chabazite and mordenite). The introduction into the alkaline aluminosilicate matrix of the formula $Na_2O \cdot Al_2O_3 \cdot 6SiO_2 \cdot 14.5H_2O$ of the acid resistant fillers, selected from mica, aluminosilicate microspheres and ground quartz sand taken in quantities of 3, 8 and 12 wt.% enabled to increase the acid resistance of the coatings by 1.25–1.5 fold compared to the known-in-the-art mineral analogs. Heat resistance of the coatings under study, in the conditions of alternate exposure of temperature (473 K) and vapors of oleum, may reach 100 cycles. The developed formulations of the anti-corrosion alkaline aluminosilicate coatings were successfully tried in 2007 in industrial conditions in repairing the deteriorated brickwork of the flue. After 5 years no sign of deterioration of the protective coating was reported.

1. Introduction

Traditionally used materials based on high-alumina cement intended for repairing damaged inner surfaces of flues do not provide a long-term effect as a result of shrinkage of the freshly laid concrete and weak adhesion of a newly laid concrete to the old concrete or brickwork. After a short term period (2…3 years), breaks occur in the earlier repaired joints, resulting in a necessity of replacement or expensive repair works by making a strengthening cage around the flue trunk. The paper covers the results of development of alternative protective composite materials based on the alkaline aluminosilicate bonds for anticorrosion application, the scientific bases of which have been proposed in 1957 by Professor Victor Glukhovsky and since then are being developed by his scientific school (Glukhovsky, 1979; Krivenko, 1971, 1995; Skurchinskaya, 1973).

Purpose of this research was to develop heat- and corrosion resistant coatings intended for protection of inner surfaces of flues from exposure of acid media with pH = 3 and pH = 5 for temperatures up to 473 K using the modified alkaline aluminosilicate bonds produced in the conditions of cavitation treatment.

2. Materials and methods

2.1. Materials

An alkaline aluminosilicate bond of the following composition: $Na_2O \cdot Al_2O_3 \cdot 6SiO_2 \cdot 14.5H_2O$ and the following ratios between basic oxides: $Na_2O/Al_2O_3 = 1$, $SiO_2/Al_2O_3 = 6$, and $H_2O/Al_2O_3 = 14.5$ were used in the experiments. The bond was prepared using a finely dispersed metakaolin (meeting the TU U V.2.7-16403272.005-99 requirements). A fineness of the metakaolin measured using a Blaine apparatus and expressed as a specific surface was 300–350 m^2/kg.

Sodium silicate solution with the following characteristics: silicate modulus (M) = 2.76–2.83 and $\rho = 1400 \pm 10$ kg/m^3 was used in the alkaline aluminosilicate bond as a liquid phase.

Rotten-stone was used as a correcting additive. The main constituent of the rotten-stone is opal-like amorphous microsilica ($SiO_2 \cdot mH_2O$). Specific surface of the rotten-stone after grinding was 250–280 m^2/kg (by Blaine).

Clinoptilolite was used to regulate a target synthesis of high-silica zeolite-like phases. Its thermoactivation was carried out by firing at T = 1073 K. Its specific surface after firing and grinding was 280–300 m^2/kg (by Blaine).

Ground granulated blast-furnace slag (GGBF slag) with the specific surface of 400 m^2/kg (by Blaine) was used as a modifying additive in order to accelerate hardening in air-dry conditions (T = 293 K and

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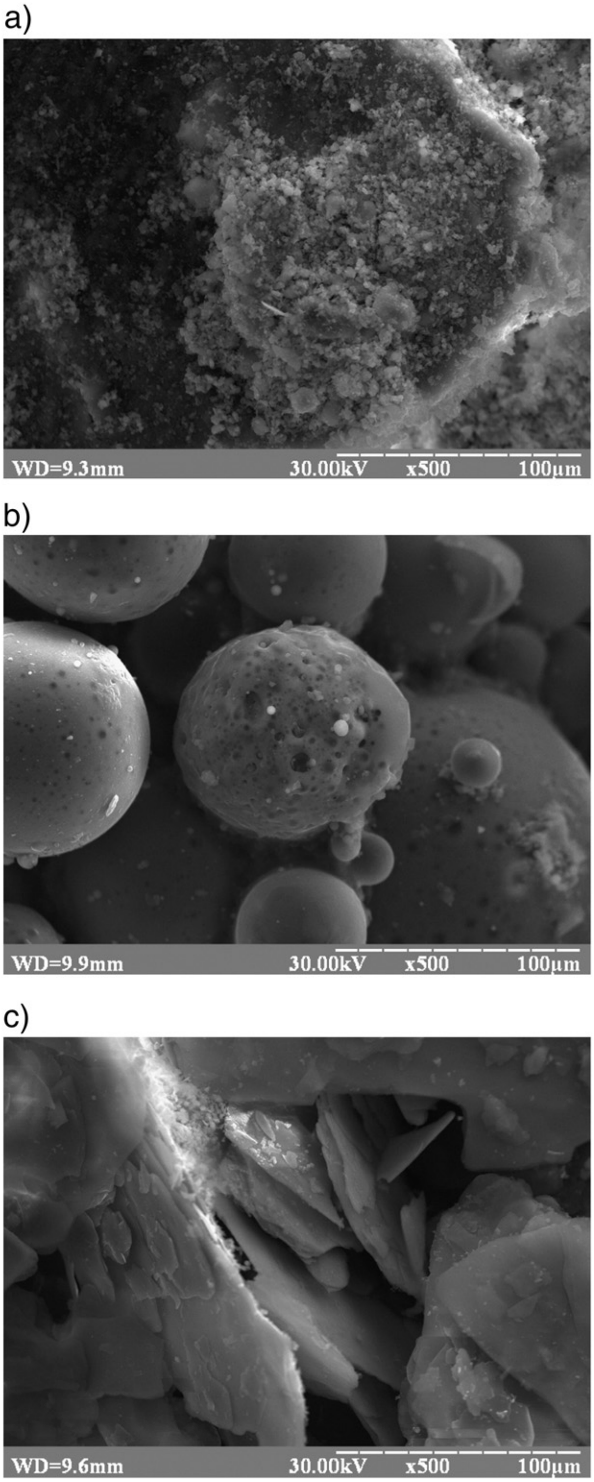

Fig. 1. SE photomicrographs of the correcting additive and fillers: a—clinoptilolite; b—aluminosilicate microspheres; c—synthetic mica (fluorphlogopite).

RH = 60%) and to enhance water resistance of the hardened coatings based on the alkaline aluminosilicate bond.

Synthetic mica – fluorphlogopite $KMg_3[Si_3AlO_{10}]F_2$ – with the flat particle-size less than 40 μm, ground quartz sand with particle-sizes: 0.14 mm and 0.325 mm (40:60) and aluminosilicate microspheres with particle-size of 10–350 μm were used in the protective coatings as acid resistant fillers. Their micrographs are given in Fig. 1. Chemical compositions of the starting materials are given in Table 1.

2.2. Experimental set-up

Formation of the acid-resistant high-silica zeolite-like phases in the alkaline aluminosilicate suspensions with the ratio of the basic structure-forming oxides: $Na_2O/Al_2O_3 = 1$, $SiO_2/Al_2O_3 = 6$, and $H_2O/Al_2O_3 = 14.5$ was provided due to a regulated low-temperature sol–gel synthesis in the fields of dynamic cavitation with the process parameters developed for this application (Guziy and Terenchuk, 2010). The Proportions between oxides in the alkaline aluminosilicate bond for synthesis of zeolites of target composition were taken in accordance with the recommendations given in (Barrer and Langley, 1958; Breck, 1973).

Determination of the phase composition of hydration products of the alkaline aluminosilicate bond was carried out using X-ray phase analysis and electron microscopy.

The X-ray phase analysis was carried out using a diffractometer in the discrete regime with the step size of 0.05° using the Cu Kα—radiation with a nickel filter and 25 kV accelerating voltage and 15 μA current by a powder method. The imaging was carried out within the range of angles $2\Theta = 10–35°$ at a speed of counter rotation of 2°/min. Identification of the hydration products was done in accordance with the following work (Semushin, 1986) and using the data base PC-PDF (*Version 2.13 a*, *Copyright JCPDS – International Centre for Diffraction Data*, *1992*), *the program* "*XPowder*" *and the AMSCD data base* (http://rruff.info).

SEM studies of the microstructure of the hardened coatings were held on non-polished rough surface of the specimen after fracture preparation which was coated with Cu using secondary electron imaging. The hydration products were identified in accordance with the data provided in (http://www.webmineral.com).

Viscosity ("spread behavior") of the alkaline aluminosilicate suspensions and protective coatings on their base was measured using Suttard's viscosimeter. Compressive strength of the hardened coatings based on alkaline aluminosilicate bond was determined on six cube specimens (20 × 20 × 20 mm) in accordance with the DSTU B V.2.7-239:2010 requirements. The same specimens were used for determination of water resistance. Water resistance was expressed as a ratio of the compressive strength of the water saturated specimen to that of the specimen that has been dried before. Bond strength, that is, adhesion of the protective coating to the concrete substrate, was determined in accordance with the GOST 14760-69 requirements. The concrete beam specimens (40 × 40 × 160 mm) with an average compressive strength of 42.5 ± 0.5 MPa (determined by a non-destructive method with the help of sclerometer) were used as a concrete substrate.

Frost resistance tests of the protective coatings on the concrete substrate were carried out in accordance with the DSTU B V.2.7-48-96 requirements: the specimens were allowed to freeze at T = 255 K during 2 h and to thaw at T = 293 K and RH = 90% during 22 h (1 cycle of testing). After a certain number of cycles the specimens were examined to check changes taking place in their appearance and loss of mass which is not allowed to be greater than 5 wt.%. After the mass loss reached 5 wt.%, the testing was stopped.

Corrosion resistance tests of the protective coatings were carried out in accordance with the GOST 27677-88 requirements using a coefficient of corrosion resistance expressed as a ratio of compressive strength of the specimens placed in aggressive media (pH = 3 and pH = 5) to that of the specimens placed in inert medium (drinking water). Thickness of the coating was 2 mm.

After the protective coatings hardened the coated and uncoated beam specimens were placed in the baths filled with the inert (drinking water) and aggressive (solutions of sulfuric acid) media in such a way that to provide a free access of the aggressive medium to the specimens, the ratio of the volume of the aggressive medium expressed in cm^3 to 1 cm^2 of the specimen surface being not less than 5:1. The test age was 90 days. This paper includes the results of 60 day-tests. A quantity of the specimens required for assessment