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Synthesis of ceramic protective SHS-coatings for refractory concretes

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Abstract

The presented investigations were performed concerning production of protective SHS-coatings based on the Al–SiO_2 system for protection of concrete. Quartz sand and kaolin were used as silicon-containing components. The thermal analysis has shown that in some cases incorporation of additions allows increasing the intensity of SHS process. The X-ray phase analysis indicated that a phase composition of coatings mainly consists of mullite, sillimanite, corundum and residual quartz. The SHS-synthesized ceramic materials, and coatings obtained on their base, were investigated regarding the physicochemical and thermal properties such as density, porosity, adhesion strength, temperature coefficient of linear expansion, fire protection and thermal resistance. It has been found that additions have an influence on the above-mentioned properties, and high adhesion strength is characteristic of coatings that contain additions of titanium dioxide and boric acid. The investigations resulted in the development of coating compositions based on the Al–SiO_2 system and various additions for protection of different structural elements.
Keywords: SHS-coating, Exothermal synthesis, Binder, Fire resistance, Thermal resistance, Mullite

SYNTEZA SHS CERAMICZNYCH WARSTW OCHRONNYCH NA BETONACH OGNIOTRWAŁYCH

Prezentowane badania przeprowadzono w odniesieniu do wytwarzania metodą SHS pokryć ochronnych bazujących na układzie Al–SiO_2, aby chronić beton. Wykorzystano piasek kwarcowy i kaolin jako składniki zawierające krzem. Analiza termiczna pokazała, że w pewnych przypadkach wprowadzenie dodatków pozwoliło na zwiększenie intensywności procesu SHS. Rentgenowska analiza fazowa ujawniła, że pokrycia złożone są głównie z mullitu, sillimanitu, korundu i kwarcu resztkowego. Zsyntezowane metodą SHS materiały i pokrycia otrzymane na ich bazie badano w odniesieniu do ich właściwości fizykochemicznych i cieplnych takich jak gęstość, porowatość, wytrzymałość adhezyjna, współczynnik liniowej rozszerzalności cieplnej, ochrona ogniowa i odporność termiczna. Stwierdzono, że dodatki mają wpływ na wspomniane właściwości, a wysoka wytrzymałość adhezyjna jest charakterystyczna dla pokryć zawierających dodatki tlenku tytanu i kwasu borowego. Przeprowadzone badania doprowadziły do opracowania składów pokryć, opartych na układzie Al–SiO_2 i różnych dodatkach, przeznaczonych do ochrony różnych elementów konstrukcyjnych.
Słowa kluczowe: pokrycie SHS, synteza egzotermiczna, spoiwo, odporność ogniowa, odporność termiczna, mullit

1. Introduction

To increase energy security in Belarus, Lithuania and other European countries, it is planned to develop energy sector based on the use of biofuels. In recent years several power units have been put into operation, and there are the projects to build new ones designed to use biofuels as well as to burn domestic and medical wastes. In these technological units, the intensive burning of fuel occurs in a boiling layer, and processes of heat exchange and chemical reactions. For this reason, the service life of conventional refractory materials and structures made of them is not sufficient because they operate in extreme conditions such as a high temperature in the range from 1000°C to 1600°C, chemically aggressive environment and wear under the action of gas and hard particle flows, and thermal cycles, etc. Therefore, on updating, development, repair and building of special-purpose units, which include thermal electrolysers, heat-treatment furnaces, mixers for holding and dosed pouring of metals, special attention is given to the development and application of refractory materials [1–3]. This is associated with solving the problems of increase operating properties and service life of these units as well as with attacking the problems of energy requirements and the saving of material resources. The cost of refractory materials often amounts to 50% of that of thermal generating units. However, under certain operating conditions the service life of installations made from refractory materials is as short as 1 to 2 years.

Now it is planned to build the Training Complex for Modelling of Fires in Living Quarters, Social Centres and Production Spaces at the operational-tactical training ground of

Ministry of Emergency Situations of the Republic of Belarus. It will be the first construction of this type on the territory of CIS. The aim of its creation is to increase the qualification level of firemen due to their training under the conditions maximally close to real situations.

In West European countries and the USA, training complexes in the form of buildings (Burn Buildings) have been successfully used since 1965. The general distinctive feature of the above-mentioned objects is that they have forms of fragments of various-purpose buildings, the bearing and filler structures of which are protected against multiple actions of fire. The burning is initiated in these “burn buildings”, and the temperature conditions maintained correspond to a real fire which makes it possible to guarantee safety of trainees.

When creating such objects, the most urgent problem is to ensure thermal protection of building structures as they should withstand multiple high-temperature fire actions (up to 1200°C), and in this case the protective material should be resistant to destruction that can result from manifold thermal impacts (heating-cooling: 1200°C – water no less than 70 thermal cycles) and have a sufficiently high strength (no less than 50 MPa).

The analysis of fire protection methods used at analogues objects indicates that this problem can be solved by constructive methods and in particular by application of composites consisting of heat-insulating and protective layers. Non-combustible heat-insulating materials are used as heat-insulating layers and refractory ceramic materials as protective layers. Metallic sheets have sufficient mechanical strength, but they are short-lived and much time is required for technical maintenance and repair of the system. When refractory ceramic plates are used, the system is quickly and easily maintained and repaired. On the basis of this knowledge there is tendency in the world practice to use refractory ceramic materials as protective layers. However these materials are rather costly.

Under the conditions of multiple actions of dangerous fire factors, the concrete structures are not only subjected to periodic high-temperature action (up to 1200°C) but also to “thermal impacts” (cold watering of a heated concrete). This results in cracking, damage of protective layer and exposure of reinforcement with starting the latter to deform under the action of high temperatures.

To increase the operating life of construction refractories of heat-generating units and of structure elements, and for an improvement of fire protection, the realization is made by using different methods that include the surface hardening of a refractory layer by exposure to high energies, the change of refractory in a working layer for a more high-strength material, the application of protective–hardening coatings, etc. From the viewpoint of practical realization, the application of protective-hardening coatings is the most efficient method as it requires the lowest labour and material costs. The coatings are applied onto the surface of internal structures of a heating unit with its subsequent going into the operating mode. In some works, it is suggested to use a self-propagating high-temperature synthesis to decrease energy consumption during the synthesis of ceramic material phases [4–6].

The self-propagating high-temperature synthesis (SHS) is in principle a process in which an exothermal reaction is realized in mixtures of chemical elements and compounds with formation of condensed products. The characteristic feature of the high-temperature synthesis process is its self-maintaining due to energy released upon the interaction of initial mixture components.

In many respects as a technological approach, the SHS method is superior to conventional synthesis methods that use high-temperature furnaces, and it holds much promise for application in manufacturing industry of modern refractory and high-melting-point materials and composites.

It is known that the SHS method finds application for production of mortars as well as of various pastes, daubing materials, etc., that are used as binders for bonding of laying components, when making a furnace lining (mortar solution) or for sealing and protection of a furnace lining against action of gases, dust, abrupt temperature drops, etc., (in the form of daubing materials and pastes).

When producing various building materials such as lining materials, refractories, light cellular concretes, and heat- and fire- protective materials, it is practical to give preference to SHS systems containing silicon dioxide (SiO_2) as this component is the basis of the majority of natural materials and building industry wastes [7–12].

From a viewpoint of practical application, concerning aluminosilicate refractories most spread in industry, the coatings obtained on the basis of the Al–SiO_2 system using the SHS technology are of special interest. The coatings applied to the surface of refractories widen the temperature range of application of a refractory base, lead to a considerable decrease of physicochemical corrosion and mechanical surface erosion as well as to increase of the temperature range and life time of refractories on their use under the conditions of static and dynamic (including cycling) action of aggressive media and high-temperature gas and dust flows.

This paper is aimed at the development of protective coatings for fire-resistant concretes, structural elements of high-temperature plants and units using exothermal synthesis processes (SHS).

2. Experimental

To obtain coatings with the aid of the method of self-propagating high-temperature synthesis, the main initial components used in this work were technogenic raw materials such as aluminium powders and natural ones including quartz sand and kaolin.

The aluminium powder is obtained by milling of primary aluminium in a ball mill. The shape of aluminium powder particles looks like plates covered by thin fatty and oxide films. An apparent density was about 200 kg/m^3 and a content of active aluminium was 91%.

The milled dust-like quartz is the product of milling of dry enriched quartz sand up to passing through a sieve № 005 of no less than 75% of a mill product.

The kaolin is a clay rock of white colour that consists of a kaolinite mineral. It is formed on failure (weathering) of granites, gneisses and other rocks containing feldspars (primary kaolins). The rewashing of primary kaolins results in their redeposition in the form of sedimentary rocks, and there occurs formation of secondary kaolins also referred to as "kaolin clays". The formula is as follows: $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$. The main kaolin properties include high fire resistance, low plasticity and binding capacity.

To activate the synthesis process, the additions of sodium silicofluoride and cryolite were used with their content not exceeding 5%. When performing investigations, the use was also made of boric acid, titanium oxide and calcium sulphate additions were applied.

The raw mixture was prepared using a dry method that involved stirring of a definite quantity of initial components preliminarily weighed on electronic scales.

The stirring was carried out in a ball mill for 15 minutes using grinding bodies made of aluminosilicate ceramics.

To prepare a covering mass, the binder solution was continuously added in a charge. The binder was a solution of sodium silicate glass with modulus 2.06. It was incorporated in the quantity necessary to obtain a paste-like mass that was brushed on a sample working surface in the form of a 1–2 mm thick layer. The consistency required for this was regulated by the binder quantity. The coated samples were dried at room temperature within 24 hours, then heated up to a temperature of 150 °C, and hold at this temperature for 2 hours with subsequent increasing of the temperature to 400–450 °C, and holding at this temperature for 2 hours in order to remove water. This was followed by heating of samples at a rate of 7–10 °C/min to complete the SHS process.

The samples were annealed in a laboratory electric furnace of the SNOL 6,7/1300 type (in air) at the temperatures of 800–1300 °C. Then they were hold at maximum temperature for 1 hour. The samples were cooled together with the furnace up to room temperature.

The thermal coefficients of linear expansion (TCLE) were determined by a NETZSCH DIL 402 PC dilatometer. The differential thermal analysis (DTA) was carried out by a MOM Q-1500 D (Paulik-Paulik-Erdey) derivatograph. The phase composition of the synthesized material was investigated by X-ray analysis using a Bruker D8 ADVANCE diffractometer. Crystal phases were identified with the aid of Powder Diffraction Standards 2003 international data file and DIFFRACPLUS software (Bruker). The microstructural study of the surface were performed with a JEOL 7600F scanning electron microscope and optical microscope LEICA DFC 280.

3. Results and discussion

3.1. Optimisation of kaolin content

The compositions of mixtures selected for the investigation contained (15–20)% of aluminium and (75–80)% of silicon-containing components that were quartz and kaolin as well as their mixtures.

The progress of SHS synthesis of coatings based on the mixtures is associated with the following chemical processes that ensure formation of crystalline phases of mullite, corundum and other aluminosilicate compounds [13]:

$$4Al + 3SiO_2 = 2Al_2O_3 + 3Si \qquad (1),$$

$$Si + O_2 = SiO_2 \qquad (2),$$

$$3Al_2O_3 + 2SiO_2 = [3Al_2O_3{\cdot}2SiO_2] \qquad (3),$$

$$12Al + 4SiO_2 + 9O_2 = 2[3Al_2O_3{\cdot}2SiO_2] \qquad (4).$$

The incorporation of kaolin into an initial mixture for obtaining a coating allows us not only to decrease the aluminium quantity required for the formation of mullite, but also to increase a sedimentation stability of suspension used during the usage of the coating. Besides, owing to the increased content of free quartz, there is practically no inhabitation of the process due to the effect of dilution and decrease of contact surface areas of interacting components under the action of clay minerals.

As is evident from a visual assessment of coatings formed with the aid of these mixtures, the most optimum compositions were those containing 15% of aluminium. The coatings were characterized by high adhesion with concrete and absence of cracks after drying and annealing. The optimum content of kaolin is up to 30%, and in this case the most high-quality coatings are obtained with the use of enriched kaolins which is probably associated with their high content of free quartz. This ensures a decrease in shrinkage effects during drying and annealing of coatings and prevents initiation of cracking.

The optical microscopy data indicate that the number of pores is increased with increasing the kaolin content in the mixture, and the structure is presented by crystalline aggregates cemented together by amorphized glassy phase.

The major factors that characterize a protective fire-resistant coating are porosity, adhesion strength and heat resistance.

As it follows from experimental results in the case of using the unmodified mixtures the coatings obtained without the use of kaolin have the highest adhesion strength and the lowest porosity. The heat resistance indexes of coatings are actually limited only by heat resistance of a refractory base and are 12–14 cycles (1000 °C - water), and material failure occurs due to the initiation and development of main cracks in the sample surface areas where the coating is absent.

The graph of dependence of porosity and adhesion strength on kaolin content of mixture is presented in Fig. 1.

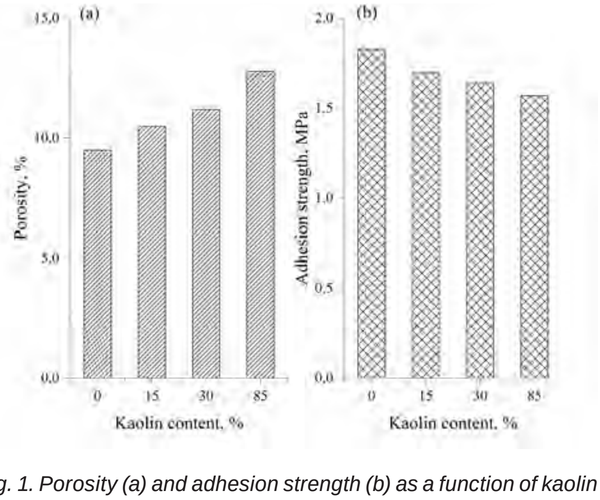

Fig. 1. Porosity (a) and adhesion strength (b) as a function of kaolin content of mixture.

As it follows from the experimental data the increase of porosity and the decrease of adhesion strength occurs with increasing the kaolin content of mixture. This is accounted for by a less active proceeding of SHS due to the increase of proportion of an inactive component. In addition, as noted above, shrinkage effects occur, when the kaolin content is increased that lead to cracking.

The TCLE measurements have shown that the coating has thermal expansion corresponding to that of mullite-corundum and chamotte refractories. This ensures obtaining the values close to those of fillers used for preparation of a concrete mixture. As ceramic materials work in compression in the best way a compression strength for most of ceramic materials is higher than a tensile one by a factor of above 6, the TCLE of a coating should not exceed that of a base material. The TCLE data experimentally obtained are given in Fig. 2, depending on the measurement temperature for the coating and concrete.

As is seen from the presented dependence, the TCLE of the coating is lower than that of concrete, and is characterized by the stability in the temperature range of 200–800 °C which is due to completion of sintering processes.

3.2. Selection of additives

The mixture composition selected for further investigations contained 15% of kaolin which ensured the uniform applying and formation of a coating with rather high adhesion. Using this composition as a basis, the synthesis of coatings was carried out with incorporation of additions activating the synthesis process. Fig. 3 illustrates the dependences of porosity and adhesion strength on the kind of addition.

As may be evident from the presented dependence diagram upon incorporation of additions activating the synthesis process, there occurs an increase in the coating-to-base adhesion strength and a decrease in porosity due to additional initiation of SHS process and participation of addition in sintering of a coating at high temperatures. Thus, titanium dioxide and boric acid in the quantity of (5–10)% are the optimum additions that ensure high adhesion strength of a coating.

The DTA data for mixtures with incorporated activating additions (Fig. 4) have revealed that upon volume heating the greatest influence is exerted by additions of fluorinated compounds. This is conditioned by the development of a gas-transportation mechanism of mass transfer (due to the formation of gaseous silicon and aluminium fluorides) as well by the removal of oxide films from the surface of reactionary aluminium particles.

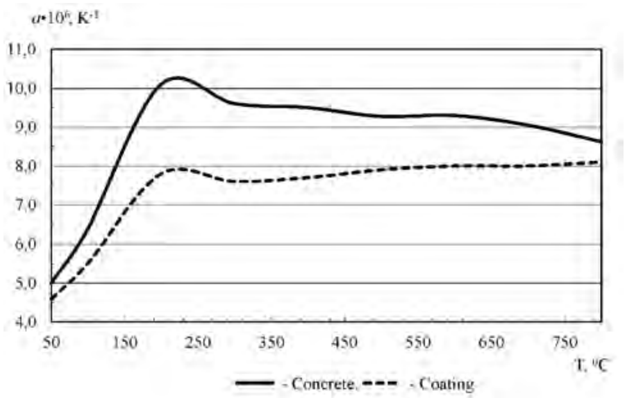

Fig. 2. TCLE depending on temperature for coating and base concrete.

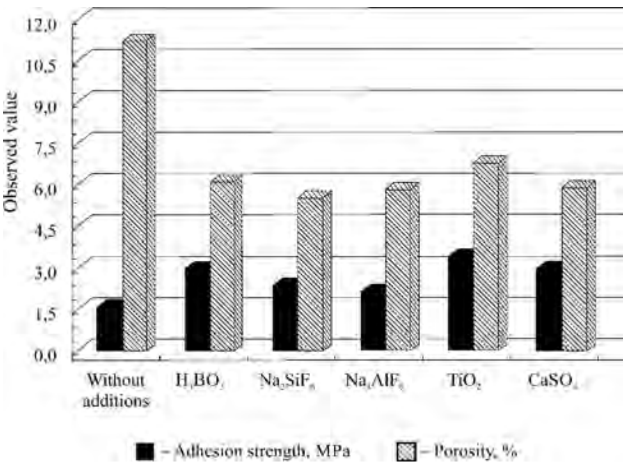

Fig. 3. Adhesion strength and porosity of obtained coatings depending on the kind of addition.

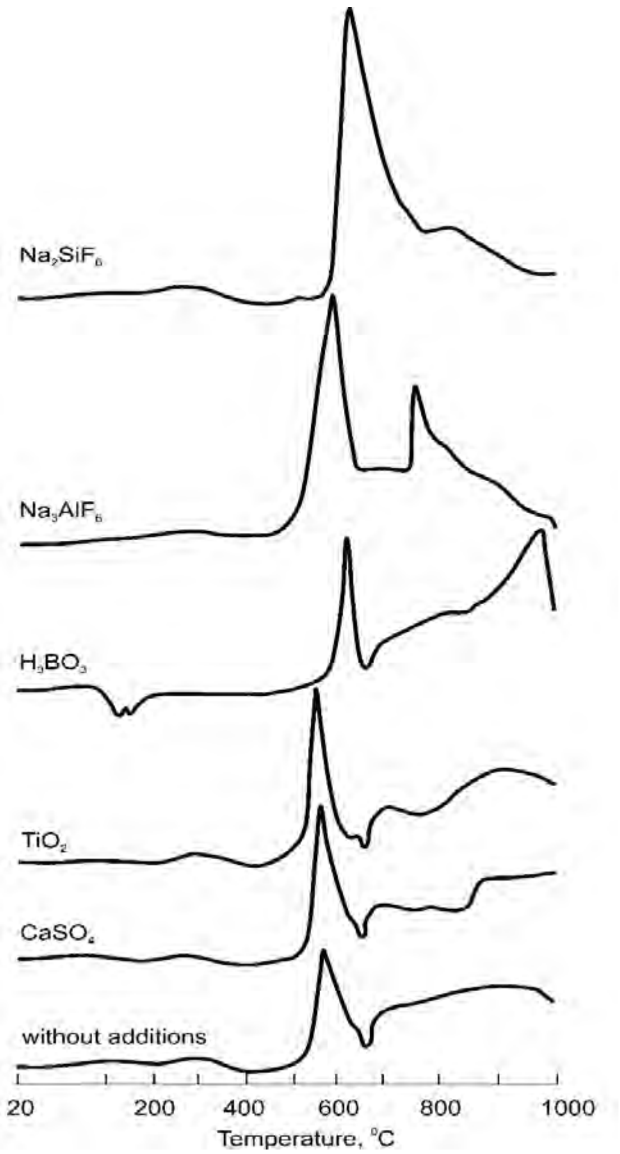

Fig. 4. Curves of DTA of mixtures depending on the kind of addition.

No effect is practically exerted by other additions as the temperature of heating initiation exceeds that of aluminium oxidation by air oxygen which in this case does not allow SHS reaction to be initiated.

The phase composition of coatings obtained on the basis of the mixture containing 15% kaolin, 70% quartz and 15% aluminium is illustrated in Fig. 5, when a binder is a liquid glass and different additions are used.

As is evident from the presented data, the formation of mullite occurs only when using kaolin as a silicon-containing component as well as activating additions such as boric acid and sodium silicofluoride.

When the mixture of kaolin and quartz is used, the formation of mullite is not achieved due to insufficient quantity of aluminium oxide that is bound not only by silica with the formation of sillimanite but also by sodium silicate which decreases probability of mullite formation.

In the SHS process, the formation of mullite is mainly associated with phase transformations in kaolins that occur during the latter thermal treatment. Thus, in the temperature range of 450–600 °C chemically bound water is removed due to kaolinite decomposition according to the following reaction:

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O \rightarrow [Al_2O_3+2SiO_2] + 2H_2O \quad (5).$$

In the temperature range of 950–1050 °C, the kaolinite mullitization process is observed to occur. At the temperature of 1100 °C on release of heat, a metakaolinite is rearranged with formation of a $3Al_2O_3{\cdot}2SiO_2$ mullite during a final stage:

$$3[Al_2O_3{\cdot}2SiO_2] \rightarrow 3Al_2O_3{\cdot}2SiO_2+4SiO_2 \quad (6).$$

Then with rise in the temperature, the quantity of mullite is continuously increased and reaches maximum at 1250–1350° C. At the temperatures exceeding 1200 °C, the long-term holding has no effect on increase of mullite yield but promotes growth of its crystals.

The coating microstructure observed by an electron scanning microscope is presented in Fig. 6.

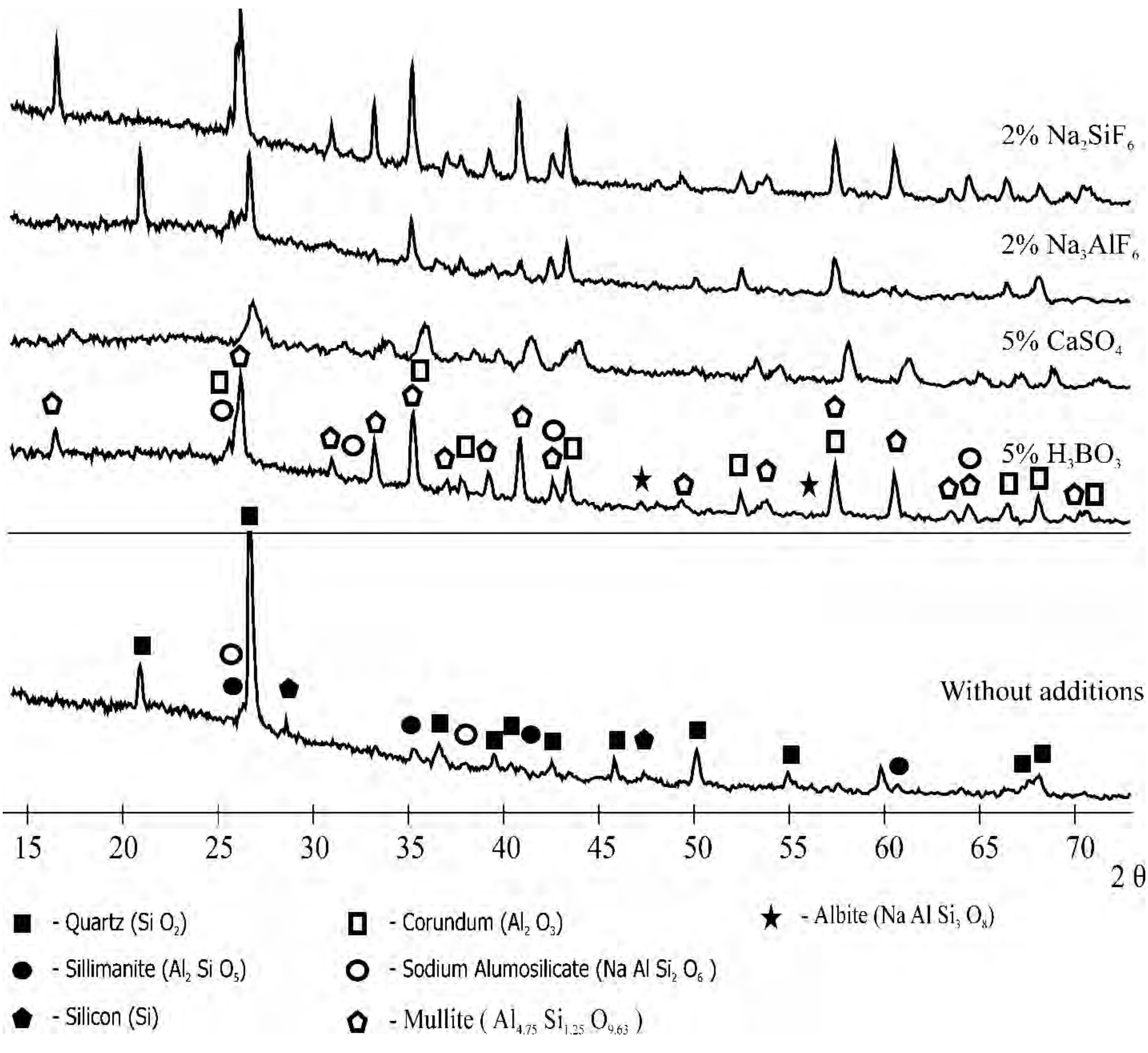

Fig. 5. X-ray diffraction patterns of coatings of the composition containing 15% kaolin, 70% quartz and 15% aluminium and obtained with the use of different additions.

3.3. Optimization of binder

To ensure the effective protection of lining of furnaces used for burning of wastes it is necessary that a developed SHS coating could be used at an operating temperature that is no less than 1000–1100 °C. In such conditions, it should have high mechanical and adhesion strengths without forming a great amount of a liquid phase that could lead to sticking of ashes and slags.

The developed coating composition used for investigation included aluminium, kaolin and quartz sand. The modifying additions were 5% titanium dioxide and 1.5% sodium silicofluoride They were incorporated into the mixture in the quantity exceeding 100% and facilitated the temperature of synthesis onset. The binder was a solution of sodium silicate glass of various concentrations that were regulated by the ratio of a commercially produced glass to added water. The ratio of sodium silicate glass to water varied in the following range (by volume %): 1:0, 9:1, 8:2, 7:3, 6:4, 5:5 and 4:6. The ratio of solution to solid phase was constant and as follows: 1 ml to 1 g of dry mixture.

After drying, the coating samples prepared on the basis of the above-mentioned SHS mixture composition and binder solutions were annealed in an electric furnace at the temperatures ranging from 800 °C to 1100 °C with interval of 100 °C for determining the temperature of starting the formation of fused areas. The coating characteristics are presented in Table 1.

It has been established that after drying the coatings obtained using low-concentration solutions of sodium silicate glass (ratios: 5:5 and 4:6) have defects in the form of cracks that are formed due to a great shrinkage. The temperature of fusion onset of coatings is above 110 °C, with changing coating strength characteristic (adhesion strength) from 2.8 MPa to 1.8 MPa.

The examinations of coating microstructures performed with the aid of an optical microscope have shown the presence of a considerable quantity of a glassy phase only when undiluted liquid glass is used (Fig. 7, magnification ×100).

Thus, when performing the investigations it has been found that the optimum ratio of a liquid glass to water by volume % should be 9:1–8:2. With this ratio an undesirable sticking of heat-treated products, slags and ashes to the surface of lining becomes less probable with retaining high operating characteristics of coatings.

4. Conclusion

The investigations were performed concerning production of protective SHS-coatings based on the $Al–SiO_2$ system for protection of concrete. Quartz sand and kaolin were used as silicon-containing components. It has been established that the use of kaolin and quartz sand mixtures decreases the probability of forming cracks in coatings during their drying and annealing with increasing the qualitative characteristics. The thermal analysis has shown that in

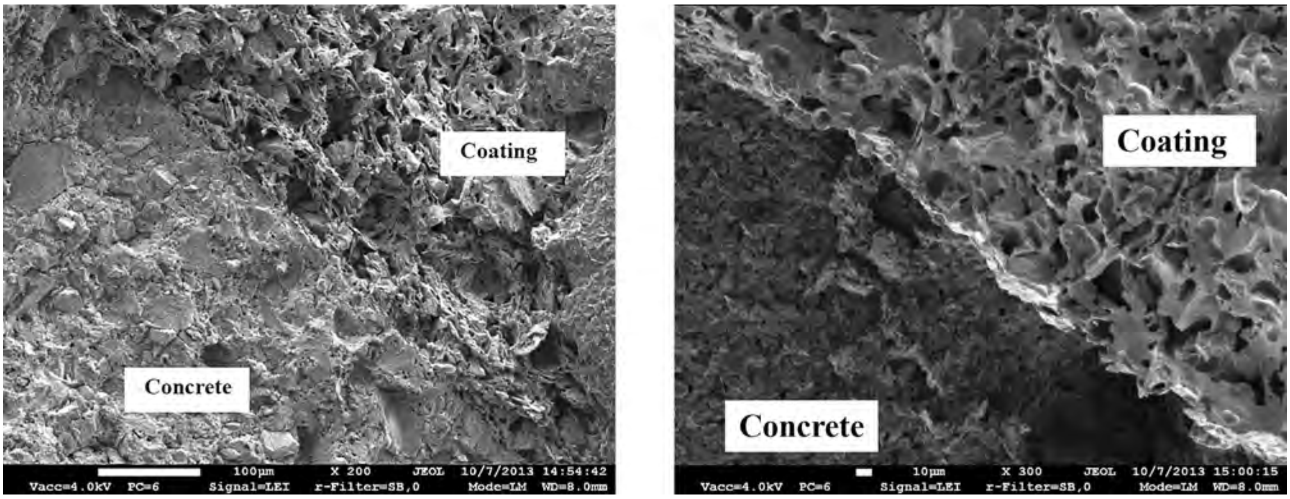

Fig. 6. Microstructure of a coating applied onto concrete base.

Table 1. Coating characteristics depending on ratio of sodium silicate glass solution to water.

Characteristic	Ratio of sodium silicate glass to water [vol. %]						
	1:0	9:1	8:2	7:3	6:4	5:5	4:6
Annealing temperature prior to fusion onset [°C]	1100	>1100	>1100	>1100	>1100	>1100	>1100
Adhesion strength [MPa]	2.8	2.5	2.4	2.1	1.8	–	–
Presence of defects	None	None	None	None	None	Cracks	Cracks
Compression strength of coating material after annealing [MPa]	80	78	75	70	70	–	–
Thermal resistance (1000 °C – water), cycles	14	15	15	13	13	–	–

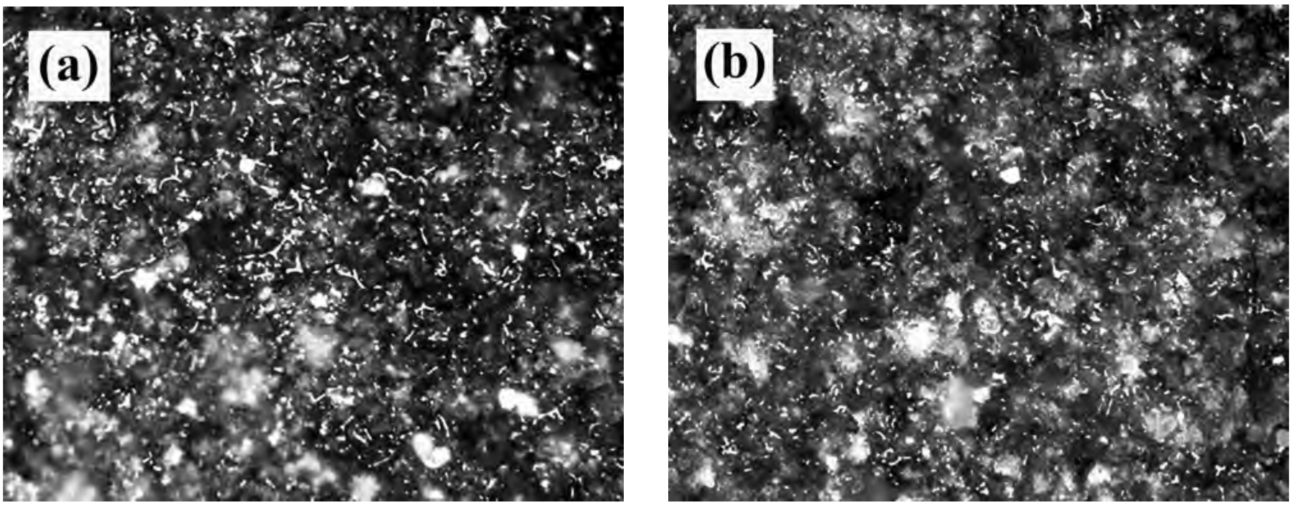

Fig. 7. Microstructure of coatings obtained with various ratios of a liquid glass to water, by volume %: a) 1:0; b) 8:2.

some cases incorporation of additions allows increasing the intensity of SHS process.

The X-ray phase analysis showed that the phase composition of coatings mainly consists of mullite, sillimanite, corundum and residual quartz. The mullite formation is ensured only in case of the use of kaolin as silicon-containing component as well as of activating additions (boric acid and sodium silicofluoride). The synthesized ceramic SHS materials and coatings obtained on their base were investigated regarding their physicochemical and thermal properties such as density, porosity, adhesion strength, temperature coefficient of linear expansion, fire protection and thermal resistance. It has been found that additions have effect on the above-mentioned properties and high adhesion strength is characteristic of coatings that contain additions of titanium dioxide and boric acid. It is shown that the optimum ratio of a liquid glass to water is varied in the following range (by volume %): 9:1–7:3.

The investigations performed resulted in the development of coating compositions based on the Al–SiO_2 system and various additions for protection of different structural elements.

Acknowledgments

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