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STUDY OF THERMOCHEMICAL TRANSFORMATIONS IN FIREPROOF COATINGS OF STEEL BUILDING ELEMENTS

Justification of prospects of use of phosphatic sheaves for receiving fireproof coverings is given. The structure of a fireproof covering on the basis of a phosphatic binding cold curing is developed and its properties are studied. The general scheme of interaction in $NH_4H_2PO_4$ – $(NH_4)_2HPO_4$ – MgO – Cr_2O_3 – H_2O system is established. The thermochemical nature of processes is investigated.

Introduction. One of the least fireproof building elements are steel bearing structures. For the majority of steels, temperature equal to 500°C is considered to be critical. At this temperature yield point of metal drops to the size of the running voltages invoked by the external loading and own mass of the structure. After reaching of this temperature, deformation of engineering structures and their almost instant destruction is observed [1].

At the same time there are no domestically produced materials of the 1st group of fireproofing, that can provide under the fire exposure up to 1100°C a thermal protection of bearing metal structures for 150 minutes [2]. Based on the above-mentioned, development of effective fireproof coverings for steel structures of the 1-st fire resistance group with application of raw material resources of the country was applicable goal of the research.

The main requirements to fire-retarding composition of the 1-st fire resistance group are:

– heat resistance, i.e., resistance to sudden thermal shock;

– fire resistance – ability to save its properties at temperature exposure up to 1100°C as much as 150 minutes;

– ability to isolate heat flow of fire activity, while maintaining the integrity, prevent the destruction of the protecting material;

– absence of toxic substances emission at fire activity;

– good adhesion to steel structures;

– workability – ability to provide fast curable coating after its applying;

– weather resistance;

– durability.

Besides, the covering should have inhibiting properties.

In view of these requirements, the selection of components was carried out to create a composite material.

The basic and most responsible component of a fireproof material providing its properties is a bonding agent. It is the bonding agent that provides and defines the main physicochemical and operating properties of the coverage.

As binders in fireproof materials on an industrial scale a number of organic and inorganic substances were tested [3-6]. They, as a rule, have their pluses as well as minuses. For example, intumescent coatings based on organic binders are manufacturable with high architectural-decorative and technical characteristics. However, they provide the limit of fire resistance of structures only up to one hour, and the products of combustion of such coatings are toxic.

Fireproof coverings on liquid glass provide limits of fire resistance up to 3 hours, but they are not manufacturable because of short duration of their storage. Besides they are fragile with low adhesion, insufficient weather resistance and consequently are short-lived. Eventually these compositions carbonized that deteriorates decorative and operational properties of the processed surfaces.

Phosphate binders are the best suited to the above-mentioned set of requirements. These types of binders provide the required fire resistance limits as they are mostly refractory compounds, they are not destroyed under the action of heat flow, save their structure and properties under the required thermal action, have good adhesion to steel structures. It is necessary to note, that structures on the basis of phosphatic binders have found wide industrial application abroad, especially in such countries, as the USA, China, Japan that proves to be true by numerous patents and publications [7–13].

In order to support business objectives the most promising of the number of phosphate binders are those at decomposition of which chemically related water will be disengaged as well as other gaseous products that in combination prevent oxygen penetration into the flame zone and thus serve as a fire extinguisher to some extent.

Such a binder, from our point of view, can be magnesiumammoniumphosphatic binder which can be prepared using commercially available materials - ammophos brand 12-52 [14], which is a mixture of ammonium dihydrogen phosphate and hydrogen phosphate.

As a curing agent of this binder we have offered to apply fine powder, derived from spent periclase-chromite refractory bricks brand PCHC [15] in rotary cement kilns.

Taking into consideration the above-mentioned, the development of flame retardant was carried out on the basis of magnesiumammonium-phosphatic binder providing fast curing of composition. Spent periclase-chromite firebrick and ammophos were used as raw material to create a binder. It was assumed that while interacting of selected raw materials double magnesiumammoniumphosphates are formed which, when exposed to high temperatures,can be decomposed to release gaseous products (ammonia). They do not support burning and, thus, block the centers of a fire. Under further exposure to temperatures decomposition of ammonia into nitrogen and hydrogen is carried out with loss of energy, which also reduces the temperature of the fire.

To ensure good heat insulating properties expanded vermiculite was used as a filler [16]. Vermiculite consisting of zeolite water loses it under temperature exposure, and thus also contributing to a reduction of combustion temperature and providing thermal insulation.

Data on the reaction of interaction of the above-mentioned raw materials and curing chemistry of magnesiumammoniumphosphatic binders is not numerous in literary source. It should be noted that for such systems a complex interaction between structure, a phase condition of initial components and durability of the forming structures are typical. Therefore, undoubtedly, it is impossible to predict precisely conditions for obtaining the binder from this technogenic raw material, as well as interaction mechanisms of double MgO $\cdot Cr_2O_3$ oxide with ammophos.

Summarizing all above-stated, it is possible to conclude, that the system accepted for research $NH_4N_2PO_4 – (NH_4)_2HPO_4 – MgO – Cr_2O_3 – H_2O$ is complex, not studied, with no information in the literature on the character of crystallization processes constituting the foundation of curing of this composition. Research of phase formation in the above system under nonequilibrium conditions is of great scientific interest.

Therefore, one of the goals of the study was to establish thermochemical transformations in fire-retardant coating, which will allow running the process of obtaining the binder and contributing to the chemistry and technology of phosphate materials.

Main part. At the first stage of work on the chosen raw material for the establishment of the optimum parity of the components a number of structures have been investigated. As a function of structures optimization strength and adhesion properties were used. From the chart, presented in Fig.1, it is seen that the maximum values of adhesion and compression strength [17] is in the range of percentage composition of ammophos 40-50 wt.%. Thus, Water-firm parity has made 0.2. Development of mechanical strength at compression of the above-mentioned system is particularly intense within the first four days (up to 90% of the final strength).

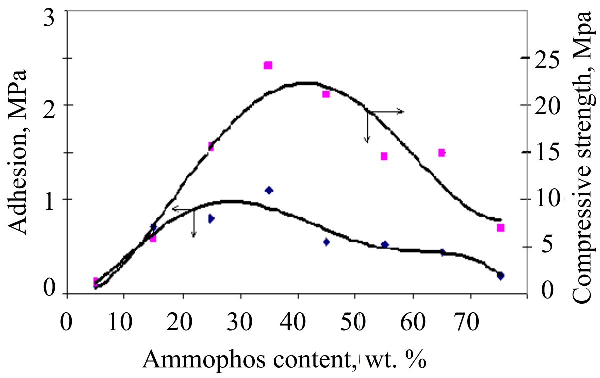

Fig. 1. Dependence of adhesion and durability under compression of fireproof composition on the content of phosphatic binder

The essential difference of values of parameters of the above-stated properties obtaining under changing percentage parity of raw components can be explained not only by rheology but also different phase structure of products of the interoperability forming in the given composition.

According to X-ray diffraction (XRD), the main phase of tumors in this system is struvite $NH_4MgPO_4 \cdot 6H_2O$. There are also diffraction peaks of smaller intensity responsible for dittmarite. With the increase of ammophos over 60 wt. % the other new formation together with struvite appears – shertellit.

After consideration of the obtained results the optimization of the content of fire-retardant coating was carried out by changing the content of these components in the following range: binder (ammophos) - 40-50 wt. %, curing agent of a binder (periclase-chromite powder) - 50-60 wt. %. The highest rates in the properties of the coating are observed under the following composition of the components: 42 wt. % of phosphate binder and 58 wt. % of curing agent.

The development of coating composition was carried out by varying the content of magnesiumammoniumphosphatic binder, a set regulator and vermiculite. A combination of requirements on durability under compression, adhesion and consistency was a function of optimization for covering. Thus requirements on covering density decrease, as well as reduction of its cost were taken into consideration. Taking into account all requirements, composition containing vermiculite 20 wt. % is ideal.

At the second stage of the study examining of the process of composition curing, as well as phase transformations occurring in the system under the action of temperatures up to 1100 ° C was the main task. The obtained results will make it possible to predict the behavior of coatings in case of fire, to manage their properties and, as a consequence, to develop effective fire-retardant materials in the future.

Influence of the amount of the filler on the resistance of the coating to thermal effects was assessed by measuring the adhesion and durability after heating the samples in the temperature range of 100-1100°C.

From the graphic dependences presented in Fig. 2 and 3, it is clear, that there is a decline of durability and adhesion at 300 and 900 ° C.

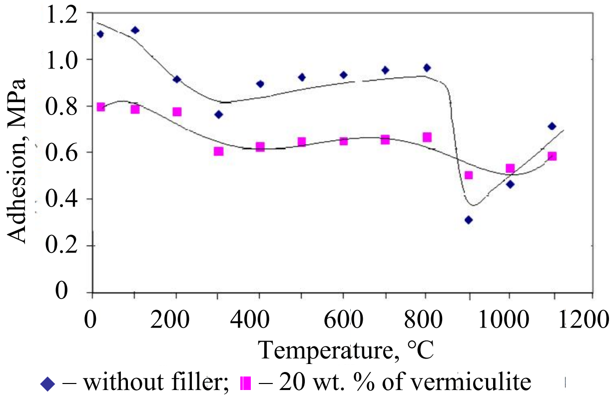

Fig. 2. Dependence of adhesion of fireproof composition and covering on its basis on temperature

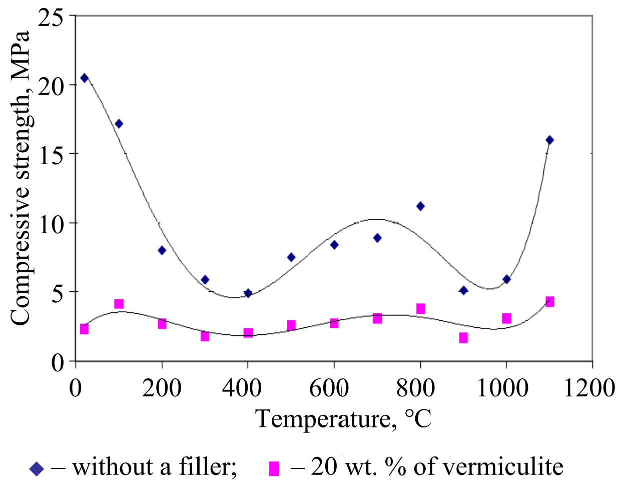

Fig. 3. Dependence of durability at compression of fireproof composition and covering on its basis on temperature

The coating has similar thermochemical processes. However, in the temperature range of 50-400°C in the thermogram there is one endoeffect with a minimum at 130°C. This is due to the fact that vermiculite under these temperatures rapidly gives up the water.

The third heat effect is exothermic-occurs in the temperature range of 600-700° C.

By differential thermal analysis thermal effects were studied that occur when heated in the compositions.

For the establishment of the nature of these thermal effects roentgenograms of investigated structures have been taken, namely: compositions without a filler and coverings with vermiculite. Also roentgenograms of coating composition after temperature exposure of 170, 260 and 690°C have been taken.

According to the data analysis of derivatograms and XRD in the composition without a filler at the temperature range from 50 to 400 ° C, there are two endothermic effects with minimums at 109 and 222°C. The first endoeffect is connected with struvite dehydration and deammonation , according to X-ray data of the sample thermally processed at 170 °C. The second endoeffect in the range of 190-260°C is provided by dittmarite dehydration and its deammonation as well as continuation of struvite dehydration. According to the X-ray diffraction analysis of the heat-treated at 280°C composition, intensity increase of dittmarite diffraction maximum is recorded.

Maximum exothermic peak for the composition is observed at the temperature of 663°C, for the coating - at 679°C. In this temperature range final dehydration and deammonation of dittmarite take place as well as polycondensation with magnesium diphosphate formation. This is confirmed by x-ray data of the composition after heat treatment at 680 ° C, which is consistent with published data on the full transition of the binder in the magnesium orthophosphate at 900°C [18].

Thus, the drop of adhesion and durability values at 300 and 900°C is connected with structural transformations in the flame-retardant coating, namely dehydration and struvite deammonation and at 300°C and crystallization of ortho-and magnesium pyrophosphates, in the temperature range of 600-900°C.

From the graphic dependences presented in Fig. 2 and 3, it is clear, that introduction of vermiculite reduces falling of durability and adhesive properties of the coating in the specified temperature intervals. Curves of graphic dependences of variation of coating properties are flatter. It provides stability of demonstration of required properties of a coating in temperature range of 100–1100°C and thus guarantees reliability of its work in case of fire.

Conclusion. Based on the above the scheme of thermochemical transformations in the system $NH_4H_2PO_4 - (NH_4)_2HPO_4 - MgO - Cr_2O_3 - H_2O$ can be described by the following reactions:

$$2MgO + 2NH_4^+ + 2H_2PO_4^- + 5H_2O \rightarrow$$
$$\rightarrow 2NH_4MgPO_4 \cdot 6H_2O,$$

$$MgO + NH_4^+ + H_2PO_4^- + H_2O \rightarrow$$
$$\rightarrow NH_4MgPO_4 \cdot H_2O + H_2O,$$
$$MgO + 2NH_4^+ + 2H_2PO_4^- + 3H_2O \rightarrow$$
$$\rightarrow (NH_4)_2Mg(HPO_4)_2 \cdot 4H_2O.$$

It is established that under the interaction of magnesium oxide and ammoniumphosphatic binder mixed magnesiumphosphatic newformings are disengaged, struvite $NH_4MgPO_4 \cdot 6H_2O$ is the most important of them.

The way to prevent durability decreasing under temperature exposure in the composition on the base of magnesiumammoniumphosphatic binder is developed.

Developed effective coating will solve the problem of fire protection of steel structures.

Preliminary economic costing of coatings on magnesiumammoniumphosphatic binder show, that in comparison with compositions on liquid glass they 5-10 times cheaper and comparing with intumescent organic fire-retarding compositions – 30 times.

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