Thermal properties of coatings based on full aluminosiloxane polymer

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Abstract

This article is devoted to the study of thermal properties, heat resistance, corrosion resistance and fire resistance of new protective coatings based on the filled aluminosiloxane polymer. The aim of the study is to determine the effect of the source composition on the physical properties of the finished coating. Thermal stability was determined by periodic heating in a thermal chamber to a temperature of 800 °C for 5 h and then cooled in water. Corrosion resistance was determined by the change in roughness. Profiles and profilometers were used to determine the roughness parameters. Fire resistance was determined by the time from the start of the test to the onset of one of the normalized boundary states. It is set, that to improve the heat resistance of steel structures it is expedient to use appropriate coatings based on full aluminosiloxane polymer which contain Al₂O₃, ZrO₂, kaolin, kaolin fiber and modifier TiO₂ as fillers. The heat resistance of protective coatings for steel decreases by 20%–30% when kaolin is added at a heating temperature higher than 753 K. The heat resistance is increased by 30%–40% when kaolin fiber is added. Depth of corrosion of materials with developed protective coatings decreases by 2.2–3.5 times. The results of the study confirm that the introduction of kaolin in the coatings increases the fire resistance of the studied materials. Thus, the performance properties of the protective coatings can be adjusted over a wide temperature range by changing the oxide and silicate fillers.

1. Introduction

A promising way to protect building constructions of industrial objects from the influence of aggressive factors is coating their surfaces with coatings that have to work durable and reliable in the conditions of abrupt changes in temperatures. The use of thermoplastic and thermoset polymers has the fire risk and fire hazard. Simply adding flame retardant chemicals to polymers to reduce fire hazard and risk is not sufficient [1, 2]. Protection of building structures is provided by various coatings, which not only increase the service life of buildings, but also provide the necessary complex of valuable physical, mechanical and chemical properties that can be achieved by regulating the phase composition and structure. Silicon-based polymers are outstanding materials for coating surfaces. These compounds have excellent properties, such as strong adhesion to most substrates and high chemical, thermal and UV resistance. Additionally, they can be converted into ceramic materials (polymer-derived ceramics) by a heat treatment and, in some cases, by chemical reactions or radiation [3]. Organic silicate coatings are prepared on the basis of the original compositions, which are obtained by mechanic-chemical dispersion of the filler in the silicon environment of the organic film-forming agent. These coatings are economically advantageous and have significant advantages over other types of coatings [4].

The siloxane resin coatings of various formulations are especially popular, in particular coatings based on functional resins of amine silicon for polysiloxanes [5].
The main disadvantage of organic protective coatings, unlike metallic ones, is the possibility of diffusion of moisture, oxygen and halide ions through them, i.e. substances that cause corrosion. The degree of penetration is determined by the molecular weight of the anticorrosion coating material and its chemical structure. However, the lack of comprehensive data on the physical and chemical processes occurring in coatings under the influence of atmospheric factors does not make it possible to direct their operational properties. Therefore, a comprehensive study of protective coatings, including studies of both thermal properties and hydrophobic properties, corrosion resistance, is relevant.

2. Literature review

The choice of construction materials that work in high temperature and fire conditions depends on the expected life and conditions of use. Choosing the composition of coating, it is necessary to consider not only the fire and heat resistance, but also the weather resistance of the finished coatings. The stability of coating to the external factors can be increased by forming the appropriate phase composition and structure [6, 7].

The stability of coating is enhanced by adjusting the barrier type coating, which virtually prevents oxygen from accessing the surface of the material [8, 9].

Aluminosiloxane polymers are used to protect metal structures very often. Their technical and technical-economic properties are predefined by thermodynamic stability of siloxane connection (Si–O). These coatings combine thermal stability and chemical inertness of silicon-oxygen frame with high physical and mechanical properties [10, 11]. The presence of aluminium-containing radicals in the main chain enables the formation of new high-temperature and heat-resistant phases at lower temperatures.

A promising material for obtaining temperature- and fire-resistant protective coatings is aluminosiloxane lacquer (KO-978). This material has high elasticity, hydrophobicity, heat resistance and adhesion to various materials. Aluminosiloxane lacquer is also stable in a wide temperature range. Its ability to form reactive highly dispersed silica during thermo-oxidative degradation has significant advantages over other organic compounds [12, 13].

Thermal properties of protective coatings were investigated comprehensively. However, by adding new ingredients it is possible to increase not only the thermal properties, but also enhance weather resistance of coatings, that considerably increase their durability and reliability.

3. The main material of research with the complete ground of the got scientific results.

3.1. The objects of research

The objects of the research are compositions of protective coatings based on aluminosiloxane lacquer KO-978 with fillers (aluminium, zirconium (IV) oxides), kaolin, kaolin fibre and mineralizer (titanium (IV) oxide) (table 1). The research of coatings was conducted on structural rimming steel (St3kp) and concrete bases.

The aluminosiloxane polymer (PAS), as the filmforming agent, makes a significant contribution to the formation of properties of protective coatings. Significant changes occur during high-temperature heating. Aluminosiloxane, in contrast to organic compounds, has high thermal resistance due to the presence of ionized by 50% bond Si–O– (375 kJ mole⁻³) [9].

Thermo-oxidation destruction occurs first at the site of the Si–C side bonds. During this process volatile products are formed. The Si–O and Si–O–Al bonds, from which the microchain is constructed, are not destroyed. Si–O–Si, Al–O bonds are formed instead of two torn Si–C chains. The filmforming agent is only partially carbonated, but not destroyed. We have found that the mechanism of thermo oxidative degradation of aluminosiloxane is most clearly shown by the following scheme:

| № of coating composition | KO—978 | A1₂O₃ | ZrO₂ | Kaolin | Kaolin fibre | TiO₂ |
|--------------------------|--------|-------|------|--------|-------------|------|
| 1                        | 30.0   | 30.0  | 36.5 | —      | 3.5         | —    |
| 2                        | 30.0   | 40.0  | 11.5 | 15.0   | 3.5         | —    |
| 3                        | 30.0   | 30.0  | 22.0 | 12.5   | 3.5         | 2.0  |

Table 1. Source composition of protective coatings.
While initial compositions are being heated, temperature- and fire-resistant mullite-sillimanite and zirconium phases are formed as the part of the coating. The introduction of 1%–3% w.mass TiO₂ supports this synthesis. Therefore, the developed compositions can be used as protective coatings.

3.2. Methodology
The acknowledged standard methods were used at study. These methods allow studying physical-mechanical characteristics of protective coatings.

Thermal stability was determined by periodic heating in a furnace to a temperature of 800 °C for 5 h and then cooled in water.

Water absorption was determined by the change in weight of the samples before and after soaking in water. A thermostat, desiccator and electronic platform scales PV-2 (measurement accuracy ±0.001 g) were used during this test.

Corrosion resistance was evaluated by the change of roughness parameters and the area-damaged coating. To determine the roughness parameters profilometer PM-130, in which the sensor is a diamond needle that moves perpendicular to the surface (tracing: length 0.5–12.5 mm, accuracy up to 0.1 μm, speed 0.5–1.2 mm s⁻¹), and a dual microscope MIS-11 were used.

The microhardness of the coatings was determined using a PMT-3 device by the change of the size of diamond pyramid imprint at a holding time of 5 s.

Fire resistance was determined by the time from the start of the test to the onset of one of the normalized boundary states. The heat resistance was determined by the change in corrosion penetration, expressed in mm per year. For this purpose, the sample was subjected to unilateral heating in a high-temperature electric furnace SNOL 8/1600L with a microprocessor thermostat.

The microstructure and phase composition of the coatings were examined using a TESLA BS-300 electron raster microscope.

3.3. Findings
It is known, that durability and service ability of building materials and constructions are determined primarily by temperature of working conditions and firmness of protective coating to the action of unfavorable weather conditions.

The proposed coating compositions (table 1) were applied to the pre-treated surfaces with a thickness of 0.4 to 0.6 mm. Curing of the coating was carried out at room temperature for 24 h to achieve the maximum degree of microhardness (at least 200 MPa). The formation of the coating is accompanied by processes of wetting and distribution of the suspension. This creates an area of contact between the phases based on the adhesive bond. Accelerated studies to determine weather resistance have shown a high insulating ability of coatings. This ability depends on the content of the film-forming material and the filler. The water absorption of coatings on concrete is 1.5–2 times higher than the similar figure for St3kp steel due to the lower integrity determined by the surface relief (table 2).

The corrosion depth of protected metal decreased 2.2–3.5-fold, thereby durability of the material is increasing 2.5–3.2-fold, respectively. The integrity of the coating decreases monotonically with increasing temperature due to heat oxidative degradation of PAS polymer at temperatures 1123–1473 K (80%–88%).

The uniformity of the covering is increased by 3%–4% if two mass fractions TiO₂ (%) are incorporated in the coating. The continuity increases by 5% when kaolin administered in the composition.

| № of coating composition | Boundary wetting angle, degrees for steel St3kp on concrete | Boundary wetting angle, degrees for steel St3kp on concrete |
|--------------------------|-----------------------------------------------------------|-----------------------------------------------------------|
| 1                        | 293 K 243 K                                              | 293 K 243 K                                              |
| 2                        | 96 91                                                   | 93 91                                                   |
| 3                        | 95 93                                                   | 91 89                                                   |

\[ \equiv \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Al} - \text{Si} - \text{CH} + \text{O}_2 \to \equiv \text{Si} - \text{CH} = \to \\
\to \equiv \text{Si} - \text{O} - \text{O} - \text{CH} = +\text{Al} - \text{O} \to \\
\to \equiv \text{Si} - \text{O} - \text{CH} = +\text{O} - \text{Al} - \text{O} \to \\
\to \equiv \text{Si} - \text{O} - \text{Si} \equiv +\text{-O} - \text{Al} - \text{O} - +\text{C} = +\text{CH}_3\text{OH} \]
That fact that corrosive processes take place in the surface layers of the coating is confirmed by the change of their roughness (table 3). Tests were conducted in dry − 60% humidity and moist − 90% humidity conditions for 1 year.

Boundary wetting angle for investigated coatings is greater than 90 degrees that confirms their high hydrophobicity. Analyzing the results of researches of weather resistance of coatings, it is necessary to note that the action of weather factors doesn’t cause deep destruction of protective coatings. The basic processes of oxidation are only in the surface layer of the polymer without a considerable reduction of filler content.

Studies have shown (table 4) that the limit of fire resistance of ordinary concrete, which is covered by the developed coating, is 88 min, and for metal − 32 min.

These results confirm the feasibility of introducing kaolin into the coatings to increase the fire resistance of the investigated materials.

The mechanism of the flame retardant action of the coating is based on the creation of a heat-insulating and temperature-resistant layer on the surface of the material. This occurs due to the swelling during heating with the formation of a porous solid structure, reinforced with filamentous crystals of aluminium silicate.

The thermal resistance is increased by 30%–40% when the kaolin fiber is added. The heat resistant coatings is increased by 20%–25% if the kaolin and kaolin fiber are introduced into composition.

The resistance of metals, alloys and other materials to oxidation at high temperatures determines their heat resistance. Surfaces in contact with hot gas corrosive agents are corroded and destroyed. As is known, it is caused by the action of liquid or gaseous products on the metal and as any heterogeneous process begins with the surface of the phase separation. The heat resistance depends on the permeability and strength of the oxide film on the surface of the materials formed as a result of gas corrosion. Usually, this film is porous and penetrates highly active oxygen at high temperatures, which increases the depth of corrosion. It is possible to reduce the porosity and increase the density of the protective film on the material surface and its strength by applying protective coatings. The corrosion resistance of metals and alloys is evaluated by the rate of Oxygen penetration into the material, and quantitatively by the reduction of linear dimensions due to corrosion expressed in mm/year. Corrosion of metallic substrates of St3kpt without coating begins at a heating temperature higher than 623 K and is most intensively in the temperature range 873–1273 K (table 5).

The application of protective coatings on their surface shifts the onset of corrosion to a temperature of 673 K. Heating to a temperature of 873 K practically does not change the corrosion index of 0.8–2.0 mm year⁻¹.

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Table 3. Indexes of roughness of coatings during tests.

| № of coating composition | Index \(R_a\) (numerator) and \(R_z\) (denominator), mkm | in dry conditions | in moist conditions |
|--------------------------|-------------------------------------------------------|------------------|--------------------|
| 1                        | 0,357/0,537                                           | 0,391/1,141      |
| 2                        | 0,381/0,510                                           | 0,268/1,217      |
| 3                        | 0,312/0,572                                           | 0,398/1,127      |

Table 4. Fire resistance of the studied materials.

| № of coating composition | Fire resistance, min |
|--------------------------|---------------------|
|                          | Steel St3 | concrete |
| Without coating          | 8         | 45       |
| 1                        | 27        | 83       |
| 2                        | 32        | 88       |
| 3                        | 32        | 86       |

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The application of protective coatings on their surface shifts the onset of corrosion to a temperature of 673 K. Heating to a temperature of 873 K practically does not change the corrosion index of 0.8–2.0 mm year\(^{-1}\). Heating to a temperature above 873 K leads to an increase in corrosion. Therefore, the least corrosion resistance is observed for the surface covered by composition No.1 (without kaolin), which is explained by its low density.

The introduction of kaolin in the protective coating increases the corrosion resistance by 20%–25% and the titanium (IV) oxide—by 10%–15%. In general, the application of protective coatings reduces the corrosion depth by 2.2–3.5 times, which accordingly increases the durability of products under high temperature and gas corrosion conditions.

The processes of forming the protective coating structure were also explored with optical microscopy\(^{[13]}\). It is found that heating to a temperature above 573 K leads to the thermal oxidative degradation of PAS and forming reinforcing frame. That creates the conditions for the formation of thermal and fire-resistant layer. Interaction between the components of the coating at a temperature above 1223 K happens with the formation of zircon and mullite (figures 1–2).

Kaolin has a special influence on the microstructure of a protective coating. If the percentage of kaolin increases from 10 to 20%, the amount of particle mullite-sillimanite phase increases by 5%–7%.

The influence of composition on the microstructure of the coatings was established. The performance properties of the protective coatings can be adjusted in a wide temperature range because the influence of oxide and silicate fillers, which the coatings comprise, is established.

It is set, that to improve the heat resistance of steel structures it is expedient to use appropriate coatings based on full PAS and as fillers - Al\(_2\)O\(_3\), ZrO\(_2\), kaolin, kaolin fiber and modifier TiO\(_2\). The influence of feed composition on the thermal properties and corrosion resistance of these coatings is established.

| Temperature, K | Without coating | No of coating composition |
|---------------|-----------------|--------------------------|
|               |                 | 1 | 2 | 3 |
| 673           | 1.4             | 0.1 | 0 | 0 |
| 873           | 3.6             | 1.9 | 1.7 | 1.5 |
| 1073          | 9.1             | 4.9 | 3.9 | 2.6 |
| 1273          | 14.1            | 7.9 | 6.0 | 4.2 |

Figure 1. The microstructures of the protective coating composite No.1 at temperatures: (a) – 1573 K; (b) – 1673 K.
4. Conclusion

It is established that the coatings based on full aluminosiloxane polymers are characterized by the high indexes of physical properties (weather resistance and weather absorption) at preservation of sufficient temperature and fire resistance.

Positive results of increase of thermal and heat resistance of metal surfaces which are protected by PAS coating were obtained. The performance properties of the protective coatings can be controlled in a wide temperature range, since the effect of oxide and silicate fillers is established. The introduction of kaolin increases the content of mullite by 5–7 wt%, which increases the temperature resistance of coatings, and the introduction of TiO$_2$ reduces the temperature of silicate formation by 50–60 K.

Introduction to the composition of the coating of kaolin increases the corrosion resistance by 20%–25%. The introduction of titanium (IV) oxide increases the corrosion resistance by 10%–15%. In general, the application of protective coatings reduces the corrosion depth by 2.2–3.5 times. The addition of kaolin fiber increases the heat resistance of the coating by 30%–40% due to the reinforcement of the coating.

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Figure 2. The microstructures of the protective coating compositive No.2 at temperatures: (a) $-1573$ K; (b) $-1673$ K.