Aluminate spinel-based SHS pigments for fire-resistant protective and decorative coatings

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Abstract. In the work, color spinel-based inorganic pigments obtained by the SHS method are used in fire-resistant protective and decorative aluminophosphate-bonded coatings. X-ray diffraction (DRON-UM1 diffractometer, filtered CuKa radiation) and IR spectroscopic (Nicolet 5700 FTIR spectrometer) analyzes revealed that the coating contained AlPO₄, Al₂{(HPO₄)}₂, and Al(H₂PO₄) phases and spinel. Thermal analysis performed on an SDT Q600 thermal analyzer showed a slight mass loss related to the polymerization of phosphates and the formation of P₂O₅ anion in the range of 500-550 °C, which was also confirmed by IR spectroscopy. The color of protective and decorative coatings is maintained at temperatures of up to 1000 °C. Optical studies (Axiovert 200M) showed that color coatings subjected to heat treatment at 300 °C have a uniform structure that does not contain cracks, and therefore they can be used for metal, concrete and brick surfaces.

1. Introduction

The creation of various composite materials increases the demand for high-quality pigments that are resistant to UV irradiation, elevated temperatures and corrosive media, which in turn stimulates the expansion of the color palette and the methods for obtaining inorganic pigments. Spinelids are considered to be the best ceramic pigments [Masl.]. They are characterized by high-temperature formation conditions.

Large volumes of spinelides are obtained, as a rule, by the ceramic method, which includes annealing the corresponding oxides at temperatures of 1200–1400 °C, and by the sol-gel method followed by calcination [1–5]. All these methods are expensive due to increased energy consumption, therefore, the reduction in the cost of spinels through the use of the energy efficient method of self-propagating high-temperature synthesis (SHS) is an urgent problem. Aluminum powders (ASD-4 and ASD-6) produced in sufficient volumes by metallurgical enterprises were used to develop the SHS procedure for obtaining aluminum spinels [6]. The high speed of processes at which the temperatures required for the synthesis of spinels are reached, simple equipment and waste-free production are also the advantages of this method.

Spinels are widely used in the ceramic industry for the production of ceramics, refractory materials; color spinels are contained in heat-resistant paints. Spinel SHS pigments with increased chemical resistance to mineral acids, high melting temperatures, water resistance, Mohs’ hardness of 7.5-8 and the ability not to fade in the sun can be used in white and color refractory protective and decorative aluminophosphate-bonded coatings. Aluminophosphate binder (APB) is a product of the interaction of aluminum hydroxide with orthophosphoric acid and possesses good binding properties due to the formation of aluminum phosphates [7–10]. Refractory SHS spinelides added to APB were used to obtain aluminophosphate compositions with refractory and decorative properties.

The purpose of this work was to obtain protective and decorative aluminophosphate-bonded coatings using spinel SHS pigments and study the phase composition and heat resistance of the compositions obtained.

2. Experimental procedure
Pigments were synthesized from ZnO, MgO, CoO, Co2O3, Co3O4, Al2O3 oxides (high grade, pure grade) and (or) cobalt salts, and aluminum powder Al (ASD-4) was used as a fuel. The synthesis was conducted in the layer-by-layer combustion mode at atmospheric pressure in air in the SHS setup.

APB was prepared from a mixture of orthophosphoric acid and aluminum hydroxide with a ratio of H3PO4:Αl(OH)3 = 100 ml: 22.5 g by heating to temperatures of 80 ÷ 100 °C with constant stirring.

Spinel-based SHS pigments were introduced into aluminophosphate binder in the amount of 10-15 mas. % with a small amount of boric acid.

The microstructure of the protective and decorative coating was investigated by optical microscopy (Axiovert 200M). Obtained pigments and composite decorative material were examined using X-ray diffraction analysis (diffractometer DRON-UM1, filtered CuKα radiation) and IR spectroscopy (Nicolet 5700 FTIR spectrometer with a diffuse reflectance attachment, KBr). Complex thermal analysis of a ceramic coating consisting of APB and spinel-based inorganic pigment was performed using an SDT Q600 thermal analyzer. The particle size analysis of SHS pigments was performed on a Mastersizer-2000 analyzer.

3. Discussion of results
Pigments were synthesized at atmospheric pressure in air in the mode of layer-by-layer combustion and natural filtration.

The main reactions that provide the SHS process are exothermic oxidation of aluminum. For white magnesium aluminate spinel and light blue pigments based on it, the leading reaction is direct aluminum oxidation during which a large amount of heat is released [11, 12]:

\[4Al + 3O_2 = 2Al_2O_3 + 3350 \text{kJ} \]  (1)

For pigments based on cobalt oxides, aluminothermic reactions develop along with direct oxidation of aluminum:

\[\text{CoO} + 2\text{Al} + \text{O}_2 = \text{Al}_2\text{O}_3 + \text{Co} \]  (2)

\[2\text{Co}_2\text{O}_3 + 8\text{Al} + 3\text{O}_2 = 4\text{Co} + 4\text{Al}_2\text{O}_3 \]  (3)

As a result, a reaction mixture is heated to temperatures above 1000 °C, after which the synthesis of spinels begins, proceeding also with the release of heat:

\[\text{MeO} + \text{Al}_2\text{O}_3 = \text{MeAl}_2\text{O}_4, \text{ where } \text{Me-Mg, Co, Zn} \]  (4)

The last stage of SHS is volume combustion related to oxidation of cobalt obtained during thermite reactions, its interaction with aluminum oxide, polymorphic transformations of Al2O3, etc.

The advantage of SHS of spinel pigments is their finely dispersed state obtained directly in the combustion wave. The particle size analysis of SHS pigments showed that the average particle size was 4–9 μm.

Pigments synthesized from magnesium aluminate spinel and cobalt chloride (MgO-Al2O3, MgO-CoO-Al2O3 system) do not contain metallic particles, and systems obtained from cobalt oxides include Co particles observed under the microscope.

Table 1 demonstrates the main and impurity compositions of synthesized medium blue pigments according to X-ray diffraction analysis.

| №  | System                | Main phases | Impurity phases                      |
|----|-----------------------|-------------|--------------------------------------|
|    |                       |             | Oxides, Metal                        |
| 1  | MgO-Al2O3 (white)     | MgAl2O4     | α-Al2O3, AlBO3                       |

Table 1. Phase composition of spinel-containing pigments obtained by SHS
Synthesized SHS-pigments were used to obtain reliable protective and decorative aluminophosphate-bonded coatings. The optimal amount of pigment introduced into aluminophosphate binder was 10–15 wt.% with a small amount of boric acid added to slow the rate of crystallization for the technologically necessary time. Obtained paint was applied to the surface and dried. The reaction of the interaction is given by:

$$\text{Al(OH)₃} + \text{H₃PO₄} = \text{AlPO₄} + 3\text{H₂O} \ (5)$$

To create a solid ceramic coating, the surface of the product covered with dried paint was exposed to heat treatment (~ 300 °C) for 1 ÷ 2 minutes. Such temperature treatment provides water resistance to coatings [7].

Figure 1 shows the X-ray diffraction pattern of the coating based on APB and aluminum-cobalt pigment (obtained in the ZnO-MgO-CoO-Al₂O₃ system). The obtained coating is a mixture of AlPO₄, aluminum phosphates, crystallized in a hexagonal and orthorhombic crystal systems, and CoAl₂O₄ spinel.

Ceramic coating is resistant to high temperatures. Figure 2 shows the complex thermal analysis of the coating consisting of aluminophosphate binder and CoAl₂O₄-based inorganic pigment. Figure shows a loss of adsorbed and crystallization water with a maximum at 66.9 °C, 176.0 °C and 231.0 °C. In the range of 500–550 °C with a maximum at 538.2 °C, a slight mass loss related to the polymerization of phosphates and the formation of P₂O₇⁻ anion is observed, which is also confirmed by IR spectroscopy (Figure 3).

$$2\text{PO₄}^2⁻ → \text{P₂O₇}⁻ + 1/2\text{O}_2 \ \ (6)$$

The coating is stable up to ~ 1000 °C. Spinels with high stability during heating do not react with phosphoric acid, so the color of the coating is maintained.

Figure 1. X-ray diffraction pattern of the ceramic coating consisting of APB and CoAl₂O₄-based inorganic pigment, where 1-CoAl₂O₄, 2-AlPO₄ (hexagonal), 3-AlPO₄ (orthorhombic).
IR spectroscopic analysis performed on the Nicolet 5700 spectrometer showed the presence of absorption bands typical for $\text{PO}_4^{3-}$ ($932.2 \text{ cm}^{-1}$), $\text{HPO}_4^{2-}$ ($980.4 \text{ cm}^{-1}$) and $\text{H}_2\text{PO}_4^{-}$ ($1095.7 \text{ cm}^{-1}$) anions in the range of 1400–900 cm$^{-1}$. The vibrations of bonds of tetrahedrally coordinated cobalt [CoO$_4$] at 687.5 cm$^{-1}$ and octahedrally coordinated aluminum [AlO$_6$] at 552.3 cm$^{-1}$ in aluminum-cobalt spinel overlap with lines of aluminum phosphate (Figure 3, curves 1 and 2).

Heat treatment of the coating at 1000 °C leads to the occurrence of an absorption band at 732.3 cm$^{-1}$, which related to the vibration of $\nu$(O-O) bond characteristic for $\text{P}_2\text{O}_7^{2-}$ polyanion [13]. In all cases, the absorption band at 497.6 cm$^{-1}$ related to $\text{H}_2\text{PO}_4^{-}$ anion was observed. Deformation vibration of bond $\delta$(Co ... O-P) is detected at 456 cm$^{-1}$, which enhances with an increase in the thermal treatment of the coating (Figure 3, curves 3 and 4). The $\nu$(Co – O) absorption band occurs at 669.5 cm$^{-1}$ at 1000 °C. The peak with a maximum of 1229.5 cm$^{-1}$ is related to the valence vibration of bond $\nu$(P = O). With an increase in the treatment temperature, the content of AlPO$_4$ in the coating increases, and the vibration of PO$_4^{3-}$ anion contained in the composition of the coating is observed at 565.3 cm$^{-1}$ (Figure 3, curve 4) [14].

Figure 2. TG, DTG, DTA thermoanalytical curves of the composition from CoAl$_2$O$_4$ -based inorganic pigment and aluminophosphate binder (maximum mass loss on the DTG curve are directed upwards).
Figure 3. IR spectra of protective and decorative coatings, where 1 is pigment based on spinel $\text{CoAl}_2\text{O}_4$, 2 is APB + pigment (after drying), 3 is APB + pigment (after heat treatment at 300 °C), 4 is APB + pigment (after heat treatment at 1000 °C).

Figure 4 shows a sample of a protective-decorative coating deposited on a brick after heat treatment at $\sim$ 300 °C.

Figure 4. Microstructure of the surface of color protective and decorative ceramic coatings based on aluminophosphate binder and $\text{CoAl}_2\text{O}_4$ -based inorganic pigment deposited on brick, Axiovert 200M.

Optical studies (Axiovert 200M) showed (Fig. 4) that after heat treatment at 300 °C, the color coating has a uniform structure, does not contain cracks and can be used for metal, concrete and brick surfaces.

4. Conclusions
Thus, SHS spinel-based inorganic pigments are acid- and light-resistant and can be used for color fire-resistant protective and decorative aluminophosphate-bonded coatings.

The coating based on APB and pigment (obtained in the ZnO-MgO-CoO-Al$_2$O$_3$ system) consisting mainly of $\text{CoAl}_2\text{O}_4$ spinel, along with AlPO$_4$ aluminum phosphates crystallized in a hexagonal and orthorhombic crystal systems and $\text{CoAl}_2\text{O}_4$ spinel, contains acidic aluminum salts with $\text{HPO}_4^{2-}$ and $\text{H}_2\text{PO}_4^-$ anions.
Thermal analysis performed on the SDT Q600 thermal analyzer showed a slight mass loss related to the polymerization of phosphates and the formation of $\text{P}_2\text{O}_7^{2-}$ anion in the range of 500-550 °C, which is confirmed by IR spectroscopy.

The color of coatings is maintained during annealing at temperatures of 1000 °C. Metallic particles contained in cobalt oxide - based pigments do not affect the quality of coatings.

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